

Review

# Thickness and Structure of Adsorbed Water Layer and Effects on Adhesion and Friction at Nanoasperity Contact

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Abstract: Most inorganic material surfaces exposed to ambient air can adsorb water, and hydrogen bonding interactions among adsorbed water molecules vary depending on, not only intrinsic properties of material surfaces, but also extrinsic working conditions. When dimensions of solid objects shrink to micro- and nano-scales, the ratio of surface area to volume increases greatly and the contribution of water condensation on interfacial forces, such as adhesion ( $F_a$ ) and friction  $(F_t)$ , becomes significant. This paper reviews the structural evolution of the adsorbed water layer on solid surfaces and its effect on  $F_a$  and  $F_t$  at nanoasperity contact for sphere-on-flat geometry. The details of the underlying mechanisms governing water adsorption behaviors vary depending on the atomic structure of the substrate, surface hydrophilicity and atmospheric conditions. The solid surfaces reviewed in this paper include metal/metallic oxides, silicon/silicon oxides, fluorides, and two-dimensional materials. The mechanism by which water condensation influences  $F_a$  is discussed based on the competition among capillary force, van der Waals force and the rupture force of solid-like water bridge. The condensed meniscus and the molecular configuration of the water bridge are influenced by surface roughness, surface hydrophilicity, temperature, sliding velocity, which in turn affect the kinetics of water condensation and interfacial  $F_t$ . Taking the effects of the thickness and structure of adsorbed water into account is important to obtain a full understanding of the interfacial forces at nanoasperity contact under ambient conditions.

**Keywords:** water adsorption; water condensation; molecular configuration; adhesion force; friction force

# 1. Introduction

Understanding interfacial properties of water adsorbed on/at solid surfaces is a central theme across many scientific disciplines [1,2]. Adsorption of water from the surrounding environment onto solid surfaces is inevitable unless the surface is chemically inert or its surface energy is extremely low. The extent of adsorption plays a crucial role in a broad range of industrial processes, such as microelectromechanical systems, nanomanufacturing, heterogeneous catalytic reactions, electronic devices/sensors, nanomechanics, and lubrication [3–6]. Indeed, water condensation causing high interfacial forces, such as adhesion ( $F_a$ ) and friction ( $F_t$ ), is a serious problem in micro/nanomaterial engineering when the surface-to-volume ratio becomes significantly large and the surface properties dominate the material performance [7–9].

Water adsorption on solid surfaces is governed by the subtle balance between water-water hydrogen-bonding (H-bonding) and water-solid H-bonding as well as dispersive interactions governed



by Lifshitz theory. These interactions determine the molecular configuration of water molecules in the adsorbed layer. The structure of the adsorbed water layer on a solid surface has been analyzed with various spectroscopic techniques and molecular dynamics (MD) simulations [10–13] and found to be quite different from bulk water (or liquid water). For instance, the structure of the adsorbed water layer is determined by the extension of water-solid interactions from the interior to the exterior of the surface. If a solid surface is hydrophilic, strong interactions between the solid surface and water molecules may result in the formation of a strongly H-bonded water layer, also denoted as ordered water, solid-like water, ice-like water, or quasi-ice, in the adsorbed layer [10]. Water condensation around nanoasperity contacts varies with not only the intrinsic properties of the contacting surfaces (e.g., atomic structure, dangling bond, wettability, chemical activity, and surface roughness), but also the working conditions (e.g., temperature, humidity, sliding velocity, and atmosphere) (Figure 1) [14–16]. Apart from the amount of adsorbed water, the structure of the adsorbed water layer also plays a significant role in interfacial forces at the nanoasperity contact, especially under ambient conditions.



**Figure 1.** (a) The molecular configuration of adsorbed water layer on solid surfaces is governed by atomic structure of substrates, terminated groups on solid surfaces, and atmosphere conditions. A dynamic equilibrium exists in adsorbed water layer on solid surfaces with continuous evaporation and chemi/physi adsorption. (b,c) Schematically showing meniscus bridge formation at contacting and near-contacting asperities at multi-asperity contact and at single nanoasperity contact, which strongly affects the interfacial forces (i.e., adhesion force and friction force). The single-asperity contact in (c) is also regarded as a microscopic prospective of the multi-asperity contact in (b).

This review focuses on water adsorption behaviors on solid surfaces and their effects on  $F_a$  and  $F_t$  at nanoasperity contacts for a sphere-on-flat geometry. The influences of surface structure and chemistry as well as atmosphere conditions on water adsorption behaviors on metal/metallic oxides, Si/Si oxides, fluorides, two-dimensional (2D) materials, and other material surfaces are summarized. The changes in the kinetics of water condensation due to these factors and their effects on interfacial forces at the nanoasperity contact, including  $F_a$  and  $F_t$ , are discussed.

#### 2. Water Adsorption on Solid Surfaces

# 2.1. Effect of the Surface Atomic Structure on Water Adsorption

The unique properties of water in the liquid state stem largely from its dipole moment and H-bonding capability [17,18]. When water is adsorbed on solid surfaces, interactions with the solid surface cause its properties to deviate from that of liquid water [19,20]. One of the most typical characteristics of adsorbed water is that an ordered structure can exist on some solid surfaces due to strong hydrogen-bonded interactions between the water molecules and substrate atoms [13,21]. Using ultrafast electron crystallography with a spatial resolution of 0.01 Å, Ruan et al. [22,23] measured the structures and dynamics of interfacial water on Cl- and H-terminated Si(111) surfaces and observed the coexistence of ordered water and crystal-like ice structures on Cl-terminated surfaces at a cryogenic temperature (Figure 2). The analysis of surface diffraction features indicates that water

molecules adsorbed at the Cl interface are undissociated. Compared with those on H-terminated surfaces, the interactions of water with Cl-terminated Si(111) are relatively stronger because of electrostatic contributions [24]. These interactions explain why the ordered structure of water forms on Cl-terminated Si(111) but not on the H-terminated Si surface. Using scanning tunnel microscope (STM), a self-assembled molecular water monolayer with a long-range order structure was shown to form on a TiO<sub>2</sub> anatase (101) surface without any other termination groups [25].



**Figure 2.** (a) Schematic illustrating the structural water adsorbed on the Cl-terminated Si(111) surface. This ordered water film structure lasts up to three to four layers and forms crystalline islands. (b–e) showing the evolution of in situ growth of ordered ice water on the Cl-terminated silicon surface at a cold temperature of 110 K. The adsorption of water on the substrate can be seen from the disappearance of 111 silicon Bragg points (b) and the formation of 111 crystal ice Bragg points, along with the diffraction ring of amorphous ice (c). The structure is stable when the rings, spots and fringes are almost unchanged as diffraction shows (d,e). Reprinted from Ref. [22,23], Copyright 2004, with permission from Science.

Both the structural and dynamic properties of the adsorbed water layer depend on the atomic-scale geometry and chemical properties of solid surfaces [26]. For example, the structure of water adsorbed on Cu(110) is a quasi-one-dimensional (1D) chain. However, the adsorbed water on Cu(111) behaviors a three-dimensional (3D) hexagonal structure. Moreover, 2D overlayers with mixtures of pentagons and heptagons were observed on Pt surfaces, but no uniform 2D ice layer has been detected [27–30]. Another example is water-silica interfaces, which are probably one of the most extensively studied systems [31–35]. Based on density functional theory and MD simulations, a well-ordered 2D structure with quadrangular and octagonal patterns of H-bond networks, also known as an ice tessellation, is expected to form on a  $\beta$ -cristobalite(100) surface due to strong H-bond interactions between water molecules and geminal silanol groups (Figure 3a). In contrast, only isolated water molecules would exist on  $\beta$ -cristobalite(111) surfaces because silanol groups on this surface do not interact with each other (Figure 3b) [36]. This surfacial atomic structure dependence of water adsorption is also found on other solid surfaces. Zhang et al. [37] investigated the adsorbed water film on 111 and 100 crystal surfaces of calcium fluorite (CaF<sub>2</sub>) using MD simulations and sum frequency generation (SFG) vibrational spectroscopy; they reported that a gap exists between surface fluoride ions and interfacial water molecules in the (111) surface (Figure 4a). This surface is modestly hydrophobic with a water contact angle of  $\sim 20^{\circ}$ . By contrast, the (100) surface is hydrophilic, has a zero contact angle, and is fully hydrated by water molecules (Figure 4b). Up to three water layers can interact with the (100) surface, whereas only two water layers interact with the (111) surface. These studies show that the different atomic structures or termination groups of solid surfaces not only affect the structure and morphology of the adsorbed water layer, but also change the hydrophobicity.





