



Hydration repulsion between membranes and polar surfaces: Simulation approaches versus continuum theories



Matej Kanduč^{a,b,*}, Alexander Schlaich^a, Emanuel Schneck^c, Roland R. Netz^a

^a Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

^b Department of Theoretical Physics, J. Stefan Institute, SI-1000 Ljubljana, Slovenia

^c Institut Laue-Langevin, 6 Rue Jules Horowitz, 38042 Grenoble, France

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ABSTRACT

A review of various computer simulation approaches for the study of the hydration repulsion between lipid membranes and polar surfaces is presented. We discuss different methods and compare their advantages and limitations. We consider interaction pressures, interaction thermodynamics, and interaction mechanisms. We take a close look at the influence of the experimental boundary conditions and at repulsion mechanisms due to the unfavorable overlap of interfacial water layers. To this end, we analyze several distinct water order parameters in simulations of interacting polar surfaces and compare the results to the predictions of simple continuum theories.

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1. Introduction

The hydration repulsion dominates the interaction between hydrophilic surfaces in an aqueous environment at nanometer separations. It

reduces the mutual perturbation of biomolecular assemblies in the congested cellular environment and ultimately prevents the collapse of biological matter. The hydration repulsion between biological membranes creates a major barrier against close contact and thereby suppresses uncontrolled membrane adhesion and fusion [1]. At the same time, the residual water layers constitute hydrodynamic pathways for the diffusion of biomolecules. In summary, the hydration repulsion is vital for the structural organization of cells and organelles as well as for their functionality. Besides electrostatic, van der Waals, and undulation interactions, it is considered a fundamental interfacial force [2–5].

* Corresponding author at: Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany.

E-mail addresses: kanduc@physik.fu-berlin.de (M. Kanduč), aschlaich@physik.fu-berlin.de (A. Schlaich), schnecke@ill.fr (E. Schneck), rnetz@physik.fu-berlin.de (R.R. Netz).

The notion of a repulsive force due to hydration water was first introduced by I. Langmuir in 1938: “The fact that the particles [...] remain separated by considerable distances and do not come into contact proves the presence of some other kind of repulsive force [...]. Hydration seems to be the most reasonable explanation” [6,7]. Pressure–distance measurements with phospholipid membranes, typical models of biomembranes, in the late 1970s and '80s showed that the hydration repulsion obeys an approximately exponential decay with a decay length between 0.1 nm and 0.6 nm [8,2,9,10]. This parameterization has been widely used in studies on interacting membranes [11–14], although the repulsion mechanisms still elude quantitative theoretical description. In an effort to rationalize the hydration repulsion, three fundamentally different mechanisms have been proposed.

1) Repulsion due to the enforced release of water molecules that are strongly bound to the membrane surfaces: This picture requires that the sum of the molecular interactions, namely lipid–lipid, lipid–water, and water–water interactions, is most favorable when a finite amount of hydration water is accommodated between the membrane surfaces. Such a scenario may occur due to strong physical binding or a good complementary fit between water and surface groups. Clearly, the resulting enthalpic repulsion would be limited to the first few water layers directly interacting with the membrane surfaces [15,16].

2) Repulsion due to the reduction in configurational entropy of membrane lipids: Initially, this mechanism proposed by Israelachvili and Wennerström [17,18] has been merely associated with steric collisions between lipids protruding from the membrane surfaces into the inter-membrane space [19], but the concept can be successfully generalized also to lipid configurational entropy [16,20].

3) Repulsion due to the unfavorable overlap of interfacial water layers: The overlap of interfacial water layers, characterized in terms of suitably defined order parameter profiles, is generally associated with changes in a system's free energy [21]. It was first suggested by Marčelja and Radić that such a mechanism could be involved in the short-range repulsion between lipid membranes [22]. The basic concept was further refined [23] and frequently discussed in terms of the water molecules' dipole orientation [24–26].

