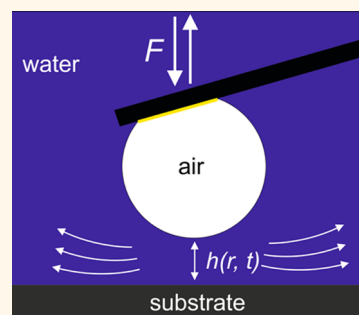


Forces and Thin Water Film Drainage in Deformable Asymmetric Nanoscale Contacts

Holger Schönherr*

Physical Chemistry I & Research Center of Micro and Nanochemistry and Engineering (C_μ), Department of Chemistry and Biology, University of Siegen, Adolf-Reichwein-Str. 2, 57076 Siegen, Germany

ABSTRACT Gas–liquid interfaces are omnipresent in daily life, and processes involving these interfaces are the basis for a broad range of applications that span from established industrial processes to modern microengineering, technology, and medical applications for diagnosis and treatment. Despite the rapid progress in understanding intermolecular forces at such interfaces from a theoretical point of view and, in particular, from an experimental point of view down to sub-nanometer length scales, the quantitative description of all relevant forces, particularly the hydrophobic interaction and the dynamic behavior of nanometer-scale confined water films, was until now unsatisfactory. This situation is particularly the case for the elusive description and understanding of the origins of the so-called hydrophobic interaction. For soft, deformable interfaces, such as those found in asymmetric contacts between gas bubbles and a solid, a complete picture has begun to emerge that has direct consequences for interfacial water at (bio)interfaces, functionalized gas microbubbles, surface nanobubbles, and beyond.



The relevance of interfaces and intermolecular interactions at interfaces was realized many decades ago and is fascinating from a scientific point of view but remains controversial in some areas. Spanning the fields of surface science in high vacuum with its ties, for example, to catalysis or to the complex situation of biointerfaces at the border of physics and physical chemistry with biology and medicine, the broad range of questions to be addressed and applications to be harnessed can be very specific but are certainly worthwhile. The complexity of the physics of surfaces and interfaces is well conveyed in the famous quote “God made the bulk; surfaces were invented by the devil,” attributed to Wolfgang Pauli; however, the rapid progress in science and technology may lead one to believe that this statement is no longer true. Despite the development and successful application of powerful experimental tools, such as the surface forces apparatus, the atomic force microscope (AFM), advanced synchrotron light sources, and free electron lasers, and the establishment of theory and closely coupled simulations covering many orders of magnitude in terms of relevant time and

length scales, one has to admit that certain fundamental questions have not been resolved, in particular, for arguably soft, deformable gas–liquid (gas–water) interfaces.

Among those are the so-called “surface nanobubbles” that have been observed at the solid–liquid interface and seem to violate established concepts of physical chemistry, in particular, wetting.^{1–3} Their existence has been intermittently debated and is still not unequivocally confirmed due to experimental limitations. Their highly unusual nanoscopic contact angles and unexpected stability have triggered significant interest. Due to the nanoscale dimensions and deformable properties of surface nanobubbles and the associated experimental challenges, contradicting results have been reported. Of even broader interest is the elusive and satisfactory *quantitative* description and the identification of the origins of the ominous “hydrophobic interaction”, which was and still is discussed controversially.⁴ Despite many reports about its range and magnitude and descriptions of the distance dependence of hydrophobic interactions at solid surfaces, its origin and a quantitative description for deformable droplets and bubbles remain open issues.

* Address correspondence to schoenherr@chemie.uni-siegen.de.

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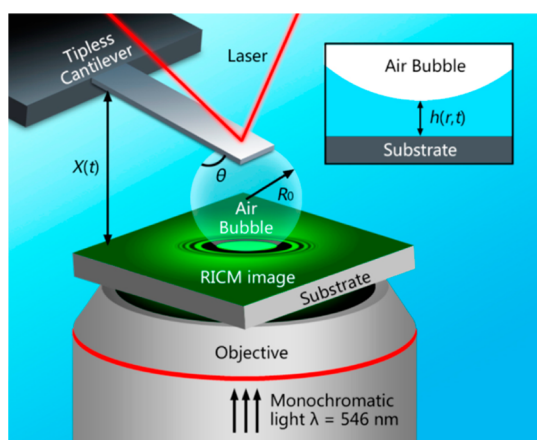


Figure 1. Combined atomic force microscopy and reflection interference contrast microscopy experimental setup used by Shi *et al.*⁵ An air bubble of radius R_0 is attached to a hydrophobic patch at the end of the bare AFM cantilever and is brought in AFM force–displacement measurement mode into contact with the transparent hydrophobized mica substrate underneath. The RICM measures the thickness $h(r,t)$ of the water film confined between the bubble and the mica continuously (compare inset). Reproduced from ref 5. Copyright 2015 American Chemical Society.