**Figure 3.** Water adsorption on different crystallographic planes obtained in molecular dynamics (MD) simulations. (**a**) Adsorbed water structure on two different adsorption sites of the  $\beta$ -cristobalite(100) surface, i.e., the bridge site of two adjacent vicinal hydroxyl groups (**a**,**b**) and that of two adjacent geminal silanols (**c**,**d**). The water molecules have been colored with black oxygen and white hydrogen to distinguish from the hydroxyl groups on the surface (colored dark gray and light grayd). (**e**) Adsorbed water structure on the  $\beta$ -cristobalite(111) surface. Reprinted from Ref. [36], Copyright 2005, with permission from APS publications.



**Figure 4.** MD simulation snapshot of the equilibrium configuration of water molecules at fluorite (111) surface (**a**) and (100) surface (**b**) (green: fluorine; cyan: calcium). Reprinted from Ref. [37], Copyright 2015, with permission from ICE Virtual Library.

#### 2.2. Effect of Surface Wettability on Water Adsorption

In generally, surface wettability (hydrophilicity/hydrophobicity) is assessed by the contact angle of a water droplet [38]. The water contact angle on a highly hydrophilic surface may be as low as nearly zero and rises with the hydrophobicity of the solid surface [39,40]. Qualitatively, water adsorption preferentially occurs on hydrophilic surfaces [41–46]. Apart from the amount or thickness of the water layers adsorbed on a surface, the surface chemistry can also alter the configuration of water molecules in the adsorbed layer. When a surface is hydrophilic, both ordered and liquid-like water structures can coexist as the outermost adsorbed layer [10,47]. In contrast, adsorbed water assumes a more liquid-like structure on hydrophobic surfaces [41]. Using MD simulations, Willard et al. [48] reported that water molecules adsorbed on hydrophobic surfaces showed diffusive behavior due to the lack of strong

interactions with the surface. Gordillo et al. [49] demonstrated that water molecules on graphite do not form H-bond interactions with the surface.

Chen et al. [41] compared the configurations of adsorbed water layer on a hydrophilic Si oxide surface (terminated with Si–OH groups, water contact angle  $<5^{\circ}$ ) and a relatively hydrophobic Si surface (terminated with Si–H groups, water contact angle  $\approx 83^{\circ}$ ) by characterizing O–H stretching vibrations using attenuated total reflection infrared (ATR-IR) spectroscopy. As shown in Figure 5a and b, the difference in the H-bonding interactions of water molecules adsorbed on these two surfaces is manifested in the peak shape of the O–H stretching mode in the range of 3000–3800 cm<sup>-1</sup>. In general, ice water shows a peak centered at ~3220 cm<sup>-1</sup> [50,51], while liquid water exhibits a broad peak centered at ~3400 cm<sup>-1</sup> [52,53]. Thus, the OH stretching band can be deconvoluted into these two components: A solid-like component with a strongly H-bonded, relatively ordered structure and a liquid-like component with a disordered structure [53].



**Figure 5.** Water adsorptions on hydrophilic OH-terminated silicon oxide surface and hydrophobic H-terminated silicon surface. ATR-IR spectra of the O-H stretching region of water adsorbed on (**a**) hydrophilic OH-terminated silicon oxide surface (Si-OH) and (**b**) hydrophobic H-terminated silicon surface (Si-H) at relative humidity (RHs) of 15%, 30%, 45%, 60%, 75% and 90%. The insets schematically show the Si-OH functional groups on a native oxide layer and the Si-H groups on the HF-etched surface. Si: blue, O: red, H: grey. The O-H stretching region is fitted with two components-strongly H-bonded water (blue lines centered at 3200~3275 cm<sup>-1</sup>) and weakly H-bonded water (green lines centered at 3400~3450 cm<sup>-1</sup>). (**c**) and (**d**) respectively illustrating the schematic of structural of adsorbed water layer on hydrophilic Si-OH and hydrophobic Si-H surfaces. The dotted yellow lines represent hydrogen bonds. Note that illustration is not to scale. Upper-right inset in (**d**) showing the schematic of clusters of water molecules on the hydrophobic Si-H surface. Reprinted from Ref. [41], Copyright 2018, with permission from ACS publications.

On the hydrophilic OH-terminated Si oxide surface, the dominance of the peak at ~3220 cm<sup>-1</sup> (blue line in Figure 5a) implies the abundance of the ordered water structure over the disordered structure (Figure 5c). This configuration is congruent with the structures previously proposed from other spectroscopic observations [13,51,54] and MD simulations [55,56]. A similar water adsorption behavior has been observed on other hydrophilic surfaces reported by Thiel, et al. and Beaglehole, et al. [57,58]. On the hydrophobic H-terminated Si surface, the main peak was observed at ~3400 cm<sup>-1</sup> (green

line in Figure 5b), indicating the weakly H-bonded disordered structure is dominating. While the thickness of water increases up to four layers of hydrophilic OH-terminated Si oxide surfaces at near-saturation humid conditions, it remains less than a monolayer coverage on the hydrophobic Si surface (Figure 5d) [59]. On hydrophobic surfaces, adsorbed water molecules would form clusters. Based on the spectral shape of the OH stretching mode (Figure 5b), the structure of these clusters appears to be highly disordered or dynamically changing, regardless of the relative humidity (RH) of the environment [60]. Using atomic force microscopy (AFM), Cao et al. [61] visualized the microscopic structures of adsorbed water on H–Si(111), graphite, and functionalized mica, and found that water is adsorbed as nanodroplets ~10–100 nm in size on these surfaces under ambient conditions.

Apart from the molecular configuration of the adsorbed water layer, the entropy of water adsorption depends on the surface wettability [60]. The water layer adsorbed on hydrophilic surfaces at low humidity seems to have much lower entropies than bulk water, and the entropy of the water layer increases as the surface becomes more hydrophobic. MD simulation studies showed that interfacial water molecules on a hydrophilic surface remained in the interfacial region longer than those on a hydrophobic surface [10–13]. The physical structure of the material surface can also determine the configuration of the adsorbed water layer. Chen et al. [62] varied the contact angle of a Si surface from  $\sim 0^{\circ}$  to  $\sim 85^{\circ}$  via aging of the H-terminated Si surface in various environments (e.g., DI water, humid air, anhydrous ethanol). Their study showed that the amount of adsorbed water as well as solid-like structure decreases with the increase in hydrophobicity of flat substrate surfaces. However, the aged surface with a gel-like structure could uptake significantly more water from humid air than flat Si surfaces with complete OH-termination (SiO<sub>x</sub>/OH) even if the latter is more hydrophilic (Figure 6).



**Figure 6.** The relationship between adsorbed water thickness and the water contact angle on  $Si_{water}$ ,  $Si_{air}$ ,  $Si_{alcohol}$ , and  $SiO_x/OH$  surfaces. Insets: schematic illustrating water adsorption on  $Si_{water}$  surface with gel-like chains network formed in DI water (upper) and the transform from hydrophobicity to hydrophilicity (bottom). The gray shadow area and the dashed line are drawn to guide eyes for these two conditions. The RH for all measurements is controlled at 35 ± 5%. Reprinted from Ref. [62].

#### 2.3. Effect of External Environments on Water Adsorption

In addition to the intrinsic surface properties of materials described above, the external environmental conditions such as RH, temperature, and storage time can influence water adsorption. Miranda et al. [63] studied water adsorption on mica at various RH conditions using SFG vibrational spectroscopy. The results of this work revealed that the structure of the adsorbed water layer evolves with RH. In the adsorption spectrum of heavy water (D<sub>2</sub>O), the sharp peak at 2740 cm<sup>-1</sup> corresponds to the O–D stretching of non-H-bonded O–D groups (free O–D stretching), while the broad peaks at 2375 and 2510 cm<sup>-1</sup> represent O–D stretching modes associated with ordered and disordered H-bonded networks, respectively (Figure 7a) [51,64]. The O–D stretching modes associated with H-bonded O–D

groups begin to emerge at RH of 23%, and the component corresponding to the ordered structure becomes stronger than the component corresponding to the disordered structure at RH  $\geq$  40%. When RH exceeds 90%, the spectrum is completely dominated by the ordered O–D peak, indicating the domination of the ordered structure over the disordered one in the adsorbed water layer. Xu et al. [65] investigated the evolution of the adsorbed water layer on a mica surface with changes in RH by modifying the water structure by contacting with the tip of a scanning polarization force microscope. The tip contact produced a circular depression in the local polarizability at low RH (<20%), and capillary condensation induced the formation of water droplets and 2D islands around the contact point at other high RHs. In contrast to the evaporation of droplets over a short period of time, the ordered structure islands can remain much longer time (Figure 7b). However, the water droplets rapidly evaporated as RH decreased from 33% to 24%. The water molecules were condensed again as RH was increased back to 35%, and the recovery of the islands ceased after 38 min (Figure 7c).



