Electroelastic Coupling between Membrane-Embedded Charges and Membrane Fluctuations: Continuum Multi-Dielectric Treatment

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Abstract

There is growing interest in understanding effects due to electronically promoted membrane-water fluctuations, which may influence voltage-gating in proteins. Membrane geometry is significantly altered by electronical interactions with membrane-embedded charged species. This paper describes an analytical continuum model for membrane-water fluctuations for arbitrarily shaped membrane-water interfaces in multi-dielectric environments. The model starts from the point charge by sphere approximation and contains all of the nonlinear effects of the problem: dielectric, elastic and solvation effects, and the linear Poisson-Boltzmann equation, directly calculating the potential due to the point charge via a method that eliminates self-energy contributions. The membrane treating a charge as a mixed liquid-water environment, e.g. one crossing the fluctuating membrane-water interface or interacting with a water phase penetrating the membrane’s hydrophobic core. We determine the energetics and optimized shapes of such aqueous deformations interacting electroelastically with the charge located at various positions in the membrane.

Introduction

Electroelastic coupling of electric fields or charges to membrane fluctuations is important for membrane stability, electromechanics, ionic transport and voltage gating [1]. This issue became especially relevant due to the breakthrough discovery [2] that the gating charges ‘‘s solvation energy is bistable: at some charge value, there is a new low-energy state with the charge solvated by a water “dimple”. The corresponding membrane fluctuations trigger the gating charge’s ‘‘s solvation, aided solvation. This prompted analysis of another route of instability, one where elastic fluctuations trigger the electrostatic energy fluctuates and increases (to ~5 and ~10 kT, q = 1.0e and 1.5e, respectively). For q = 0.5e, there is no stable state where the water dimple is in contact with the membrane surface. All other conformations are of higher energy. Higher q asymmetrically may reflect insufficiency relaxed free volumes.

LMC Reaction Path Following of the Charge across the DOPC Membrane

Figure 3. Dependence of total, electronic and elastic energy profiles on charge position for DOPC. For all h values, electronic and total energies are differences, with reference since the uncharged membrane had the charge immobile in bulk water (6 Å). The first plot portrays electronic energy profile for a flat water layer (orange water profile). The other plots are energy profiles for membrane free in solution: total energy with respect to the formation of charge for different q values. The charge was unidirectionally constrained to cross the membrane using LMC, with the initial position, then the reaction coordinate was monitored. All other degrees of freedom, were fixed. Higher q asymmetrically may reflect insufficiency relaxed free volumes.

We determined the energetics and optimized shapes of such aqueous deformations interacting electroelastically with the charge located at various positions in the membrane.

Solution Method

We determine the energetics and optimized shapes of such aqueous deformations interacting electroelastically with the charge located at various positions in the membrane. The electrostatic energy increases at the pore entrances due to membrane deformation and fluctuations near the region in between –7 and -4 Å. Lower pores the membrane deformation is larger.

Figure 2. Profiles of the electronic and elastic energy profiles as functions of the charge position. The elastic energy is in kT. For q = 0.5e, the elastic energy decreases slightly and then drops sharply. For a charge bound at |z|, the elastic energy always drops sharply. The electronic energy increases at the pore. For the uncharged membrane (ν = 0), the electronic energy drops sharply as the charge moves towards the membrane surface.

We addressed the question of bistability of the membrane-water fluctuations and used an analytical model for membrane-water fluctuations for arbitrarily shaped membrane-water interfaces in multi-dielectric environments. The model starts from the point charge by sphere approximation and contains all of the nonlinear effects of the problem: dielectric, elastic and solvation effects, and the linear Poisson-Boltzmann equation, directly calculating the potential due to the point charge via a method that eliminates self-energy contributions. The membrane treating a charge as a mixed liquid-water environment, e.g. one crossing the fluctuating membrane-water interface or interacting with a water phase penetrating the membrane’s hydrophobic core. We determine the energetics and optimized shapes of such aqueous deformations interacting electroelastically with the charge located at various positions in the membrane.

Speculations and Future Directions

Membrane-barrier charges can induce large amplitude fluctuations (dimples), which can be described as “atomic elastic” model. To describe such a change in the lateral component of the lipid hydrophobic core we modeled a “pore forming” mechanism.

A cylindrical water-filled membrane-spanning pore reduces the electrostatic barrier for charge translocation several-fold. Overall energetics depends on the pore radius, q, the membrane charge, and the fold in the barrier pore radius. Estimates of this wide, depending on interaction between membrane water and solute, and a large reorganization of the membrane-water network. Our semianalytical approach is based on elastic energy fluctuations and increases (to ~5 and ~10 kT, q = 1.0e and 1.5e, respectively). The energy peaks correspond to the occurrence of a water dimple.

References

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