In this issue of *ACS Nano*, Shi *et al.* report on the elucidation of forces at an asymmetric contact between a gas bubble in water and surfaces with systematically varied hydrophobicity and the temporal evolution of the water confined in this nanoscale contact.⁵ In their elegant experimental approach (shown schematically in Figure 1), Shi *et al.* combined established sub-nanonewton resolution force measurements from AFM with simultaneous reflection interference contrast microscopy (RICM) for measurements of tip–sample gaps with nanometer-scale z-resolution in order to follow the interaction forces and the thickness of the water confined between the bubble and the surface in real time. In their experiments, which were conducted using various approach and retraction rates to assess the thin film drainage dynamics and, importantly, the impact of the bubble deformation, the solid mica surface was functionalized with hydrophobic silanes to adjust hydrophobicity.

The force data obtained in the absence of the hydrophobic interaction on bare mica (as a reference and test for the conditions and models applied) as well as on mica

with different hydrophobicity were described *quantitatively* with a theoretical model proposed (for selected data, see Figure 2). The model comprises the Reynolds lubrication theory and the augmented Young–Laplace equation and takes the effects of the disjoining pressure into account.⁵ The data could be described with a hydrophobic interaction free energy per unit area $W_H(h)$ with a decay length between 0.8 and 1.0 nm, depending on the surface hydrophobicity.

From a fundamental point of view, this study, together with other recent efforts addressing droplets and solid surfaces,^{6,7} contributes to the description of the physics of the mutual interaction and dynamics of bubbles, droplets, and solid substrates in a concerted manner by explicitly considering the deformation of soft interfaces and thereby eliminating previous uncertainties and ambiguities. The ingenious approach by Shi *et al.*, which relies on and expands previous AFM force spectroscopy⁸ and AFM-RICM techniques⁹ by using them synchronously, appears to be generalizable and, hence, carries the promise that a consistent and complete picture can rapidly be obtained.

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A comparison of the data by Shi *et al.*⁵ with recent data of decay lengths reported for hydrophobic surfaces⁷ indicates good agreement. A shorter decay length reported previously for interacting oil droplets⁶ was qualitatively rationalized by the different ways the interfaces may react to rearrangement of interfacial water molecules. The rigidity of the hydrophobizing silane monolayer in the experiments is certainly different from the oil droplet studies. Hence, one can expect a range of decay lengths of the hydrophobic interaction depending on the systems' particular chemistry (hydrophobicity) and rigidity.

OUTLOOK AND FUTURE CHALLENGES

Interfacial Water. These results are noteworthy considering interfacial water for biologically relevant interfaces and man-made biointerfaces (e.g., to control protein adsorption). In a classic example, the groups of Whitesides and Grunze demonstrated that the tilt angle of the same oligoethylene glycol-terminated thiols in self-assembled monolayers, caused by the different underlying metal, determines whether or not the interface resists protein adsorption.¹⁰ This experimental