**Figure 7.** (a) Sum frequency generation (SFG) spectra of a water (D<sub>2</sub>O) film on a mica surface as a function of RH at room temperature (296 K); The spectrum of the bulk waver/vapor interface is added as a comparison (the bottom trace). (b) SPFM images (6  $\mu$ m × 6  $\mu$ m) showing the evaporation of a droplet of water left on the mica surface after breaking the capillary neck formed around the atomic force microscopy (AFM) tip during contact. (c) SPFM images (3.4  $\mu$ m × 3.4  $\mu$ m) showing the size of the water islands at different RH. Reprinted from Ref. [63,65], Copyright 1998, with permission from ACS publications & APS publications.

Similar to observations on the mica surface, the water layer grows gradually with increasing RH on other hydrophilic surfaces [66,67]. However, the evolution of water structures on highly-hydroxylated Si oxide surfaces with a water contact angle less than 5° is fairly diverse. Figure 8a presents the thickness of the adsorbed water layer, as well as the ordered and disordered components with varying RH, on the Si oxide surface. The values recorded are estimated based on the ATR–IR spectra of O–H stretching measured on the substrate surface. At low RH (<30%), the ordered O–H peaks are dominant, so the adsorbed water mainly has a solid-like structure on the Si oxide surface that propagates for up to ~3 layers from the surface. The solid-like structure, also denoted as the ice or ordered structure, competes with the liquid water structure in the RH range of 30–60%, above which the liquid structure dominates the adsorbed water (Figure 8b). Similar results on the RH dependence of adsorbed water

structures have been obtained by MD simulations [41]. Rahaman et al. [67] studied the dynamics of water adsorption on calcite surfaces as a function of RH and found that water molecules appeared to be much more tightly bound to the surface at low RHs than at high RHs, indicating the domination of an ordered water layer under these conditions.



**Figure 8.** (a) Adsorption isotherm of adsorbed water layer on silicon oxide surface estimated based on the ATR-IR spectra of O-H stretching region measured at room temperature. Regions A, B, and C are marked to demonstrate the growth of ice-like water at low RH (< ~30%), transitional growth from ice-like structure to liquid-like structure at middle RH (~30% < RH < ~60%), and the growth of liquid water at high RH (> ~60%). (b) Schematic illustrating the structural evolution of adsorbed water layer on hydrophilic silicon oxide surface. Reprinted from Ref. [10], Copyright 2005, with permission from ACS publications.

RH-dependent water adsorption behaviors have been studied on hydrophobic graphene surfaces. No adsorbed water exists on the surface of graphene/mica at RHs below 2%, and a polygonal island structure can be observed at RHs above 90% [68]. Furthermore, water molecules are capable of adsorbing inside single-walled carbon nanotubes (SWNTs). As RH increases, the amount of water adsorbed in the SWNTs increases at temperatures between 8.0 and 22.1 °C (Figure 9a) [69,70]. Here, the environmental temperatures have a significant impact on the water adsorption in SWNTs. More water molecules are adsorbed in SWNTs at lower temperatures, especially at RHs below 90%, than at higher ones, thereby indicating that a hydrophobic-hydrophilic transition in SWNTs can be realized by cooling treatment [19,71]. Ketteler et al. [72] demonstrated that the water film coverage on a TiO<sub>2</sub> (110) surface increases with increasing RH but decreases with increasing temperature. Using grand canonical Monte Carlo simulations, Puibasset et al. [73] compared the adsorption of water in disordered mesoporous silica glass (Vycor-like) at temperatures of 300 and 650 K. The results showed a hysteresis loop in the adsorption/desorption data at low temperatures and a reversible curve at high temperatures. The results described above demonstrate that the structure of interfacial water is sensitive to temperature.



**Figure 9.** (a) Water adsorption isotherms inside single-walled carbon nanotubes (SWNTs) as a function of RH measured at different temperatures, including 8.0 °C (squares), 18.4 °C (triangles), and 22.1 °C (circles). (b) Schematic illustration showing a monolayer water adsorbed inside SWNTs at 8.0 °C. Reprinted from Ref. [19,71], Copyright 2008, with permission from Science.

#### 3. Effect of Water Adsorption on Adhesion at Nanoasperity Contact

#### 3.1. Brief Introduction of Water Adsorption-Dependent Adhesion Forces

 $F_a$  is the force required to separate two contacting or near-contacting surfaces. In general, the components that can contribute to  $F_a$  between surfaces are capillary force ( $F_c$ ), van der Waals force ( $F_{vdW}$ ), electrostatic force ( $F_E$ ), and chemical bonding force ( $F_B$ ) [14,73–75]. In dry or vacuum conditions,  $F_a$  is mainly determined by the attractive force of two contacting surfaces, such as  $F_{vdW}$ ,  $F_E$ , and  $F_B$ , due to the lack of adsorbed water. If the tip and sample sit in air for a sufficiently long time, surface charges are expected to fully dissipate [76]. Thus,  $F_E = 0$ .  $F_B$  can also be neglected when the contacting surfaces are fully saturated with non-reactive functional groups. Therefore,  $F_a$  is dominated by  $F_{vdW}$  under dry or vacuum conditions. At ambient conditions, water molecules can condense around the contact interface and form a meniscus (bridge) around the annulus of the contact area [77]. This meniscus attracts the two surfaces to come in close contact and causes greater adhesion. In this case, the adhesion between surfaces is mainly dominated by  $F_c$  and  $F_{vdW}$ .

A typical technique to quantify interfacial adhesion involves measurement of the pull-off force using AFM. Extensive experiments carried out in humid air show that  $F_a$  is dominated by the capillary interaction, which varies with RH as well as the surface wettability or surface chemistry [14,15]. The RH-dependent  $F_c$  plays an important role in adhesion behaviors. For example, as RH increases,  $F_c$  has been reported to monotonically increase [78], monotonically decrease [79], exhibit a maximum [80, 81], increase in a step-wise manner [82], or remain constant [83] (Figure 10). The discrepancies among these reports may be due to the differences in the humidity measurement ranges, sample preparation processes, and measurement methods. Thus, experimental details must be considered before conclusions on the influence of RH on  $F_a$  are drawn. Researchers believe that RH and surface wettability are among the factors determining  $F_a$  at single-asperity contact [77,80,81]. In general, trend c in Figure 10 is most frequently observed for hydrophilic contact surfaces (i.e., silanol group terminated Si<sub>3</sub>N<sub>4</sub> [65], mica [84] or SiO<sub>2</sub> surface [80,81]), which is usually attributed to the formation of water meniscus around the contact. When either or both of the contact surfaces are hydrophobic, the  $F_c$  has a limited contribution to  $F_a$  due to weak capillary condensation. In this case, adhesion is dominated by other RH-independent factors, such as  $F_{vdW}$  and surface topography (Figure 10e) [15,85–87].



**Figure 10.** Possible trends of adhesion force versus RH curves in AFM measurements. (**a**) Monotonic increase (two different types); (**b**) Monotonic decrease; (**c**) Increasing to maximum and then decreasing; (**d**) Step-wise increase; and (**e**) RH independence. Reprinted from Ref. [15], Copyright 2015, with permission from Taylor & Francis.

The variations in adhesion caused by capillary effects are strongly related to the configuration of the condensed water bridge around the annulus of the contact area. For instance, Asay and Kim [81] calculated the  $F_a$  at single-asperity contact between silicon oxide surfaces based on Xiao and Qian's model [80] and found that the theoretical values, including  $F_c$  and  $F_{vdW}$ , are much smaller than the experimental results at all RH conditions tested. The capillary effect alone cannot explain the high  $F_a$  observed on the hydrophilic silicon oxide surface; this was explained to be due to the ignorance of the solid-like water structure. In this case, the contribution of the rupture of H-bond bridges between strongly H-bonded networks at the center of the contact region must be considered in the adhesion. In the following subsections, the effect of water condensation on adhesion is reviewed from its contribution to  $F_{vdW}$ ,  $F_c$ , and the force of solid-like water bridge breaking.

