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Entropy Driven Like Charched Condensation

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Like charged systems are expected to have repulsive interactions. However, attraction has been observed in a variety of systems, in the presence of multivalent counterions. This includes DNA condensation, as found within virus capsids or chromosomes and the attraction between similarly charged biopolymers such as microtubule or F-actin. Each system exhibits different behaviour and the observations cannot reside within a consistent framework.

We studied the interaction between mixtures of neutral and negatively charged lipids in pure water and in a variety of salt solutions. This is a good model system to study like-charge attraction because the membrane charge density can be controlled by the neutral/charged lipid stoichiometry. The strength of vdW interaction between the membranes, the elastic properties of the membrane and its dimensions can be controlled by the lipid tail structure.

In the meeting results showing how entropy derives long-ranged condensation of liked-charged membranes when no salt is added and under various conditions will be presented. The critical conditions needed for membrane condensation will be discussed.

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Free Energy and Conformation of Hydrocarbons in Lipid Bilayers

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Molecular dynamics simulations combined with umbrella sampling allows probing the free energy landscape for small molecules within a lipid bilayer. We have applied this method to several hydrocarbon molecules, some of which are biologically relevant substrates of membrane transporters. Molecules of hexane, decane, hexadecane, and nonacosane have been tested in bilayers of DOPC, and decane and hexadecane in DPPC. It has been found that these hydrophobic molecules overwhelmingly favor localization to the center of the bilayer, and that there is a significant cost to remove a molecule from the bilayer center, on the order of tens of kJ/mol. The free energy of removal is consistently dependent on the length of the molecule, varying from ~25 kJ/mol for hexane to ~70 kJ/mol for nonacosane. In addition to calculating the energy cost of removing these molecules from the center of the bilayer, it has been observed that long hydrophobic molecules such as alkanes tend to adopt two conformations in the center of the bilayer, either in the plane of the bilayer, between the terminal methyl groups of the lipid tails, or parallel to the bilayer normal, interdigitating with the lipid tails. Further constrained simulations may be used to calculate the rate of exchange between these two modes.

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Monte Carlo Simulations of Sterol Superlattice Mosaics in Bilayers Yield Simultaneous Agreement with Concentration and Chemical Potential Data

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Multiple experiments suggest that at certain mol fractions ($\chi_{\mathrm{sterol}} = C_r$) sterol molecules, cholesterol (chol) and ergosterol (erg), form superlattice (SL) structures occupying particular acyl chain sites in a lipid bilayer. We have constructed a theoretical model, which we have tested successfully against our own nystatin-erg channel data and the fluorescence measurements of sterol concentration [1]. Our Monte Carlo (MC) simulations show that mosaics of SLs, with structures strongly dependent on χ_{sterol} , form in bilayers for all χ_{sterol} studied. Here we successfully test the model against the chemical potential data using Kirkwood's coupling parameter method. Holding all interaction energies (sterol/sterol, sterol/lipid) constant the model successfully predicts simultaneously the observed increase in chemical potential [2] and no marked increase in sterol concentration at $\chi_{\mathrm{sterol}} = 0.4$ [1].

1. Chong, P.L-G., and M. Olsher. 2004. Fluorescence Studies of the Existence and Functional Importance of Regular Distributions in Liposomal Membranes. Soft Mat. 2:85-108.

2. Ali, M.R., K.H. Cheng, and J. Huang. 2007. Assess the nature of cholesterol-lipid interactions through the chemical potential of cholesterol in phosphatidylcholine bilayers. PNAS 104:5372-5377.

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The Temperature Dependence And Quantized Nature Of The Lipid Membrane Permeability

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We investigate the permeability of phospholipid membranes for fluorescence dyes and ions. We find that the permeability is strongly enhanced close to the chain melting transition of the membranes. Close to transitions, fluctuations in area and compressibility are high, leading to an increased likelihood of spontaneous lipid pore formation. Fluorescence Correlation Spectroscopy (FCS) reveals the permeability for rhodamine dyes across 100 nm vesicles. Using FCS, we find that the permeability of vesicle membranes for fluorescence dyes is within error proportional to the excess heat capacity. To estimate defect size we measure the conductance of solvent-free planar lipid bilayer. Microscopically, we show that permeation events appear as quantized current events. Furthermore, we demonstrate that general anaesthetics lead to a change in membrane permeability that can be predicted from their effect on heat capacity profiles. Depending on temperature, the permeability can be enhanced or reduced. We demonstrate that anaesthetics decrease channel conductance and ultimately lead to 'blocking' of the lipid pores in experiments performed at or above the chain melting transition. Our data suggests that the macroscopic increase in permeability close to transitions and microscopic lipid channel formation are the same physical process.

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Headgroup and Interfacial Hydration in Some Headgroup-Modified Analogues of Dimyristoylphosphatidylethanolamine: A DSC and FTIR Spectroscopic Study

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The thermotropic phase behavior and organization bilayers composed of dimyristoyl phosphatidylethanolamine and some of its headgroup-modified analogues were investigated by differential scanning calorimetry and by fourier-transform infrared spectroscopy. As expected, chemical modification of the lipid headgroup resulted in changes in the gel/liquid-crystalline phase transition temperatures of the analogues that were positively correlated with the capacity for inter headgroup hydrogen-bonding to the phosphate moiety, and negatively correlated with the size of the headgroup substituent. However, such changes also drastically altered the nature of the lamellar crystalline phases formed by these compounds as well as the lateral packing interactions between the hydrocarbon chains. Moreover, although the chemical modifications of the polar headgroup did not alter the net charge of the lipid headgroup, they did nevertheless, markedly alter the susceptibility of these membranes to penetration by interfacially active molecules such as antimicrobial peptides. Our studies suggest that many of the effects of the chemical modification of the lipid headgroup can be rationalized in terms of their effects on the hydration of, and hydrogen-bonding interactions in the polar/polar interfacial regions of the lipid bilayer.

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Giant vesicles under oxidative stress

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We use optical microscopy to observe giant unilamellar vesicles (GUVs) during the initial steps of membrane oxidative damage. A photo-sensitive molecule consisting of a porphyrine linked to a lipid headgroup (PE-porf) is incorporated in the lipid bilayer, thus generating singlet oxygen at the bilayer surface. This system enables studies on the effects of lipid peroxidation in a more controlled fashion, allowing threshold determinations of membrane oxidative damage. We show that irradiation of GUVs containing PE-porf induces immediate increase in vesicle surface area, with accompanying morphological changes. Because porphyrin is rapidly photo-bleached, the oxidation process is halted during the initial formation of hydroperoxides and membrane disruption is avoided. The increase in surface area is quantified as a function of irradiation time and the amount of PE-porf incorporated. The increase in area was related to the migration of hydroperoxides to the polar interface. The coupling of lipid peroxidation to morphological changes of natural membranes may be involved in the activation of different cellular responses to oxidative stress.

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Miscibility Phase Behavior Of GUV Membranes Containing Ternary Mixtures Of PS Lipids, PC Lipids, And Cholesterol

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Vesicles containing ternary mixtures of phospholipids and cholesterol produce coexisting liquid phases over a range of compositions and temperatures.