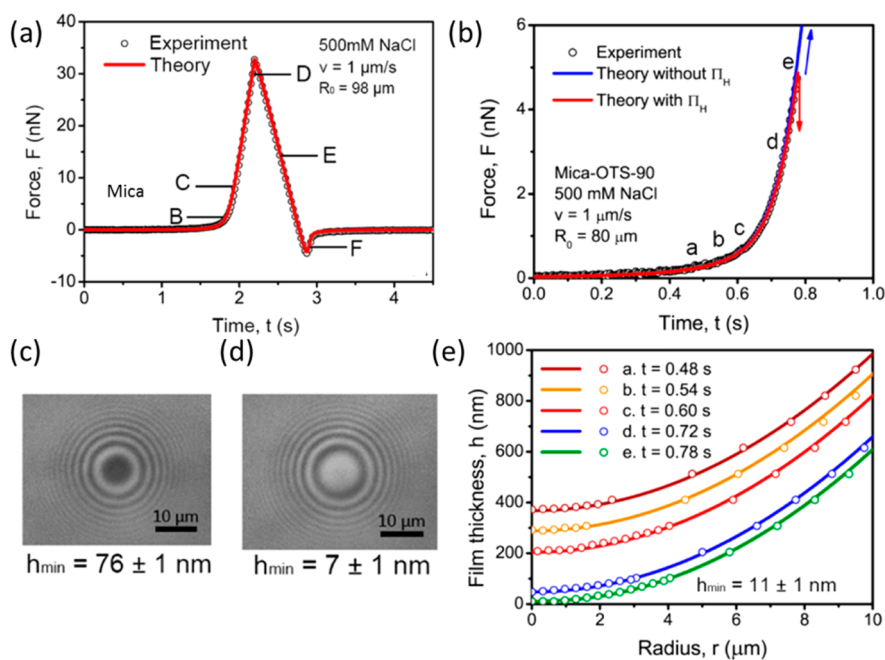


Figure 2. (a) Interaction force F as a function of time t during interaction between an air bubble and a hydrophilic mica surface in 500 mM NaCl solution and superimposed fit of the model. At this high salt concentration, the electrical double-layer interaction between the bubble and the mica surface was highly screened, eliminating its contribution to the overall disjoining pressure. The disjoining pressure due to van der Waals interaction is repulsive at all separations. Hence, a thin water film is maintained between the bubble and the mica. (b,e) Experiments and models of the (b) force between and (e) thickness of an air bubble and a hydrophobic mica surface (contact angle 90°). (c,d) Interference fringe patterns, from which the film profiles were deduced corresponding to positions (c) B and (d) D in panel (a). Figure adapted from ref 5. Copyright 2015 American Chemical Society.

finding, though surprising at the time, was rapidly rationalized, and the role of interfacial water has been further established by experimental work including force measurements and also by advanced simulations. With the recent progress in simulations, the results discussed by Shi *et al.* will lead to new insights in future simulations because the contribution of the underlying hydrophobic interaction can explicitly be taken into account.

Functionalized Microbubbles. Direct impact is also identified for gas microbubble approaches developed for medical diagnostics and therapy in theranostic applications.^{11–13} Not only do they promise to provide access to a full description of the forces and eventually the processes in *in vitro* experiments, but they also may give important hints for the complex and crowded *in vivo* situation. This appears to be beneficial for loading suitably decorated theranostic microbubbles with external payloads *via* adsorption.

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In addition, guided assembly or even targeting of deformable objects, including (functionalized) bubbles and droplets, to preselected positions at adequately functionalized and designed surfaces can be envisioned. By carefully

controlling and exploiting the forces and drainage of water films in nanoscale contacts in addition to established colloidal forces, complex assemblies may be constructed by assembly of nano- to mesoscale building blocks.¹⁴ Considering that previously reported approaches relied on patchy particles¹⁵ and soft hydrogel micro building blocks,¹⁶ entirely new two-dimensional and three-dimensional architectures may be envisioned.

Nanobubbles. While an exploitation of the findings by Shi *et al.*⁵ in terms of assembly, as sketched above, requires further effort and development, the relevance for gas–liquid interfaces, such as those found for nanobubbles, is more immediate. The generation of small bubbles that are amenable to combined and synchronous AFM and RICM analysis is currently at the heart of several large-scale efforts: In addition to the mentioned theranostic microbubbles,¹¹ the use of plasmonics to generate small

bubbles has garnered a great deal of attention.¹⁷ In view of energy harvesting and conversion and the quest for sustainable uses of solar energy, among others, dynamic processes involved in bubble nucleation and growth and bubble interactions are required. Depending on the dimensions, scale may be an obvious issue. Unfortunately, the exquisite resolution of RICM as a diffraction-limited optical technique is constrained to the surface normal direction, in which it provides nanometer-scale resolution. Even though interference techniques have been employed to study surface nanobubble appearance and dynamics by Karpitschka *et al.*,¹⁸ the nanobubble profile cannot be reconstructed from the data. Likewise, even though the role of hydrodynamic forces in AFM imaging (*i.e.*, the origin of repulsive forces during imaging and the deformation of nanobubbles) was unraveled by Walczyk *et al.*,¹⁹ a direct application of the elegant approach by Shi *et al.*⁵ is only applicable for larger bubbles. However, data obtained in carefully controlled experiments with microbubbles still provide input for nanobubble research.

Finally, in encompassing and addressing all relevant current and future directions in this area of deformable soft interfaces, interactions, and confined nanometer-scale liquid films, it is fair to conclude that further theoretical modeling and simulation, parallel to experimental refinement and efforts, are required. These will certainly progress rapidly; as briefly discussed in this Perspective, the close link between theory and experiment has been laid as a foundation.

Conflict of Interest: The author declares no competing financial interest.

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