#### 3.2. Effect of Water Adsorption on van der Waals Force

 $F_{vdW}$ , which is named after the Dutch scientist Johannes Diderik van der Waals, refers to the distance-dependent interaction between atoms or molecules [74]. Unlike ionic or covalent bonds, these attractions do not result from a chemical bond. They are comparatively weak and, therefore, more susceptible to disturbance.  $F_{vdW}$  vanishes quickly with increasing distance between interacting molecules [88]. Normally, the value of  $F_{vdW}$  is approximate to the pull-off force at the contact interface measured in vacuum. The pull-off force is determined from the force–distance curve based on the maximum deflection in the attractive region just before the AFM probe snaps off to the freestanding position [76]. In ambient conditions, the presence of water at the contact interface can vary the  $F_{vdW}$ ; in this case, estimating  $F_{vdW}$  from the experimentally-measured  $F_a$  becomes difficult [76]. Thus,  $F_{vdW}$  is usually estimated from a theoretical calculation.

The  $F_{vdW}$  in a typical sphere/plane geometry (Figure 11) contact can be calculated by [89]:

$$F_{\rm vdW} = A_{Hamaker} R/6a^2. \tag{1}$$

This force is a function of the sphere radius (*R*) and Hamaker constant ( $A_{Hamaker}$ ) of the medium in which the two objects are placed. According to Israelachvili [76], the separation *a* for most solid contacts can be taken as ~2 Å to make use of the continuum theory at the atomic scale. Then, the values of  $F_{vdW}$  in air ( $F_{vdw}^{air}$ ) and water ( $F_{vdw}^{water}$ ) can be estimated.  $F_{vdW}$  can be expected to take a value between these two limiting cases as RH increases from zero to saturation. At intermediate RHs,  $F_{vdW}$  can be expressed by the following crude approximation to account for the filling angle ( $\phi$ ) [77,80,90],

$$F_{\rm vdW}(\phi) = F_{\rm vdW}^{\rm water} \{1 - \frac{1}{\left[1 + R(1 - \cos\phi)/a\right]^2}\} + F_{\rm vdW}^{\rm air} \{\frac{1}{\left[1 + R(1 - \cos\phi)/a\right]^2}\}$$
(2)

*r*<sub>DM1</sub>

**Figure 11.** A geometric model of a liquid meniscus formed between a sphere and a flat substrate. Here,  $\phi$  is the filling angle, *R* the sphere radius,  $h_{\text{DMT}}$  the DMT indentation depth,  $h_{\text{m}}$  the height of meniscus,  $r_{\text{K}}$  the Kelvin radius (or meridional radius) of meniscus,  $r_{\text{m}}$  the meniscus-only portion of the total radius from the contact center, and  $r_{\text{DMT}}$  the DMT contact radius. Reprinted from Ref. [91], Copyright 2017, with permission from ACS publications.

Meniscus

Substrate

In general, condensation of the water meniscus between the sphere–plate contact interface decreases *A*. For example, in the case of Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> contact,  $A_{Hamaker}$  is  $1.04 \times 10^{-19}$  and  $1.9 \times 10^{-20}$  J when the medium is air and water, respectively [92]. Then, Equation (2) demonstrates that the growth of the water layer causes a decrease in  $F_{vdW}$  with increasing RH. Thus, the contribution of  $F_{vdW}$  to  $F_a$  decreases with increasing RH (Figure 10b). Chen et al. [4] measured the  $F_a$  on a hydrophobic H-terminated Si surface (water contact angle ~83°) and found that the force decreases substantially as the test environment transits from humid air to liquid water. During this process,  $A_{Hamaker}$  is reduced by 80% [80,85,93]. On a hydrophobic Si surface, water adsorption is very weak (Figure 5d), so  $F_c$  is negligible and  $F_{vdW}$  decreases, leading to a considerable decrease of  $F_a$ . Furthermore, the decrease in  $F_a$  at high RHs (as shown in Figure 10c) may be partly attributed to the decreasing  $F_{vdW}$ . However, the situation is complicated for hydrophilic surfaces (Figure 10a,c,d). Water condensation caused by the capillary effect becomes significant in RH-dependent adhesion behaviors.

#### 3.3. Effect of Water Condensation on Capillary Force

The meniscus condensed between two neighboring surfaces can induce attractive interactions (such as  $F_c$ ), which are the physical basis for many adhesion phenomena [14,15]. In earlier research, the  $F_c$  for a sphere-on-plane geometry was simply defined based on the contact angles of a sphere ( $\theta_1$ ) and plane ( $\theta_2$ ) [80],

$$F_{\rm c} = 4\pi\gamma R(\cos\theta_1 + \cos\theta_2) \tag{3}$$

where  $\gamma$  is the surface tension of the liquid and *R* is the radius of sphere. Equation (3) is valid for macroscale contact, where *R* is much larger than the height of the sphere immersed in the meniscus, or in the case when one or both of the contact surfaces is/are hydrophobic. In this model, the effect of the environment (such as RH) on the capillary-related *F*<sub>a</sub> is very limited. Adhesion behaviors on hydrophobic surfaces (such as self-assembled monolayers [80,94], CaF<sub>2</sub> [83], Au-coated Si<sub>3</sub>N<sub>4</sub> [95], and HOPG [85]) may be independent of RH due to the negligible growth of the adsorbed water layer [41]. For instance, the water adsorbed on a hydrophobic Si surface with complete H termination ( $\theta_2 = ~83^\circ$ )

reveals a cluster-like structure, and its average thickness is less than one layer even when RH reaches the near-saturation level (Figure 5d) [4,59]. In this case, the capillary interaction is much weaker compared with other attractive forces (i.e., the van der Waals component), and its contribution to adhesion can be neglected [80,83,85,94].

On some hydrophilic surfaces, the dependence of adhesion on surface wettability may be predicted by using Equation (3), although an exact value cannot be obtained. For example, Seo et al. [94] obtained different hydrophilic graphene surfaces by UV/O<sub>3</sub> treatment and found that the adhesion energy (estimated from  $F_a$ ) increases gradually with surface hydrophilization. The variations in adhesion as a function of surface wettability obey the model in Equation (3). Many research groups have shown the possibility of controlling interfacial adhesion by adjusting the wettability of a surface [91–93]. As shown in Figure 12, upon either *n*- or *p*-type doping with subsurface polyelectrolytes, graphene surfaces become more hydrophilic [59], water adsorption is enhanced, and  $F_a$  (i.e., the pull-off force) increases significantly. This behavior is consistent with the wettability-dependent adhesion modulation [96].



**Figure 12.** (a) Schematic illustrations showing graphene wettability modulation by doping-induced Fermi level shifts. (b) Water contact angle (left axis) measured by environmental scanning electron microscopy and the work function (right axis) measured by scanning Kelvin probe microscopy of n-doped (by high molecular weight (HMW) poly(allylamine hydrochloride) (PAH) and poly-L-lysine (PLL)), the p-doped graphene (by HMW poly(sodium 4-styrenesulfonate) and poly(acrylic acid) (PAA)), and undoped graphene on SiO<sub>2</sub>. (c) Adhesion force measurements on doped and undoped graphene samples using an octadecyltrichlorosilane-coated silicon AFM probe. Hydrophilic SiO<sub>2</sub>/Si was used as a control substrate and showed the lowest adhesion force. Reprinted from Ref. [96], Copyright 2016, with permission from ACS publications.

The schematic shown in Figure 10 reveals that the adhesion behavior strongly depends on RH. However, the contribution of this factor to adhesion is not considered in Equation (3). Taking graphene as an example,  $F_a$  remains low at low humidity due to the lack of a capillary meniscus. In this case,  $F_{vdW}$  should play a dominant role. However, when RH > 23%, an adsorbed water layer begins to form and expands from the initial liquid island to the entire graphene surface, thereby increasing the  $F_c$  and  $F_a$  as RH rises to ~45% [88]. Several other studies demonstrated that the increase of RH above 50% may result in a decrease of  $F_a$ , especially on hydrophilic surfaces (Figure 10c) [80,81,93]. Xiao and Qian [80] built a new formulation to fit this complex RH-dependent adhesion behavior and explain the observed decrease in  $F_a$  at high RH. The authors indicated that the decrease in capillary pressure force governed this behavior when the dimension of the meniscus became comparable with the tip size.

