

I. Szleifer, M. Schick, Phys. Rev. Letters, 96, 098101, 2006]. The partition coefficients are calculated as a function of chain length, degree of saturation, and temperature. Perhaps our most important, model-independent, observation is that the partition coefficients must depend upon the relative compositions of the two liquid phases which coexist. For given phases in coexistence, we find that saturated anchors prefer the denser liquid-ordered phase and that their partition coefficients generally increase with the length of the anchor. Unsaturated chains and other bulky anchors prefer the less dense liquid-disordered phase. The fraction of anchors in the liquid-ordered phase decreases with decreasing degree of saturation of the anchors. For a given number of double bonds, the partition coefficient depends upon their location, with those near the chain ends causing a smaller decrease in the fraction of anchors in the liquid-ordered phase than double bonds closer to the middle of the anchor. The effect of doubling the number of chains in an anchor is to increase the partitioning into the liquid-ordered phase when the tails are nearly as long or longer than those comprising the bilayer, but is minimal when they are relatively short. A reduction of temperature also increases the partition coefficient of long chains, but again has little effect on shorter ones.

1480-Pos

Xerogel-Supported Lipid Bilayers: Effect of Surface Curvature and Surface Chemistry on Bilayer Properties

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Aerogels are a special class of interconnected nanoscale colloidal-like particles or polymeric chains derived from highly cross-linked inorganic or organic gels that are dried under specific conditions to preserve the tenuous solid network. Aerogels have been used or considered for use in various technical applications such as laser experiments, sensors, thermal insulation, optics, electronic devices, catalysts, cosmic dust collection and X-ray laser research. Xerogels are similar to aerogels but are dried by solvent evaporation at ambient conditions which results in a decreased porosity. Here, we demonstrate a different use of xerogels, as a scaffolding material to support lipid bilayers. We prepared various xerogel structures including silica, titania, alumina, iron oxide, phloroglucinol-formaldehyde (PF), resorcinol-formaldehyde (RF) and cellulose acetate, characterized the surfaces and confirmed lipid mobility by fluorescence recovery after photobleaching (FRAP). Subsequently, we studied DOPC/DSPC phase-separated lipid bilayers supported on silica xerogels vs. smooth mica. It was concluded, using atomic force microscopy and FRAP, that the bilayers on silica xerogel follow the surface curvature rather than being smoothly suspended on the silica interconnected colloidal particles. We used the nanometer-scale corrugations induced in the bilayer to observe the effect of curvature on the phase-separation of ternary mixtures (DOPC/DSPC/Cholesterol). It was observed that the cholesterol concentration of miscibility was significantly greater for silica xerogel-supported ternary bilayers (> 60 mol% chol) compared to smooth mica-supported ternary bilayers (~40 mol% as expected for free bilayers). This is explained as curvature-induced movement of cholesterol from the bilayer to the fusion vesicles in the medium. In summary, this study illustrates the use of xerogel structures as supports for lipid bilayers and is promising in terms of enlightening the details of curvature and surface chemistry on the behavior of the biomembranes.

1481-Pos

What is the Difference Between a Supported and a Free Lipid Bilayer?

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Supported Lipid Bilayers are an abundant research platform for understanding the behavior of real cell membranes as they allow for additional mechanical stability and enable characterization techniques not reachable otherwise. However, in computer simulations these systems have been studied only rarely up to now. Here we present a systematic study of the changes that a support inflicts on a phospholipid bilayer using coarse-grained molecular modeling. We characterize the density and pressure profiles as well as the density imbalance induced by the support. It turns out that the changes in pressure profile are strong enough that protein function should be impacted leading to a previously neglected mechanism of transmembrane protein malfunction in supported bilayers. We also determine the diffusion coefficients and characterize the influence of different corrugations of the support. We then determine the free energy of transfer of phospholipids between the proximal (close to the surface) and distal leaflet of a supported membrane using the coarse-grained Martini model. It turns out that there is at equilibrium about a 2-3% higher density in the proximal leaflet. These results are in favorable agreement with recent data obtained

by very large scale modeling using a water free model where flip-flop can be observed directly. We compare results of the free energy of transfer obtained by pulling the lipid across the membrane in different ways. There are small quantitative differences but the overall picture is consistent. We are additionally characterizing the intermediate states which determine the barrier height and therefore the rate of translocation. Simulations in atomistic detail are performed for selected systems in order to confirm the findings.

