

# Concluding remarks for FD 146: Answers and questions

Frank H. Stillinger

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## Introduction

In view of the attractiveness of the basic science involved, and the significance of its applications, it was quite natural and appropriate that a *Faraday Discussion* in 2010 would be devoted to the Wetting Dynamics of Hydrophobic and Structured Surfaces. Powerful motivation for continued scientific and engineering advances in this area arise from sources as diverse as the fundamental role of hydrophobic interactions in molecular biology, the importance of natural and artificial self-cleaning surfaces, the production of water-repellant textiles, and the technological requirements of microfluidics. The high rate of current related research activity is hard to miss; even as the nearly two dozen invited papers for this *Faraday Discussion* were being prepared by their authors, collected by the conference organizers, and distributed to participants, the scientific literature exhibited a continuing stream of publications in the same scientific area covered by this *Faraday Discussion*, but from yet other research groups.<sup>1</sup> As further evidence demonstrating widespread creative involvement in this pervasive subject, one can cite two other recent and closely connected *Faraday Discussions*, namely FD129 “The Dynamics and Structure of the Liquid–Liquid Interface”, and FD141 “Water—From Interfaces to the Bulk”.

This *Faraday Discussion* 146 arrived with an important distinction in comparison with its forerunners. The formal meeting was immediately preceded by a three-day Graduate Research Seminar (April 9–11, 2010), held locally at the Virginia Commonwealth University School of Engineering. This introductory activity was arranged for the benefit of involved undergraduate, graduate, and postdoctoral students, numbering roughly 40, who would also be part of the following FD 146. Beyond its social amenities, this Graduate Research Seminar offered five formal lectures by established experts (Widom, Yeomans, Evans, Klein, and Quéré) who would also be involved as invited speakers in the *Faraday Discussion* sessions to follow. In addition, this Graduate Research Seminar included student oral presentations, and two poster sessions. The organizers’ intentions behind arranging this introductory meeting were to familiarize the young participants with major aspects of the general scientific field, with its terminology, and with at least some of its more seasoned practitioners. Evidently this strategy was successful in bringing the student group into more comfortable interaction with ongoing research activities; during the subsequent three-day *Faraday Discussion* itself, many of the technical questions and comments directed at the invited speakers were posed confidently and with insight by the younger population of students and committed scientists, an encouraging sign for the intellectual future of the field. A broader implication is that at least some future *Faraday Discussions* might benefit similarly by arranging analogous preliminary meetings for their own groups of devoted students and early-career scientists.

In addition to the formal invited lectures presented at *Faraday Discussion* 146 (April 12–14, 2010), the program also included its own pair of poster sessions.

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Department of Chemistry, Princeton University, Princeton, NJ, 08544, USA

Among those poster presentations, three were selected for awards to recognize their excellence. Those awards were announced publicly at the close of Session 6, Tuesday afternoon.

Viewed in a conceptually coarse-grained way, the contributed papers FD146: 1–23 can be crudely classified into two categories, “experimental”, and “theoretical/simulational”. In this naively simplified view there were 12 of the former and 11 of the latter. This near-unity ratio may reflect a little something about the prejudices of research funding sources, but perhaps more importantly it is roughly consistent with the distribution of opportunities for substantial scientific advances in the immediate future. The listing of abstracts for the poster session that was distributed to participants presented a somewhat different ratio; with a nearly 50% incremental dominance of the former over the latter. Considering the fact that poster presenters demographically tend to be significantly younger on average than invited speakers, this discrepancy may be a harbinger of a future trend in research activity surrounding this Faraday Discussion’s chosen subject.

A successful scientific meeting is a positively memorable event, and this FD146 qualifies for that description. For those participants who traveled from Europe to attend and contribute to the meeting, expecting to return on schedule, there was an additional unpleasant memory that arose unexpectedly. On the last day of the meeting, April 14, the Icelandic volcano Eyjafjallajökull began to emit a seriously disruptive amount of gas and ash, with the unfortunate result that airline travel across the Atlantic Ocean was interrupted for several days.

Remarks below have been divided into three parts. The first involves a brief view of some aspects of the collection of invited papers, as well as the discussions that they stimulated, and the poster presentations. These can fairly be taken as representing the current scientific and technological status of the field. This is followed by two lists of suggestions for possible future research, one for experiment and one for theory/computation. These lists include, but extend well beyond, the Faraday Discussion’s selected topic of Wetting Dynamics of Hydrophobic and Structured Surfaces. Nevertheless they represent only a small fraction of the opportunities for future advances. The reason for adopting this broader viewpoint is the generally acknowledged necessity of establishing as many intellectual ties as possible to other areas of the physical and biological sciences, with the expectation that those connections and the conceptual feedbacks that they can generate will yield fundamental and useful insights for aqueous surface chemistry, physics, and biology.