 $F_c$  describes the force exerted on neighboring surfaces due to the surface tension of the condensed liquid and the curvature of the meniscus. According to the thermodynamic equilibrium between solid and liquid (Young's equation) and between liquid and vapor (Young-Laplace equation) [14], the  $F_c$  exerted on the asperity by the meniscus comes from both the capillary pressure (pressure difference  $\Delta p$  outside and inside the meniscus due to the curvature) and the surface tension:  $F_c = F_p + F_s$  [97]. Xiao and Qian [80] proposed a relationship between  $F_c$  and the filling angle ( $\phi$ ) between the tip and the

water meniscus for a typical sphere-plate contact geometry (Figure 11).  $F_p$  and  $F_s$  can be estimated based on the contact angles of a sphere ( $\theta_1$ ) and a plane ( $\theta_2$ ) [89] as follows:

$$F_p(\phi) = \pi \gamma R(-\sin\phi + \frac{\cos(\theta_1 + \phi) + \cos\theta_2}{\frac{a}{R} + 1 - \cos\phi}\sin^2\phi)$$
(4)

$$F_s(\phi) = 2\pi\gamma r_1 \sin(\theta_1 + \phi) = 2\pi\gamma R \sin\phi \sin(\theta_1 + \phi)$$
(5)

where *a* is the minimum distance between the sphere and the plane [80]. At thermal equilibrium, the filling angle ( $\phi$ ) is determined by the Kelvin equation [98,99],

$$\frac{kT}{\gamma v_0} \ln \frac{P}{P_s} = \Delta P / \gamma = \frac{1}{R \text{Sin}\phi} + \frac{\cos(\theta_1 + \phi) + \cos(\theta_2)}{a + R(1 - \cos\phi)}$$
(6)

where  $v_0$  is the molecular volume of water and  $P/P_s$  is RH.

The height of the water bridge at the contact interface and the related  $F_c$  can be calculated from Equations (4)–(6). A significant decrease in  $F_c$  at high RHs is a consequence of a marked decrease in the Laplace pressure relative to the size of the water bridge, which is considered to play a dominant role in the drop in  $F_a$  with RH in many studies [15]. Bartošík et al. [93] investigated the  $F_a$  between a hydrophilic silicon oxide surface and a Si AFM tip and found that the  $F_a$  increases at low RH and then decreases at high RH and this trend is reversible. Similar behaviors were predicted for different radii of the contacted asperity tip (Figure 13a) based on the formulation given by Xiao and Qian [80] considering the variation in  $F_{vdW}$ . When RH is fixed, the  $F_a$  dominated by capillary interaction has been observed to increase linearly with the increase of tip radius. All calculated constituents, including  $F_c$ , tension force, and  $F_{vdW}$ , show a linear dependence on the tip radius (Figure 13b). The transition of  $F_a$  with RH can be explained by changes in relative contributions of these individual components. As shown in Figure 13c, the decrease in  $F_c$  caused by the Laplace pressure mainly contributes to the drop in  $F_a$  at high RHs. However, the variations in  $F_{vdW}$  also play a significant role in the adhesion behavior.



**Figure 13.** (a) The calculated total adhesive force between Si<sub>3</sub>N<sub>4</sub> AFM tip and hydrophilic silicon substrate as a function of the tip radius and RH for water–surface and water–tip contact angles  $\theta_1$  and  $\theta_2 = 40^\circ$ . (b) The profiles of the total adhesive force and its constituents for 50%RH and (c) a tip radius of 10 nm. Reprinted from Ref. [93], Copyright 2017, with permission from ACS publications.

In summary, the formation of a liquid meniscus at the contact interface is insignificant at very low RHs, so  $F_c$  is relatively weak and  $F_{vdW}$  may dominate the adhesion behaviors on both hydrophilic and

hydrophobic surfaces [81,93,95]. For hydrophilic surfaces, when the adsorbed water layer begins to form with increasing RH, the increase in  $F_c$  becomes more significant compared to the decrease in  $F_{vdW}$ , resulting in an increase in total  $F_a$  (Figure 13c). As RH further increases to higher ranges (>~60%),  $F_a$ decreases with decreasing  $F_c$  and  $F_{vdW}$ . Although a quantitative description involving continuum theory has been proposed in previous years [14], the experimental results remain inconsistent with theoretical calculations because of the complexities of real interfacial conditions and the limits of the model parameters. For example, Asay and Kim [81] investigated the RH dependence of the  $F_a$  between silicon oxide surfaces at single-asperity contact and found that the variations in  $F_{vdW}$  and  $F_c$  cannot fully explain the observed magnitude of RH dependence. The presence of solid-like structural water adsorbed on the silicon oxide surface (Figure 5c) can play a significant role in the adhesion behaviors on this hydrophilic surface.

#### 3.4. Effect of Adsorbed Water Structure on Adhesion

The results shown in Figures 5–8 indicate that solid surfaces exposed to air can adsorb water molecules and the thickness of the adsorbed water layer and molecular configuration of the water layer change depending on RH and surface chemistry [10,41,62,63,65]. On hydrophilic surfaces, such as a highly-hydroxylated Si oxide surface with a contact angle less than 0°, a strongly H-bonded solid-like arrangement of water molecules is found in the adsorbed layer formed at low RHs and a weakly H-bonded liquid-like structure grows and forms multilayers as RH exceeds 30–40% [41]. This difference in structures at various RHs significantly influences interfacial properties in nanoasperity contact systems.

Figure 14a schematically shows the typical states of solid-adsorbate-solid contacts immediately before the separation of hydrophilic surfaces in different RH regions [81]. At low RH, the sphere is separated from the substrate surface by the solid-like water. Between RHs of 30% and 60%, both ice-like and liquid water structures can coexist in and around the contact area. At RHs above 45%, the contact just before snap-off is composed of two parts: solid-solid water contact at the center; and liquid-liquid water annular contact at the outer edges. A further increase in RH decreases the contact area of the central solid-solid water bridge region at the snap-off moment such that it eventually becomes zero near the saturation RH. Physically, the surface energy of the adsorbed water layer varies with the evolution of its molecular configuration as a function of RH. The surface energy of pure liquid water at room temperature is 72.8 ergs/cm<sup>2</sup> [100], while solid-like adsorbed water is estimated to close to the cohesion energy of ice (103.3 ergs/cm<sup>2</sup>) due to the involvement of more H bonds per molecule in the latter case [36,101]. As a result, the use of bulk water surface tension is expected to underestimate the interfacial tension at low RH.

Figure 14b demonstrates the RH-dependence of  $F_a$  of a silicon oxide nanoasperity contact. When the surface energy of pure liquid water is used, the calculated values consisting of  $F_{vdW}$  (Equation (2)) and  $F_c$  (Equations (4) and (5)) are significantly lower than the experimental data in the RH range of 10–80% [81]. This underestimation stems from the negligence of the RH-dependence of the adsorbed water structure, i.e., the solid-like water bridge formed at the center of nanoasperity contact (Figure 14a). Solid–solid water rupture contributes significantly to  $F_a$  at nanoasperity contact. The force required to achieve spontaneous rupture of the solid-like meniscus, denoted as  $F_h$ , can be approximated from the relation  $F_h = dW/dz$ , where  $dW = 2\gamma_h dA_{ice}$  [81]. Here, the surface energy ( $\gamma_h$ ) of the strongly H-bonded solid-like water (~103.3 ergs/cm) is used [36,102]. The area of the solid-like meniscus ( $A_{ice}$ , Figure 14a) at a critical distance (dz) over which the AFM tip snaps off can be calculated by the relation  $A_{ice} = \pi(h + 2R)(2h_{solid} - h)$ , where h is the total thickness of the adsorbed water,  $h_{solid}$  is the thickness of the solid-like water layer, and R is the radius of the AFM tip. The theoretical simulations of AFM tip separation propose that dz is the equilibrium distance between water molecules [36], i.e.,  $dz = 2^{1/6}\sigma$ (Lennard-Jones parameter  $\sigma = \sim 3.15$  Å) [103]. Thus,  $F_h$  as a function of h is written as:

$$F_{\rm h}(h) = \frac{2\pi\gamma_{\rm h}(h+2R)(2h_{\rm solid}-h)}{2^{1/6}\sigma}$$
(7)

After considering the contributions of solid-solid water rupture, as well as capillary interactions and  $F_{vdW}$ , the theoretical prediction (thin solid line in Figure 14b) can reproduce the shape and magnitude of the experimental adhesion behavior.

As shown in Figure 14b, the growth of a solid-like water meniscus can markedly increase  $F_a$  at RH < 30%. By contrast, high adhesion can be prevented if the formation of the solid-like meniscus is suppressed. For example, a simple method employing the equilibrium adsorption of gas-phase alcohol molecules on OH-terminated surfaces can effectively reduce interfacial adhesion [104–106]. When a mixture of *n*-propanol and water molecules is readily adsorbed on the OH-terminated silicon oxide surface, a binary adsorbate layer is formed on the substrate surface (Figure 15a). Here, *n*-propanol is assumed to locate at the adsorbate/vapor interface while water locates inside the adsorbate layer; unlike the liquid/vapor interface, the propanol molecules do not form a paired dimer-like structure at the adsorbate/vapor interface (Figure 15b). Then, *n*-propanol adsorption from the gas phase can effectively decrease the  $F_a$  between the silicon oxide surfaces (Figure 15c), mainly due to the weak H-bonding interactions between two *n*-propanol layers adsorbed on the two contacting surfaces, which provides very low attractive interactions when the two surfaces separate.