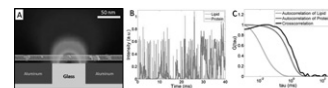
1482-Pos

Microscopy with Nanoapertures to Reveal Membrane Organization with 1 Microsecond and 100 Nanometer Resolution

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Current hypotheses for plasma membrane organization depend critically on a variety of length and time scales that are outside the resolution of conventional experimental techniques. Our novel approach utilizes nanoapertures to examine membrane organization and dynamics with near-field optical fluorescence microscopy without incorporating a scanning probe or perturbing the membrane. Conventional microscopy excitation sources and fluorescent probes are used to enable fluorescence correlation spectroscopy (FCS) on living cell membranes with super-resolution. The nanoapertures confine the excitation light to a sub-diffraction limit length scale, providing a 25-fold decrease in the illuminated area of the membrane as compared to diffraction-limited illumination.



Nanoapertures have been fabricated to create illumination areas 25 times smaller than diffraction limited illumination spots. (A) The aperture (blue) with 200 nm diameter aperture filled with glass allow for near-field illumination of membranes without inducing membrane curvature or requiring a scanning probe. Intensity vs. time of randomly diffusing lipids and slowly diffusing proteins can be analyzed with FCS, as revealed in (B) and (C). In (D) the FCS data are shown for individual components (auto-correlation) that may differ in a complex (concentration). These rates may depend on local membrane structure and state of cell activation.

1483-Pos

Budding and Vesiculation Induced by Conical Membrane Proteins

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Conical inclusions in a lipid bilayer generate an overall spontaneous curvature of the membrane that depends on concentration and geometry of the inclusions. Examples are integral and attached membrane proteins, viruses, and lipid domains. We propose an analytical model to study budding and vesiculation of the lipid bilayer membrane, which is based on the membrane bending energy and the translational entropy of the inclusions. If the inclusions are placed on a membrane with similar curvature radius, their repulsive membrane-mediated interaction is screened. Therefore, for high inclusion density the inclusions aggregate, induce bud formation, and finally vesiculation.

1484-Pos

A Comparison of the Membrane Properties of the Lipid Modifications of Proteins

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Though ubiquitous in nature and relevant for ~10% of all cellular proteins, posttranslational lipid modifications of proteins show an astonishing variety. Common motifs include myristoylations, palmitoylations, prenylations, and cholesterol modifications. All these structures show characteristic membrane properties. In recent years, we have studied a number of systems and elucidated the structure and dynamics of membrane embedded lipid modifications of proteins using solid-state NMR methods. In the presentation, a comparison of the membrane properties of several systems will be given: Farnesylated/hexadecylated Ras, myristoylated GCAP, myristoylated Src, and a transmembrane model peptide featuring lipid modifications of varying lengths between 2 and 16 carbons. Membrane embedded lipid chains show a remarkable structural and dynamical variety. For instance, the 16:0 Ras lipid chain can vary its length between 8.7 and 15.5 Å to perfectly match the hydrophobic thickness of the host membrane. Also, the myristoylation of GCAP perfectly adapts to the thickness of the host membrane. In contrast, the myristoyl chain of Src exceeds the length of the host membrane lipids because of Born repulsion of the positively charged amino acids in the direct vicinity of the N-terminal myristoylation. The projected length of a lipid modification in the membrane is adjusted by the introduction of *gauche* defects, which can be precisely determined from the ²H NMR data. The compression or elongation of a protein lipid chain with respect to the chains of the phospholipid host membrane is accompanied by characteristic changes of the segmental mobility, which is manifested in a distinctive correlation of ²H NMR nuclear relaxation times and order parameters. Thus, in spite of fulfilling the same biological function of membrane anchoring, the structural and dynamical features of protein lipid chains are distinctly different suggesting an additional role in biology.