## Present status

The formal program began with a comprehensive introductory lecture delivered by Prof. P. J. Rossky. Its emphasis was on the molecular level interactions and cooperative phenomena that underlie the macroscopic observations central to this *Faraday Discussion*. Ultimately these regimes at quite different length scales need to be much more deductively connected than they are at present. This introduction was followed by two sessions (five invited papers) devoted primarily to superhydrophobic surfaces, two subsequent sessions (seven invited papers) for dynamic transitions at various surfaces, one session each for liquid–vapor interfaces and nanobubbles (three invited papers) and for hydrophobic surfaces (two invited papers), and two final sessions (five invited papers) focusing on heterogeneous surfaces. These presentations and the audience questions that they generated can be described overall as indicative of a vigorous and imaginative scientific field that is in its intellectual adolescence. The experimental and theoretical advances reported (and this is true of the poster presentations too) involve clever experimental and theoretical techniques, but much has yet to be accomplished. The scientific areas covered by *Faraday Discussion* 146 will remain lively and productive; they are unlikely to “dry up” intellectually in the foreseeable future.

It is worth mentioning that six of the invited talks presented reported classical molecular dynamics simulations results that utilized either the simple point-charge model “SPC”<sup>2</sup> to describe water intermolecular interactions (146/17<sup>3</sup>), or its extension “SPC/E”<sup>4</sup> that incorporates polarization self energy (146/06,<sup>5</sup> 146/13,<sup>6</sup> 146/18,<sup>7</sup> 146/22,<sup>8</sup> and 146/23<sup>9</sup>). A significant number of distinctively different alternative model interactions have been proposed to describe water.<sup>10,11</sup> Therefore it is at least temporarily beneficial for the subject under consideration here to have simulation efforts focused on essentially a single model. This allows consistent comparison of results that examine different physical situations to produce a more comprehensive view of the molecular phenomena that water and its solutions produce. In the future it will inevitably become advantageous to graduate to simulations consistently based on a different and more physically accurate interaction model for water.

As a minor side issue arising both in one of the public presentations as well as during informal conversations, the semantic appropriateness of the adjectives “hydrophobic” and “superhydrophobic” was raised for the situations in which these words are normally invoked. It is generally acknowledged that however weak it might be, there is always a net attraction between a droplet of pure water or other liquid and a nearby solid (uncharged) substrate, due at least to van der Waals interactions. So one can argue that “phobia” is really always “philia”, but with highly variable magnitude. No serious alternative terminology has been proposed, however.

The fact that water, aqueous solutions, and their related surface phenomena were thematically central for FD146 invites a bit of historical perspective. Dispersed within the vast inventory of valid scientific contributions concerning water that have accumulated over many years are a few bizarre claims. And indeed the final refutations of these bizarre claims speak well for the normal operation of the scientific method. Notorious specific examples are “polywater”,<sup>6</sup> “cold fusion”,<sup>13</sup> and “dilution memory”.<sup>14</sup> By contrast the invited and contributed research presentations at FD146 were consistently representative of “normal” scientific inquiry, constituting valid and useful progress.

## Prospects for experiment

Many of the distinguishing properties that pure liquid water exhibits in thermodynamic equilibrium are magnified as it is supercooled below the freezing point. These magnifying properties include negative thermal expansion, high isothermal compressibility and isobaric heat capacity, and isothermal reduction in shear viscosity with increasing pressure. These metastable bulk-phase properties have been widely explored and well documented.<sup>15</sup> However there has been relatively little attention devoted to the water surface properties in the supercooled regime that would bear on the subject of this *Faraday Discussion*. Specifically, the surface tension  $\gamma(T)$  needs careful determination for supercooling toward  $-35^\circ\text{C}$ , the range where several bulk properties hint at an impending divergence,<sup>15</sup> to establish if it exhibits its own singularity. The obvious corollary issue is how the static contact angle  $\theta_c(T)$  for supercooled water droplets on various hydrophobic and superhydrophobic surfaces behaves as temperature declines. The water droplets typically examined experimentally for investigations of the types covered in this *Faraday Discussion* have the advantage of relatively low ice nucleation rates because of their small volumes, a major advantage in attempting to probe the deep supercooling regime.