**Figure 14.** (a) Schematics of the silicon tip (covered with a native oxide layer) position on silicon oxide surface and solid-adsorbate-solid contact area as a function of RH. (b) Simulation of the contributions from capillary force term  $F_c$ , van der Waals term  $F_{vdW}$ , and the solid-like water bridge term  $F_h$ . The bottom dotted line represents the maximum  $F_c$ . The middle-dashed line represents  $F_c + F_{vdW}$ . The solid lines represent the sum of three components,  $F_h + F_c + F_{vdW}$ . Reprinted from Ref. [81], Copyright 2006, with permission from AIP publications.



**Figure 15.** (a) ATR-IR spectra of the binary adsorbate layers of n-propanol and water on silicon oxide with the water contact angle of  $\sim 0^{\circ}$ . (b) Schematic illustration of the structure for the binary adsorbate layer of n-propanol and water on silicon oxide. Reprinted from Ref. [104], Copyright 2012, with permission from ACS publications. (c) Adhesion force between the silicon tip (covered with a native oxide layer) and silicon oxide substrate measured with AFM as a function of n-propanol partial pressure. Reprinted from Ref. [105], Copyright 2005, with permission from Elsevier.

#### 4. Effect of Water Adsorption on Friction Force at Nanoscale

According to analytical theories developed thus far [16,107], the nanoscale  $F_t$  between two contact surfaces can be divided into three main parts: adhesive friction force for two contacting surfaces ( $F_{adh}$ ), deformation-related friction force ( $F_{def}$ ) resulting from energy dissipation due to deformation of the contacting asperities; and stick-slip friction force ( $F_{stick-slip}$ ),

$$F_{\rm t} = F_{\rm adh} + F_{\rm def} + F_{\rm stick-slip}.$$
(8)

The contributions of  $F_{def}$  and  $F_{stick-slip}$  to the total  $F_t$  depend on the intrinsic properties of the contacting surfaces, such as their surface roughness, hardness, elastic modulus, and bond energy of substrate materials, [108–110] as demonstrated in Ref. [16]. In the following subsections, the role of adhesive interactions in friction behaviors is reviewed with consideration of the effect of water condensation. In the geometry shown in Figure 11, the water meniscus exerts some  $F_c$  that must be added with the applied load to obtain the effective total force pressing on the contact area and leading to high friction during relative sliding motion.

#### 4.1. Nucleation of the Water Meniscus During Sliding Process

Physically, the water meniscus between contacting or near-contacting interfaces requires time to grow until thermodynamic equilibrium is established [102]. If the contact time is too short, the water meniscus would not have enough time to form. For example, at high sliding speeds, there is insufficient time for the capillary to fully form [102]. At lower velocities, longer contact times allow water bridges to grow, which induces higher capillary-related  $F_t$ . In this section, the critical factors influencing water meniscus nucleation during the sliding process and the related time-dependence of friction are reviewed.

In contrast to the increase in friction with velocity under dry conditions due to thermally activated stick and slip [102,111], the  $F_t$  dominated by capillary effects decreases logarithmically to an asymptotic value with increasing velocity at various temperatures (Figure 16a) [102]. The critical velocity ( $v_c$ ) at the intersection of these two regimes can be used to determine the mean capillary nucleation time ( $\tau$ ) corresponding to the onset of capillary bridge formation. The critical transversal distance for one asperity travelling with respect to the contacting substrate before capillary nucleation stops is the contact diameter (d), which can be estimated by using a formula valid in the case of a stiff contact [102]:  $d = 2[(R/Y) \times (F_N + F_a)]^{1/3}$ . Here, R is the radius of asperity, Y is the reduced tip–sample Young's modulus [102], and  $F_N$  is the normal load. Then,

$$\tau = \frac{2[(R/Y) \times (F_N + F_a)]^{1/3}}{v_c}$$
(9)

The  $\tau$  calculated by Equation (9) is temperature dependent, as supported by other studies [112,113]. As shown in Figure 16b, the values of  $\tau$  range from 4.2 ms to 0.7 ms as the experimental temperature increases from 299 K to 332 K at 37 ± 2% RH; thus, the condensation of the water meniscus can be viewed as a thermally-activated process with an energy barrier [112–119]. According to thermal activation theory, the  $\tau$  of a meniscus bridge can be predicted by the Arrhenius law [112,114,117]:

$$\tau = \tau_0 exp[\Delta E/(k_{\rm B}T)],\tag{10}$$

where  $1/\tau_0$  is the attempt frequency,  $\Delta E$  is the nucleation energy barrier,  $k_B$  is the Boltzmann constant, and *T* is the absolute temperature. The data in Figure 16b show an exponential dependence of  $\tau$  on 1/T, consistent with the thermal activation model (Equation (10)). By fitting friction data at different temperatures, Szoszkiewicz et al. [102] demonstrated that  $1/\tau_0$  ranges from 4 GHz to 250 GHz and  $\Delta E = 7.8 \times 10^{-20}$  J, which is significantly larger than thermal energy ( $k_BT$ ). Similar values of  $\Delta E$  were also obtained in real-time heating experiments [116]. Thus, an increase in experimental temperature can facilitate water condensation at the sliding interface, which induces higher  $F_t$  [102,114,116].



**Figure 16.** (a) The variation of friction with velocity at different temperatures. The load was 15 nN, the tip radius was 25 nm, the RH was at  $37\% \pm 2\%$ . (b) By fitting the data to calculate the attempt frequency and energy barrier. Reprinted from Ref. [102], Copyright 2005, with permission from APS publications.

#### 4.2. Effect of Surface Wettability on Water Condensation at Nanoasperity Contact

As described in Section 2.2, the thickness and configuration of the adsorbed water layer are a function of the surface wettability of a solid substrate, which in turn influences the condensation of water meniscus at the sliding interface. The water meniscus formed between two hydrophilic contacting surfaces may be absent when one or both of the contacting surfaces is/are hydrophobic. This is the reason why the  $F_t$  on hydrophobic surfaces is relatively insensitive to RH [120–122]. Borruto et al. [123] summarized four possible models to demonstrate the possibility of a water layer existing between four different types of coupling. When both contacting surfaces are hydrophilic (Figure 17a), a water meniscus can form, and a thin water film may be restricted to the contact region. In this case, the condensed water does not produce a layer that is capable of hydrostatic lift. When the two contacting surfaces are hydrophobic (Figure 17b), direct solid contact occurs, and no water layer is formed between the surfaces. When the asperity surface is hydrophilic but the substrate surface is hydrophobic (Figure 17c), the latter tends to stay dry while the former tends to become wet. A thick water layer may form in the contact region since this region has hydrostatic lift. When the asperity surface is hydrophobic and the substrate surface is hydrophilic (Figure 17d), repulsion of the small surface of asperity can have a slight influence on the large surface of the substrate. Thus, a lifting layer of water may form at the contact interface.



**Figure 17.** (a) Four possible models of existence of water layer between contacting interface. (a) Hydrophilic asperity contacting with hydrophilic substrate. (b) Hydrophobic asperity contacting with hydrophobic substrate. (c) Hydrophobic asperity contacting with hydrophilic substrate. (d) Hydrophilic asperity contacting with hydrophobic substrate. Reprinted from Ref. [102], Copyright 1998, with permission from Elsevier.

Kaibara et al. [124] investigated adhesion behaviors for the four cases shown in Figure 17, and their results support the belief that the water meniscus makes significant contributions to adhesion only when both contacting surfaces are hydrophilic. However, although water meniscus may form

readily when one or both contact surfaces is/are hydrophobic (Figure 17b-d), the differences in the restricted water layers at the contact interface may still result in different friction behaviors. For example, the interfacial F<sub>t</sub> measured in ambient air increases gradually with hydrophilization of the contact surface [120]. Opitz et al. [121] compared friction behaviors on hydrophilic and hydrophobic Si surfaces slid against a Si AFM tip in ambient air and in an ultra-high vacuum (UHV,  $10^{-11}$  mbar). The thickness of the adsorbed water film on the hydrophobic Si surface measured by dynamic scanning force microscopy and scanning tunneling microscopy is one order of magnitude lower than the hydrophilic Si. As shown in Figure 18, compared with the hydrophobic Si surface, a much larger  $F_{t}$  can be obtained on the hydrophilic Si surface in ambient air due to the capillary effect. On the hydrophobic Si surface, the  $F_t$  is nearly identical in air and UHV at the same load, thus supporting the absence of a water meniscus (Figure 18a). Water condensation can cause massive differences in  $F_t$  on the hydrophilic Si surface between UHV and ambient air conditions. In particular, as the water vapor partial pressure increases,  $F_c$  becomes the governing factor of friction from low RH to high RH (Figure 18b). Similar results are provided in another report by Opitz et al. [125]. Different mechanisms can be used to explain running-in behaviors of the nanoasperity friction on hydrophilic and hydrophobic surfaces. For example, on OH-terminated Si surfaces, the Ft decreases remarkably when the outermost hydrophilic termination groups are removed [126–128].



