

9 Summary and outlook

We have analyzed the phase behavior and properties of interfacial and confined water, seen in experiments and simulations, from the point of view of statistical physics and based on the theory of phase transitions and critical phenomena. Such kind of analysis is obligatory, as in the phenomena considered above, we deal with macroscopic systems in various phase states. We show that the main regularities in the behavior of the confined water and water near surfaces are similar to those of other fluids. This conclusion is fully applicable to the surface critical behavior of water, the surface phase diagram of water, and the effect of confinement on the liquid–vapor phase transition. Comparison with other fluids allows distinguishing between the features typical for most fluids and features that are peculiar for water. Obviously, peculiar features of water are connected with hydrogen bonding, which dominates in the water–water interactions in an extremely wide range of thermodynamic conditions. Near any boundary, number of water–water hydrogen bonds unavoidably decreases, which is reflected in various surface properties of water. Besides, polyamorphism of bulk liquid water in supercooled region appears also in the behavior of interfacial and confined water.

Due to the strong water–water interactions, many surfaces on the earth are in fact hydrophobic, as they relatively weakly interact with water. Therefore, interfaces between liquid water and hydrophobic surface gain much importance in various biological, geological, and industrial processes. Accordingly, the depletion of liquid water density near surfaces is abundant, and solvophobic (hydrophobic) attraction between surfaces in liquid water is frequent phenomena. There is no increase in water ordering near hydrophobic surfaces. Similar to other fluids, weakly attractive surface has only disordering effect on a liquid water. For all one-component fluids, long-range interaction with a wall makes impossible a drying transition below the bulk liquid–vapor critical temperature. Accordingly, a vapor layer never appears between a liquid and a wall. Manifestations of a microscopic drying layer, which may be considered as a liquid–vapor interface completely attached to the wall, appear for strongly hydrophobic (paraffin-like) surfaces and at high temperatures only. In a wide range of thermodynamic conditions, depletion of water

density near hydrophobic surface in both vapor and liquid phases or in supercritical states is caused by the missing neighbor effect, and it is governed by the bulk correlation length.

Wetting transition of water may occur in a rather narrow interval of the water–wall interactions. This feature may be common for all one-component fluids interacting with a wall via a long-range attractive potential. The first layering transition of water on the hydrophilic surface is located at temperatures essentially exceeding the bulk freezing temperature. Although water is not unique fluid that possesses such peculiarity, this feature may be of special significance as the critical temperatures of the first layering transition are close to ambient and biologically relevant temperatures. Hence, strong fluctuations of interfacial (hydration) water in biological systems due to the proximity of the 2D critical point should be expected. The temperature-induced break up of the hydrogen-bonded network of hydration water occurring via a percolation transition is intrinsically related to the critical point of quasi-2D water, and it also occurs at biologically relevant temperatures. Remarkably, the hydration water in thermodynamic conditions, typical for living organisms, is highly sensitive to external perturbations. This may be one of the factors that are responsible for the biological function of hydrated biomolecules.

A specific rearrangement of the hydrogen-bonded network of liquid water relative to the bulk case takes place near hydrophilic surfaces. This rearrangement is aimed at preserving more energetically favorable water–water hydrogen bonds to compensate the missing neighbor effect. Therefore, a strong orientational ordering of water molecules in the first surface layer near hydrophilic surfaces is seen even in the absence of water–surface hydrogen bonds. Much weaker signatures of orientational ordering are seen in the second surface water layer, and they are practically absent in the third layer. So, the second water layer connects orientationally ordered first layer with the third layer with almost isotropic orientation of water molecules. As a result, there are two specific water layers near hydrophilic surfaces, whose local structure strongly differs from the bulk liquid water, whereas local structure of water becomes essentially bulk-like starting from the third layer. This peculiar feature of water appears in various phenomena: there are only one or two layering transitions of water; “bound” water of about one to two layers thick is not freezable and shows properties different from

those of the bulk ones; two-step sequential wetting scenario assumes condensation of two surface layers as a first step.

Ability of water molecules to form various kinds of local order in condensed state causes variety of its crystalline and amorphous phases at low temperatures. The transitions between liquid water phases with different local orders at low temperatures strongly affect the properties of water at ambient conditions. This effect is presumably responsible for various water properties, which makes water different from most other fluids and often called “anomalous” (liquid density maximum, heat capacity minimum, etc.). Naturally, the bulk polyamorphism appears also in water properties near surfaces. A transition of liquid water to strongly tetrahedrally ordered water upon cooling is the most important manifestation of this phenomenon as it occurs at ambient pressures. This transition is extremely difficult to detect in bulk water due to unavoidable crystallization. However, it is observed in many systems containing a confined water owing to the drastic change in various properties.

Despite the intensive studies of interfacial and confined water, many aspects of its behavior remain not well studied or even unclear. There are only a few studies of the phase diagram of confined water and of water adsorbed on the surface. Most of these studies are the simulations with very simple smooth surfaces. Clearly, experimental studies and simulations with more realistic surfaces are necessary. Repulsion between hydrophilic surfaces in liquid water gained much less attention than attraction between hydrophobic surfaces. However, this effect may be responsible, for example, for the destruction of some solids in environment with varying humidity. The liquid–liquid transitions of water, confined in various pores, should be studied because of their importance not only in understanding the properties of interfacial water but also aiming to locate these transitions in bulk water.

Further studies of interfacial water are necessary to clarify its role in functioning of living systems. This is a long-standing problem, and many efforts have been already made to understand the physical mechanisms behind the crucial role of water in biological function. Some aspects of this problem were clarified, but the self-consistent picture is far from being completed. There is an understanding that hydration water forms an environment for biomolecules, which enables their conformational dynamics and serves as a media for the mass

and charge transfer along biosurfaces. There are numerous evidences that the changes of the state of the hydration water (formation of a spanning water shell via percolation transition upon hydration, its qualitative changes upon varying temperature or pressure or due to addition of cosolvents) are directly linked to the important biological processes. To understand the origin of the crucial role of water in biological function, it is necessary to relate particular states of hydration water to various physical properties of hydrated biosystems. We hope that knowledge of the water properties in various phase states and at various thermodynamic conditions summarized in our book will help in solving this problem.