The simple structure of the isolated water molecule (nominally exhibiting symmetry  $C_{2v}$ ) implies that it is achiral (geometrically unchanged under mirror imaging). Consequently its liquid behavior on a patterned surface of low symmetry that itself displays a definite handedness will not change if that substrate’s pattern handedness is reversed (*i.e.*, mirror imaged). However many substances have optically active chiral molecules with stable liquid ranges that are convenient for experiment. An example is 3-methyl hexane (m.p.  $-119.4^\circ\text{C}$ , b.p.  $92^\circ\text{C}$ ). The pure *D* and *L*

enantiomers of such substances would exhibit identical liquid–vapor surface tensions as a function of temperature, and would behave identically on an achiral substrate (*e.g.*, contact angle as a function of temperature). However mixtures of the two mirror-image enantiomers could be expected to show a composition dependence of the equilibrium liquid–vapor and liquid–substrate interfacial free energies. This in turn should lead to measurable *D*, *L* mixing effects on droplet contact angles.

At least equally instructive would be how these pure enantiomorphs and their racemic mixtures would behave next to chiral solvophobic substrates. In particular chiral ligands could be grafted onto a suitable flat substrate such as silicon or gold, against which *D* and *L* enantiomers would then in principle behave differently. In the case of the just-mentioned optically active alkane liquid 3-methyl hexane, perfluorinated optically active ligands should produce non-wetting surfaces. Several distinct possibilities arise when these chirally-distinct surfaces are brought into near contact, depending on whether they display the same or opposite chirality, and even whether the intervening liquid is chiral, a racemic mixture, or even non-chiral.

It should not escape attention that some polyatomic substances exhibit two-dimensional crystal structures in their liquid–vapor interfaces over a non-trivial temperature range above their bulk thermodynamic melting points. This unusual phenomenon has been established for the normal alkanes  $C_nH_{2n+2}$  in the chain-length range  $16 \leq n \leq 50$ ,<sup>16,17</sup> and as would be expected it affects the static and dynamical properties of substantially planar interfaces.<sup>18</sup> The influence of this surface crystallization on static and dynamical properties of small droplets, specifically their contact angles at various lyophobic substrates, is largely unknown and so deserves experimental investigation.

The aqueous surface phenomena receiving attention at this *Faraday Discussion* would benefit from being viewed in the wider scientific context of other classes of liquids and their own characteristic surface phenomena. An extreme related area might be identified as involving liquid metals; these typically display much larger surface tensions than those for aqueous fluids, and have virtually no tendency to wet organic substrates. The most obvious candidates for “temperature-convenient” measurement are mercury [m.p.  $-38.87^\circ\text{C}$ , b.p.  $356.58^\circ\text{C}$ ,  $\gamma(20^\circ\text{C}) \cong 475 \text{ dyn/cm}$ ] and gallium [m.p.  $29.78^\circ\text{C}$ , b.p.  $2403^\circ\text{C}$ ,  $\gamma(\text{m.p.}) \cong 718 \text{ dyn/cm}$ ]. However the former has a well-deserved bad reputation on account of the toxic nature of its vapor around room temperature. But by contrast the very high boiling point of the latter indicates that it has a far lower tendency to vaporize until very strongly heated. It would be edifying to classify various ionic-crystal, semiconductor, and metallic substrates as “mercuriophobic” and “galliophobic” (alternatively “mercuriphilic” and “galliophilic”) *via* contact angle observations, as well as to determine quantitative details of mean forces as a function of distance acting between pairs of solid objects embedded in these metallic liquids.

On account of their historical role in this subject and their frequent mention in the literature, the leaves of the Lotus (*Nelumbo nucifera*, *Nelumbo lutea*) have become the “poster child” of superhydrophobicity. Consequently this phenomenon has traditionally been called the “Lotus Effect”. But in addition to the Lotus many other plant species also possess this beneficial characteristic.<sup>19</sup> Considering the fact that the superhydrophobicity leads to leaf self-cleaning as well as to reduction in opportunities for bacterial and fungal infections, it is natural to ask if this property might not also be useful for other plant species that do not currently exhibit it. In particular ornamental flowers, shrubs, and trees forced to survive in dirty urban environments might benefit from this characteristic. More specifically, genetic engineering (a.k.a. recombinant DNA<sup>20</sup>) has become a major contributor to optimizing the productivity of a wide variety of important crops. It would therefore be potentially valuable to identify and isolate the gene(s) that generate superhydrophobic leaf surfaces in various species, and to see if gene insertion could be exploited for additional agricultural advantage.