**Figure 18.** (a) A comparison of friction coefficients between hydrophobic and hydrophilic surfaces in air and ultra-high vacuum (UHV). The friction force of hydrophilic silicon is greater in air than in UHV while the friction force of hydrophobic silicon is almost the same under these two conditions. (b) The friction force of hydrophilic silicon versus residual pressure and a schematic model of water coverage in various coverage regimes determined by the friction behaviors. Reprinted from Ref. [121], Copyright 2002, with permission from Elsevier.

Water adsorption can also significantly alter the friction behaviors on 2D material surfaces. Graphene surfaces are well known to provide extreme low friction due to their low surface energy [129–131]. However,  $F_t$  increases substantially when the graphene surface is oxidized (Figure 19) [126]. This result indicates that the growth of OH groups on graphene oxide (GO) surfaces may enhance water adsorption and facilitate the growth of water bridges between the AFM tip and GO surface, thereby augmenting the effect of  $F_c$  and increasing  $F_t$ . Moreover, the comparison of friction between GO and rGO (thermally reducing oxygen-containing functional groups) surfaces by Kwon et al. [132] also supports this hypothesis. Due to the decrease of oxygen-containing functional groups after thermal treatments, the friction force on rGO surface is drastically reduced compared with the more hydrophilic GO surface at the same RH.



**Figure 19.** The friction measurements on graphene surface (**a**) and the friction forces as a function of load on pristine graphene (PG), graphene oxide (GO), and fluorinated graphene surfaces (**b**). Reprinted from Ref. [126], Copyright 2018, with permission from ACS publications.

#### 4.3. Effect of Water Condensation on Friction Force

Once water condensation occurs, it exerts a strong impact on friction, especially at nanoasperity contact, depending on the temperature, sliding speed, RH, and surface wettability (Figures 16, 18 and 19) [102,121,126]. In the multi-roughness peak model developed by Bocquet et al. [117], the  $F_a$  caused by capillary action between contact surfaces is related to the number of capillary menisci formed. The environmental humidity affects the size of the capillary meniscus (Kelvin radius) formed [133], the sliding speed provides the growth time of the capillary meniscus, and the thermal activation process of capillary condensation is determined by these two factors. Riedo et al. [134] proposed that similar effects can be observed in the dynamic case of sliding friction and at the nanoscopic scale.

When limited to the curvature radius of the meniscus, only the asperity gap less than the order of the Kelvin radius ( $r_m$ ) (Figure 11) can condense water to form the meniscus bridge. Based on the thermal activation process [102,117,134], a meniscus bridge with a volume of  $v_m$  form only when an energy barrier  $\Delta E(e)$  is overcome:

$$\Delta E(e) = \frac{\gamma v_m}{r_m} = \rho k_B T \ln(P_s/P) v_m \tag{11}$$

where  $\rho$  is the density of the liquid in unit molecules/m<sup>3</sup>. Assuming the activated process, the time needed to form a bridge of volume  $v_{\rm m}$  can be estimated by Equation (10). Here,  $t_0$  is the condensation time of the liquid monolayer. In the case presented in Figure 20, Riedo et al. [134] assumed that a gap of height *h* defines the volume of a potential liquid bridge  $V_{\rm m} = hA$ , where *A* is the bridge cross-section and considered as a constant for simplicity. Then, the maximum height  $h_{\rm max}(t)$  of the water bridge formed after time *t* can be defined as:

$$h_{\max}(t) = \frac{\ln(t/t_A)}{A\rho \ln(P_s/P)} \tag{12}$$

Meniscus bridges will not form at the multi-asperity contact shown in Figure 20 if the spacing of the near-contacting asperities is greater than  $h_{\text{max}}$  at a given residence time. Due to the surface roughness, nucleating sites exhibit a broad height distribution. To a first approximation, the total number of near-contacting and contacting with height  $h < h_{\text{max}}$  is equal to  $N(t) = h_{\text{max}}(t)/\lambda$ , where  $\lambda$  is the full width of the interstitial height distribution [117,135]. Then,

$$N(t) = \frac{1}{\lambda A \rho} \frac{1}{\ln(P_s/P)} \ln(\frac{t}{t_a}) = \frac{1}{\lambda A \rho} \frac{1}{\ln(P_s/P)} \ln(\frac{v_a}{v})$$
(13)

where v is the sliding speed and  $v_a$  is the critical speed corresponding to the condensation of the water monolayer. When the sliding speed, RH, or temperature changes, a continuous variation in the number of capillary bridges forms in the area of contact. Then, considering the contributions of  $F_{def}$  and  $F_{stick-slip}$ ,  $F_t$  can be predicted with following equation [134],

$$F_t = \mu(F_N + F_{ss}) + \mu[F_c N(t)] + m \ln(\frac{v}{v_B})$$
  
=  $\mu(F_N + F_{ss}) - \mu[2\pi R\gamma(\cos\theta_1 + \cos\theta_2)] \times [\frac{1}{M\alpha \ln(P_c/P)}] \ln(\frac{v}{v_a}) + m \ln(\frac{v}{v_B})$  (14)

Here,  $F_{ss}$  is the  $F_a$  of the two solid surfaces without considering the capillary effects. The term  $m \ln(v/v_B)$  corresponds to the  $F_{stick-slip}$  when m > 0, and  $v_B$  is a characteristic sliding speed [111,136].

Riedo et al. [134] studied the velocity and humidity dependence of nanoscopic sliding friction on CrN and diamond-like carbon (DLC) surfaces with a Si AFM tip. A logarithmic decrease in friction on partially hydrophilic CrN surfaces was observed as the sliding speed increased, and the slope varied drastically with RH. In contrast, a logarithmic increase in friction occurs on partially hydrophobic DLC surfaces (Figure 21). Similar results have been reported in previous literature [16,137,138]. In these works, the model of Equation (14) is employed to explain the characteristics of both time- and RH-dependent capillary-dominated friction on hydrophobic and hydrophilic surfaces.



**Figure 20.** Schematic diagram showing multi-asperities contact in ambient air where water meniscus forms at contacting and near-contacting asperities. When the height *h* between two asperities is larger than  $h_{\text{max}}$ , water meniscus cannot be formed at near-contacting asperities. The radii of tip and Kelvin radii are *R* and  $r_{\text{m}}$ , respectively. The cross section of a single water meniscus is *A*. Reprinted from Ref. [126], Copyright 2018, with permission from IOP publications.



**Figure 21.** (a) Friction force as a function of sliding velocity on partially hydrophobic diamond-like carbon (DLC) surfaces at  $P/P_S = 0.34$  and 0.65 (*P* is the vapor pressure and  $P_S$  is the saturated vapor pressure). Inset: LT-CrN films at  $P/P_S = 0.65$ . (b) Friction force as a function of sliding velocity on hydrophilic surface (HT-CrN) at  $P/P_S = 0.01$  and 0.34. Reprinted from Ref. [134], Copyright 2002, with permission from APS publications.

#### 4.4. Effect of Adsorbed Water Structure on Friction Force at Single-Asperity Contact

The multi-asperity contact model in Equation (14) can successfully predict the friction behaviors on rough surfaces, but may not be applicable to solid interfaces with subnanometer- or nanometer-scale surface roughness. In this case, the sliding interface can be modeled by a single-asperity contact if the elastic deformation of the solid is larger than the topographic features of the initial surface [139,140]. As discussed in Sections 2 and 3, strongly H-bonded solid-like water can grow on hydrophilic surfaces, not only affecting  $F_a$  [41] but also playing an important role in the resulting friction behavior [91].

