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From simple surface models to lipid membranes: Universal aspects of the hydration interaction from solvent-explicit simulations

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ABSTRACT

A review of atomistic simulation approaches including explicit water for the study of hydration forces between polar surfaces is presented. In particular, we discuss different methods for keeping the chemical potential of water constant and compare advantages and limitations of each method. It turns out that modifications of hydration forces due to surface softness can be accounted for by a convolution over the surface shape profile. Universal aspects of the hydration interaction observed in simulations of different surface chemistries are highlighted, while special attention is given to hydration forces between self-assembled phospholipid membranes.

1. Introduction

Interactions between biological surfaces result from the interplay of contributions of different physical origins. They include dispersion interactions and electrostatic interactions screened by ions in the aqueous electrolyte. For large-enough surface separations, these two contributions can be treated in a continuum approximation known as DLVO theory [1–3], which neglects the atomic structure of the matter. In this case, the surfaces are considered as media with homogeneous properties (such as charge density and dielectric constant) that interact across the electrolyte. In the case of flexible surfaces, the model has to be augmented to account for the repulsive contribution of out-of-plane shape fluctuations, known as undulation or Helfrich repulsion [4,5]. An important contribution not captured by these continuum approximations is the so-called hydration repulsion, which acts between hydrophilic surfaces of diverse kinds [1]. In fact, the interaction between charge-neutral phospholipid membranes is dominated by this contribution over a wide range of separations [6,7]. Experimentally, the interactions between lipid membranes are quantified in terms of pressure-distance curves, which can be obtained using a surface force apparatus [8] or, more commonly, from diffraction experiments on membrane multilayers [6,9,10]. In the latter case, the water layer thickness (i.e., the surface separation) is measured as a function of a defined, externally applied osmotic pressure. In these experiments, it was found that the hydration repulsion obeys an exponential decay with a decay constant λ between 0.1 nm and 0.3 nm [7]. This parameterization has been widely used in modeling the interactions of adjacent membranes [11–14], although the mechanism of the hydration repulsion is still not fully understood. There have been several attempts to rationalize the repulsion between membrane surfaces, based on the notion that the water structure near polar surfaces is perturbed. Marcelja et al. predicted an exponential decay of the repulsion based on a general order-parameter description [15]. Later theoretical studies [16–18] focused on the orientational polarization of water at polar surfaces. These studies achieved qualitative agreement with experimental observations and in particular reproduced the exponential decay of the interaction pressure. Other explanations based on a lipid-protrusion mechanism [19] have been reviewed critically [20]. But despite the progress achieved with continuum models, it has become a consensus view during the last decades that in order to explain the hydration interaction on a quantitative level, the structure of the solvent has to be taken into account explicitly [7,21]. In recent years, this insight has drawn the attention towards the application of atomistic simulations, where water molecules are treated explicitly including all relevant degrees of freedom. In this article we review various approaches to study the interactions between surfaces in aqueous environments using atomistic simulations with a focus on the hydration interaction and its universal aspects.

2. Structure and molecular interactions from atomistic simulations

Even without quantifying the interaction between surfaces, qualitative aspects of the hydration repulsion between membranes were elucidated using atomistic molecular dynamics (MD) simulations. Those aspects included structural and molecular details. Raghavan et al. observed significant orientational polarization of water between phospholipid membranes in MD simulations [22]. This polarization

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has been interpreted in terms of the order parameter introduced by Marcelja et al. [15]. Essmann et al. identified a layer of hydration water molecules with stronger hydrogen bonds at phospholipid membranes [23]. This led to the picture that strongly bound water has to be squeezed out of the head group region upon close membrane contact, resulting in repulsion at short distances. In a later work Perera et al. [24] compared water organization and molecular interactions between membranes with phosphatidylcholine (PC) and phosphatidylethanolamine (PE) head groups in order to explain their different swelling behavior. They concluded that the difference in the structure of the solvation shell around PC and PE head groups is responsible for the difference in swelling. Faraudo et al. reported an anomalous dielectric response of thin water layers confined between charged surfaces [25]. In a later study, the electrostatic interaction of charged surfaces across a thin water layer containing counter ions was investigated [26]. It was found that the electrostatic repulsion was much stronger than predicted in a continuum Poisson–Boltzmann treatment, which was rationalized by the anomalous dielectric response of the confined water. This deviation would explain the additional repulsion measured in experiments on interacting charged surfaces. For a quantitative description of the hydration mechanism in atomistic simulations, the thermodynamics involved in the interaction of surfaces has to be taken into account. This is discussed in the following sections.