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## Prospects for theory/simulation

The geometric patterns of water-molecule hydrogen bonds present at a hydrophobic or superhydrophobic interface, and how they compare with patterns inside the bulk liquid at the same temperature and pressure have not been aggressively investigated, although they could be an important source of scientific insight. In particular, the occurrence frequency with which successive hydrogen bonds are arranged to form closed polygons of different sizes is a fundamental characteristic. Although some attention has been expended in this direction for solvation of small hydrophobic solutes such as methane,<sup>21</sup> more detailed simulational examination of extended hydrophobic/superhydrophobic surfaces is warranted. Of course this hinges on the definition of “hydrogen bond”, a concept that does not enjoy a unique definition, in spite of the consensus opinion of its basic relevance. But whether a geometric or a potential energy definition is chosen, it should be consistent with the agreed-upon presence and arrangements of hydrogen bonds between neighboring molecules in the crystal polymorphs of ice.<sup>22</sup>

Beyond hydrogen bond topology issues, the precise way that the distribution functions of various orders for water vary with distance from a hydrophobic or superhydrophobic surface has not yet been theoretically specified in sufficient detail. This concerns specifically the spatial rate at which surface perturbations of molecular distribution functions die away to be replaced by their bulk characteristics as the normal distance from the surface increases. That may indeed involve hydrogen-bond polygon size distribution variations, but it also simply involves number density and polarization density variations. These spatially decaying perturbations would be involved in the long-range tail of the water-mediated interaction between a pair of hydrophobes, such as a pair of flat surfaces, where the prevailing temperature, pressure, and distance were such that the drying phenomenon was avoided. In addition to the conventional descriptions provided by statistical mechanics of condensed matter systems, it may also be useful to examine the predictions of Casimir–Lifshitz theory for the effect of electromagnetic field fluctuations which (depending on the complex dielectric functions of the materials involved) can yield long-range attractions or repulsions.<sup>23</sup>

Within the macroscopic description regime, droplet contact angles can indeed be well defined and measured. This is true not only for static equilibrium contact angles  $\theta_c$ , but also for the advancing and receding contact angles  $\theta_a$  and  $\theta_r$  under droplet transport circumstances. But because water static and dynamic phenomena at hydrophobic and structured surfaces span length scales from the molecular to the macroscopic regimes, a basic issue is how, or even whether, contact angles can be precisely and uniquely defined for very small droplet systems. Computer simulations typically incorporate  $10^3$  to  $10^4$  molecules, which for liquid water involve droplet diameters of roughly 10 nm or less. Simply estimating contact angles in these simulations roughly from graphical images of instantaneous configurations is ultimately not a very satisfying procedure. If instead an objective and precise algorithm for extracting contact angles from molecular distribution functions were to become available, the effects of variable droplet size and of substrate type on those contact angles would become accessible and would yield useful insights into the physics and chemistry involved.

The capillary length  $l_c$  for a given liquid roughly represents the outcome of the competition between the liquid–vapor surface tension  $\gamma$  and the strength  $g$  of the gravitational field. It is defined by the elementary relation:

$$l_c = (\gamma/g\rho)^{1/2}.$$

Here  $\rho$  is the mass density of the liquid under consideration. For pure liquid water at the earth’s surface and at room temperature this length is approximately 2.7 mm. This is the order of magnitude of the vertical thickness of a puddle of water sitting

atop a flat and horizontal superhydrophobic surface, in other words an essentially macroscopic length. However it is an engaging fact that the effective value of the gravitational acceleration  $g$  can be increased by up to a factor of  $10^6$  in an ultracentrifuge.<sup>24</sup> This would formally reduce  $l_c$  for room-temperature water to approximately 2.7  $\mu\text{m}$ . It would be a challenging theoretical problem then to deduce the structure of the water hydrogen bond network geometry in such extreme  $g$ -flattened “puddles”, as well as to derive the  $g$  dependence of the contact angle. Nevertheless, water models currently in use for numerical simulation could probably supply a qualitatively accurate description.

The development of more accurate models (*i.e.*, approximations) for water molecule interactions and their utilization in simulations remains a major theoretical challenge. As stressed earlier there are advantages for various research groups at any given period to employ a common model interaction, however improvements eventually must be aggressively sought. In the long run some variant of the *ab initio* quantum mechanical method for calculating the potential energy in a group of interacting water molecules “on the run” may be the most advantageous strategy.<sup>25</sup> However at present that approach is not yet capable of dealing with the typical numbers of molecules in simulations at the accuracy required to contribute effectively to the subjects under consideration in *Faraday Discussion* 146. Instead, more precise and descriptive “semi-empirical” potentials should be devised. Specifically it would be useful to include intramolecular vibrational degrees of freedom, and the dependence of their frequencies on hydrogen bonding. Furthermore, it is important to recognize that the dipole moments of water molecules depend on their environment, so that moment magnitudes and directions will not be the same in bulk phases as in interfaces. Further research will be required to determine how best to represent these attributes in terms of minimally complex mathematical functions whose sums combine to produce the necessary  $N$ -molecule interaction potential energy function.

Presuming that a future *Faraday Discussion* devoted to the same or similar subjects as this one will occur in the foreseeable future, it will be instructive then to see if the kinds of qualitative suggestions listed here for both experiment and for theory/simulation will have generated substantive advances.

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