Chen et al. [91] recently investigated the friction behaviors between a silica microsphere and a Si substrate at single-asperity contact and found that  $F_t$  strongly depends on the structure and amount of the adsorbed water layer. As shown in Figure 22a,  $F_t$  generally decreases logarithmically with increasing sliding speed to a cutoff value. Above this cutoff value, the logarithmic speed dependence of  $F_t$  can be divided into two regimes. When RH is lower than 50%,  $F_t$  is a function of both speed and RH; at RH > 50%,  $F_t$  is a function of speed only. These complicated speed and RH dependencies can be explained by the structure of the water layer adsorbed on the surface and the water meniscus around the annulus of the contact area. The  $F_t$  at the single-asperity contact varies linearly with the volume  $V_m$  of the condensed water meniscus (Figure 22b) when the solid-like water layer structure formed on the silica surface plays a critical role in friction at RH < 50% (Figure 8).

$$F_{\rm t} = \rm{intercept} + \beta \times V_{\rm m} \tag{15}$$

Here, the slope ( $\beta$ ) of the fitting line physically represents the force needed to drag a unit volume of the meniscus. The water meniscus volume is estimated by  $V_{\rm m} \propto \ln(v_{\rm a}/v)[\ln(1/R)]^{-1}$ , which is derived by combining Equations (10) and (11). When the solid-like water structure ceases to grow and the liquid-like structure dominates the newly condensed water layer at RH > 50%, the water volume dependence of  $F_{\rm t}$  becomes weak (Figure 22c), thus indicating that the contribution of liquid water to  $F_{\rm t}$  is very limited.

Adsorbed water with liquid-like and solid-like structures present different H-bonding interactions. The average H-bond number of liquid water is approximately 2.5 per molecule while ice is 4 per molecule [141]. Therefore, variations in friction behaviors caused by the condensation of liquid-like and solid-like water may be related to the structure or dynamics of H bonds among water molecules being sheared at contact or dragged in the meniscus. The supporting evidence can be found in the work by Chen and Salmeron et al. [137] who compared the sliding speed dependence of  $F_t$  on surfaces terminated with hydrophilic groups of –OH, –COOH, and –NH<sub>2</sub> and the hydrophobic group of -CH<sub>3</sub> under liquid conditions. The surfaces terminated by hydrophilic groups containing the H acceptor and donor moieties are capable of forming H-bonding networks exhibiting decreases in friction with sliding speed (Figure 23a,b). This behavior is in contrast to surfaces with hydrophobic groups which cannot form such networks (Figure 23c). Under some applied stress, the domains of glassy H-bond networks are disrupted, leading to slippage. At low sliding speeds, the network is reconstituted after stress is released and grows more substantially with more time. Larger domains can then be formed to arrest the motion of the surfaces.



**Figure 22.** The sliding speed and RH dependence of friction forces at a single asperity contact between a silica microsphere and a hydrophilic silicon substrate. (**a**) Three-dimensional plot of the friction map at various RH and *v* conditions. The color from red to cyan denotes  $F_t$  changing from large value to small value. (**b**) Friction force  $F_t$  versus meniscus volume  $V_m$  for the contact between the hydrophilic silicon surface and the silica microsphere ( $F_n = 2 \mu N$ ) moving at various *v* in RH < 50%. The inset picture showing the condensation of solid-like water at a single asperity contact. (d)  $F_t$  versus  $V_m$  for the high RH regime (>50%). The thick red line in (**c**) is the same trend line found for RH < 50% in (**b**). Reprinted from Ref. [91], Copyright 2017, with permission from ACS publications.



**Figure 23.** Semilog plot of the friction force vs. sliding velocity between a  $Si_3N_4$  tip and samples of: (a) APS monolayer on mica; (b) Polyethylenimine monolayer on mica to produce a saturated layer of hydroxyl groups, and (c) APS coated mica sample after treatment with hydrochloric acid. RH = 35%. Reprinted from Ref. [91], Copyright 2006, with permission from the APS publications.

### 5. Perspectives

Water adsorption cannot be avoided in most solid surfaces exposed to ambient air, and the amount and structure of the adsorbed water layer strongly depends on not only the atomic structure and chemistry of the absorbing surface, but also the surrounding environment. The strongly H-bonded solid-like arrangement of water molecules is found in the adsorbed layer formed on hydrophilic surfaces at low RH and the weakly H-bonded liquid-like structure could grow to form multilayers above the solid-like layer at high RH [41,142,143]. In contrast, on hydrophobic surfaces, only liquid-like water layer exists, and its average thickness is normally less than a monolayer even at high RH [41]. The molecular configuration of adsorbed water has a strong influence on interfacial forces (involving  $F_a$  and  $F_t$ ) especially on two hydrophilic contacting surfaces. The condensation of the water meniscus in the contacting interface causes capillary interaction and increases  $F_a$ , which is added to the effective total normal load and, naturally, leads to a high  $F_t$  during the sliding process. The effect of the adsorbed water structure on the adhesion and friction behaviors of hydrophilic contacting interfaces must also be taken account. The strong H-bonded networks formed in the water meniscus connecting surfaces, but also increases the sliding resistance during relative shear motion.

Further experimental studies and computational calculations with appropriate potential fields are still required to detect the role of water condensation in nanotribological behaviors. Because experimental characterization of interfacial water structures within and around the nanoasperity contact is extremely difficult (if not impossible), the contribution of the solid-like component of the adsorbed water layer to adhesion or friction can be further elucidated from computational simulations. The dynamic structure and molecular details of the interfacial water meniscus could be revealed further through computational simulations.

Water condensation can cause  $F_c$ , which is normally considered an additional applied load contributing to the effective total force during the sliding process. A widely accepted model for friction describes the relationship between  $F_t$  and normal forces  $(F_n + F_a)$ , i.e.,  $F_t = \mu(F_n + F_a)$ , where  $\mu$  is the friction coefficient [108,144]. Although both  $F_a$  and  $F_t$  at the nanoasperity contact increase with the growth of the water meniscus, the increase in amplitude of these two components may not be consistent. For example, Yu et al. [145] compared the RH dependence of  $F_a$  and  $F_t$  between hydrophilic Si oxide contact interfaces at the nanoscale levels and found that the increase in  $F_a$  is slow when RH < 30% but fast as RH rises from 30% to 50%. However,  $F_t$  increases rapidly at low RH but slowly at high RH. These results indicate that simply adding  $F_a$  to the total normal load may be inappropriate. This inconsistency may relate to the difference in configurations of the condensed water layer evolving with RH in two different experimental conditions— $F_a$  is measured while applying tensile stress normal to the surface, while  $F_t$  is measured while applying compressive normal to the surface and shear stress tangential to the surface. Thus, the real contribution of capillary-related adhesion to friction should be further detected, especially on account of the evolution of the adsorbed water structure.

This review mainly focuses on the adsorbed water at the outermost surface of solids involved in tribological contacts. Interestingly, water molecules intercalated between 2D materials and substrates can also affect the interfacial friction force on the 2D material surfaces. For example, water molecules can intercalate under the graphene or  $MoS_2$  layers covering hydrophilic substrates. This confined water layer was found to significantly enlarge friction at graphene or  $MoS_2$  surfaces [146–150]. The enhancement of friction by intercalated water can be primarily attributed to the activation of graphene flexural modes and the high frequency modes involving O-H vibrations which effectively promote energy transfer to the substrate. However, the thickness and structure of the confined water layer are difficult to determine, which may be another factor to affect the interfacial forces.

Not only the condensation of pure water, but other types of liquid may also form the annulus of a capillary-condensed ring around the contact zone and play an important role in the interfacial forces [151]. The liquids studied so far include aqueous electrolyte solutions [152,153], polymer melts [154], liquid alkanes [155], various lubricant liquids [156], ionic liquid [157], alcohols [105], or their mixture. The chemical and physical properties of adsorbed liquids, such as chemical activity, surface energy, viscosity, molecular configuration, molecular polarity, cationic species, are likely to become important determinants. They may induce interfacial tribochemical reactions, hydrodynamic

effects, ion exchanges, liquid-solid phase transitions, thereby affecting the interfacial adhesion and friction forces [15,155–158].

Finally, besides interfacial forces, surface wear caused by frictional shear stress is likely to complicate the dynamics [4,159]. Tribochemical reactions may occur between water molecules and the solid surface when the activation energy of these reactions is reduced by an external mechanical action [5,160–167]. The structure and surface energy of the adsorbed water layer on dynamically changing tribological interfaces may also play vital roles in the mechanochemistry involved in the material removal phenomenon. In most cases, adsorbed water layers with different molecular configurations influence interfacial reactions via a coupling manner. Thus, distinguishing their individual contributions is difficult. Furthermore, well-designed model experiments coupled with computational simulations of the evolution of adsorbed water configurations could provide further insights into the removal mechanism of various solid-adsorbate-solid interfaces.

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