While theory provides conceptual insight and scaling laws for each of the proposed mechanisms, it cannot predict the contribution of each mechanism on a quantitative level, since this depends on molecular details such as the conformational behavior and subtle differences in the interaction enthalpy of molecular groups. Quantitative description of the hydration repulsion between membranes thus requires rigorous modeling of all components including all relevant degrees of freedom. During the last decade, this insight has drawn the attention towards the application of atomistic molecular dynamics simulations [27]. In the present paper, we review various approaches to study the hydration repulsion between biomembranes using computer simulations and discuss the obtained results. We take a close look at the influence of the experimental boundary conditions and finally address the – still underexplored – role of the overlap of interfacial water layers for the hydration repulsion between lipid membranes. For this purpose, we combine continuum-theoretical arguments as proposed by Marčelja and Radić [22] and Cevc et al. [23] with the results of atomistic computer simulations of interacting polar surfaces.

2. The interaction of surfaces in water

Interaction of extended surfaces in the aqueous environment is commonly described in terms of pressure–distance relations, where the interaction pressure Π is measured as a function of the surface separation D_w . Π is then related to the derivative of the Gibbs free energy, G , with respect to D_w . When the surface area A is kept constant and D_w is varied by force exertion, while the system is in contact with a

bulk water reservoir of temperature T and water chemical potential μ , the corresponding pressure–distance relation reads:

$$\Pi_{\mu,T,A}(D_w) = -\frac{1}{A} \left(\frac{\partial G}{\partial D_w} \right)_{\mu,T,A}. \quad (1)$$

Importantly, μ is dictated by the reservoir and is independent of D_w in this scenario. Eq. (1) conceptually applies to the so-called surface force apparatus (SFA) experiments in which surface-functionalized plates are brought into close proximity while the interaction pressure is recorded [28]. This approach has also been used for the study of interacting membranes immobilized at solid surfaces [29]. Pressure–distance relations between lipid membranes are also commonly determined by subjecting membrane multilayers to hydrostatic pressures or so-called equivalent pressures of known magnitude [2]. The latter are realized under atmospheric pressure p by controlled competition for the hydrating water, i.e., by shifting the chemical potential μ of the surrounding water to lower values. According to the Gibbs–Duhem equation, such a shift $\Delta\mu$ corresponds to an equivalent pressure

$$\Pi_{p,T}(D_w) = -\frac{\Delta\mu}{v_w}, \quad (2)$$

where v_w denotes the volume of a water molecule. Equivalent pressures can be applied, for instance, by bringing membrane multilayers into contact with aqueous polymer solutions separated by flexible, semi-permeable membranes. The equivalent pressure is then equal to the osmotic pressure exerted by the polymers in solution. Alternatively, the hydration level can be controlled via vapor exchange with a water reservoir with shifted chemical potential. Significant shifts $\Delta\mu$ can be reached by saturated salt solutions, or by lowering the temperature of the reservoir, and can be expressed in terms of the vapor pressure p^v ,

$$\Delta\mu = k_B T \ln \frac{p^v}{p_0^v}, \quad (3)$$

where p_0^v denotes the vapor pressure of pure water at temperature T .

The water layer thickness D_w in all cases has to be measured independently. In SFA experiments, this can be done by light interferometry. In hydrostatic or equivalent pressure setups D_w is deduced from the measured lamellar periodicity L_z , either gravimetrically [30,2] from the volumes of lipids and water molecules (v_l and v_w) and from the number of water molecules per lipid n_w ,

$$D_w = L_z \frac{n_w v_w}{n_w v_w + v_l}, \quad (4)$$

or structurally [31] via scattering approaches.

The various experimental approaches to determining pressure–distance curves are not strictly equivalent, as membranes are subject to different boundary conditions: In SFA experiments, a mechanical force perpendicular to the membrane surfaces is exerted while the water layer thickness is varied. Under idealized conditions the area per lipid is kept constant at the same time. In equivalent-pressure experiments at atmospheric pressure conditions, on the other hand, the chemical potential of water is the only control parameter, and membranes are free to structurally respond to dehydration in all spatial directions. Finally, in an experiment exerting hydrostatic pressures, the membranes experience isotropic compression as they get dehydrated. In all these cases, the chemical potential of water is a key aspect of the interaction. It thus has to be taken into consideration also in computer simulations of surfaces interacting in the aqueous environment.

The chemical potential of water is a measure for the change in free energy upon the insertion of a water molecule into a system. It consists of two contributions, the ideal part, $\mu^{\text{id}}(\mathbf{r}) = k_B T \ln \rho(\mathbf{r})$, which only

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