The microscopic structure of bulk and confined water is currently studied by using X-ray or/and neutron diffraction techniques which are complementary techniques. These diffraction techniques allow to access to the intermolecular pair correlation function $g(r)$ (31) of a system which is the probability density of finding another atom lying in another molecule at a distance r from any atom. In X-ray measurements, $g(r)$ is the pair correlation function of the molecular centers, to a good approximation equal to the oxygen-oxygen correlation function. In neutron measurements, $g(r)$ is the weighed sum of the three partial functions relative, respectively, to the oxygen-oxygen pairs, oxygen-deuterium pairs and deuterium-deuterium pairs. In particular, it is heavily dominated by deuterium-deuterium and oxygen-deuterium partial correlation functions.

The structural and dynamic properties of water may be affected by both purely geometrical confinement and/or interaction forces at the interface. Therefore, a detailed description of these properties must take into account, the nature of the substrate and its affinity to form bonds with water molecules, and the hydration level or number of water layers. To discriminate between these effects, reliable model systems exhibiting hydrophilic or hydrophobic interactions with water are required. This looks the appropriate strategy to be developed to access to some understanding of the behavior of water close to a biological macromolecule, as presented in the following sections.

In the past few years, computer simulations and theoretical treatments of the structure and dynamics of water in different kinds of environments have been undertaken (32–40). Some important results are now available. For instance, molecular dynamics simulations indicate that the water density increases up to 1.5 g/cm^3 in the first few angstroms of the shell around a protein and give information concerning the pair correlation functions and orientations of water molecules (41). Instead, it has been shown experimentally that a thin layer of water vapor is formed between liquid water and a hydrophobic surface (42).

The purpose of this chapter is to account for the more recent developments about the structure and the dynamics of bulk and confined water as a function of temperature. Examples relative to interactions of water molecules with model systems as well as with biological macromolecules will be presented.

THE STRUCTURE AND DYNAMICS OF LIQUID WATER: A SHORT REVIEW

In spite of an enormous amount of experiments performed with liquid water under different external conditions (1–9), many of its properties remain not fully understood. The main reason is the complexity of the intermolecular potential resulting from the formation of intermolecular hydrogen bonds. Such bonds are strongly directional and their study imposes the consideration of quantum effects.

Most of the recent theoretical developments have been achieved by computer simulations of the molecular dynamics using several sophisticated, effective potentials (3,10). Such potentials are written ad hoc to simulate at the best both the microscopic structure and the thermodynamic and transport properties. A general problem is that, either the potential imposes a too much strong and ice-like structure to reproduce the thermodynamic properties, or it reproduces well the pair correlation function $g(r)$ and then, the so-called water anomalies are not well reproduced. Many progresses have been achieved