3. Interaction thermodynamics in atomistic simulations

The interaction of biological surfaces in aqueous environments is commonly quantified in terms of pressure-distance curves, where the interaction pressure Π is measured as a function of the separation D between the surfaces. At given temperature T and hydrostatic pressure p, the interaction pressure is related to the derivative of the Gibbs free energy, G, with respect to the surface distance, D, while the chemical potential of water, μ, remains constant:

$$\Pi(D) = -\frac{1}{A}\left(\frac{dG}{dD}\right)_{\mu,T,p}, \quad (1)$$

where A denotes the surface area. Thus, in order to determine Π in a computer simulation, the chemical potential of water has to be taken into consideration. μ is a measure for the change in free energy upon the addition of a water molecule to a system. It consists of two contributions, the ideal part, $\mu^{id}(\mathrm{r}) = k_B T \ln \rho(\mathrm{r})$, that depends on the water density, $\rho(\mathrm{r})$, and the excess part, $\mu^{ex}(\mathrm{r})$. In thermal equilibrium, μ is spatially constant in the simulated system. However, in an inhomogeneous system, μ^{id} and μ^{ex} both depend on the position r while only their sum is a constant,

$$\mu = \mu^{ex}(\mathrm{r}) + k_B T \ln \rho(\mathrm{r}). \quad (2)$$

4. Finite objects interacting in explicit water

The most direct way to control the chemical potential of water while studying the interaction of surfaces is to let objects of finite extension interact in a sufficiently large volume filled with explicit water molecules (see Fig. 1a). Since the water molecules involved in the interaction of the objects can exchange with the surrounding bulk water, the chemical potential will quickly converge to a constant value throughout the simulation volume. For large-enough volumes, this value will be sufficiently close to the corresponding reference value in pure bulk at the same pressure and temperature, denoted as μ_0. Due to its simplicity, this approach has been widely used for the study of various objects with different surface properties [27–33]. These studies have greatly progressed the understanding of surface interactions in aqueous environments.

4.1. Simple model objects

Wynween et al. studied the interaction of polarizable cylinders in water [27]. While for low polarizabilities (representing hydrophobic surfaces) the cylinders displayed attractive interaction, for high polarizabilities (representing hydrophilic surfaces) the interaction was repulsive. The latter was attributed to the solvation force exerted by the explicit solvent. This work demonstrated the importance of treating the water explicitly in MD simulations on solvation forces. Choudhury and Pettitt investigated the interaction of hydrophobic graphene plates in water [28]. They calculated the potential of mean force (PMF) between the surfaces as a function of their distance using Free-Energy-Perturbation [34]. The decomposition of the PMF into enthalpic and entropic contributions showed that the hydrophobic collapse (i. e., the complete de-wetting of the region between the surfaces) is driven by entropy. A similar approach was taken by Lu et al., but with a focus on the interaction of purely hydrophilic plates [29]. Here, the PMF was globally repulsive but showed modulations at the length scale of water molecules. These modulations indicate the layered structure of the water molecules confined between rigid surfaces. Despite its non-monotonic decay, the authors fitted the PMF with an exponential function and obtained a decay constant of $\lambda = 0.26$ nm, in agreement with the range observed in experiments. Huang et al. used MD simulations in order to study the interaction of hydrophobic ellipsoids in water with a focus on the kinetics of the hydrophobic collapse [30]. In a more recent investigation by Hua et al., this strategy was extended towards structured plates with hydrophobic and hydrophilic sites [31]. PMFs were calculated from the normal forces on the plates. For predominantly hydrophilic plates, the interaction was globally repulsive and showed modulations, consistent with the results of Lu et al. [29].

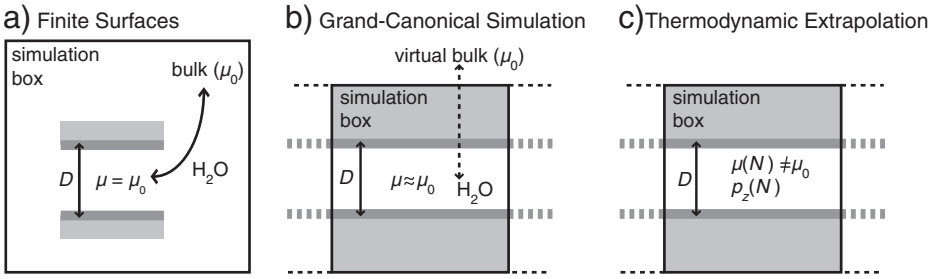

Fig. 1. Schematic comparison of different approaches for the treatment of the constant chemical potential of water in atomistic simulations of interacting surfaces. a) Finite objects interacting in a reservoir of bulk water. b) Grand-Canonical simulations: water exchange with a virtual bulk reservoir. c) Thermodynamic Extrapolation: correction for the shift in the chemical potential.