

phospholipid 1-palmitoyl-2-[16-fluoropalmitoyl]-phosphatidylcholine (F-DPPC) on bilayers composed of the fully saturated phosphatidylcholines 1,2-distearoyl-*sn*-glycero-3-phosphocholine (DSPC) and 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC). In both bilayer systems, DSC thermograms indicate a disappearance of pretransition peaks (T_p) along with a rise in main transition (T_m) hysteresis at elevated F-DPPC mol%. Fluorescence intensity measurements reveal an inverse relationship between F-DPPC mol% and the emission intensity of the environment-sensitive probe 1,6-diphenyl-1,3,5-hexatriene (DPH) below the main transitions of the respective lipids. These trends suggest a growth in interdigitated domains with the incorporation of additional F-DPPC into the bilayer. Significant drops in intensity values were observed at lower F-DPPC mole percentages in the DSPC system than the DMPC system, indicating that the latter lipid has a higher threshold for F-DPPC-induced interdigitation. Our results support that F-DPPC encourages the interdigitated phase ($L_{\beta I}$) in saturated bilayers and highlight the stabilizing effect that long acyl chains have on this phase.

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Not All Hybrid Lipids are Linactants

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Hybrid lipids are thought to be able to perform the function of linactants at membrane domain interfaces: They can reduce line tension and stabilize nanoscopic lipid raft domains in biomembranes. Hybrid lipids are lipids with one saturated chain and one unsaturated chain. Here we provide evidences that only certain hybrid lipids behave like linactants. In this study, we compared three hybrid lipids (i.e., 16:0-18:1PC (POPC), 16:0-18:2PC, and 16:0-22:4PC) in their abilities to reduce lipid domain size and shift phase boundary. The Lo-Ld phase boundaries of hybrid-lipid/di18:0PC(DSPC)/cholesterol systems were determined from giant unilamellar vesicles (GUV) using fluorescence microscopy. We found that 16:0-22:4PC behaves similarly to a fluid-phase lipid: The Lo and Ld lipid domains in 16:0-22:4PC/DSPC/CHOL mixtures are macroscopic and the phase coexisting region is very wide. On the other hand, 16:0-18:2PC/DSPC/CHOL system has a much narrower Lo-Ld phase coexisting region; however, the lipid domains are still macroscopic. Only POPC/DSPC/CHOL system contains nanoscopic lipid domains. These results were compared with Monte Carlo simulations. Based on the magnitudes of interaction energies, it appears that only mono-unsaturated hybrid lipids behave like linactants, while poly-unsaturated hybrid lipids behave more or less like fluid-phase lipids.

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Elasticity of the Lipid Bilayer Edge. Trends in Line Tension

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The line tension or excess free energy per unit length of a bilayer edge is an essential measure of the toughness of a lipid bilayer and its ability to support nanoscopic pores. Well-converged values for the line tension of model pure lipid bilayer edges are important for evaluation of the tendency of additives to stabilize or destabilize the edge. Experimental measurements of bilayer edge line tension are challenging, and new approaches are still under development. In this study we report trends for line tensions and microscopic details of the lipid bilayer edge from a series of atomistic simulations of phosphatidylcholine lipids with varying degree of saturation and tail lengths. The simulation line tensions we obtain are higher than those reported from experiments. The choice of force-field on the resulting ribbon properties was investigated and found to not affect the results. The energetics of edge formation as an area expansion perturbation to the bilayer state was also explored and explains the simulation line tensions within a factor of two.

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Image Analysis of Phase Separated Langmuir Monolayers Containing Polyunsaturated Fatty Acids

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Results from epifluorescence microscopy studies and image analysis of phase separated Langmuir monolayers of ternary mixtures containing polyunsaturated fatty acids (PUFAs), sphingomyelin, and cholesterol will be presented. Experiments were done using a Langmuir trough and inverted microscope under a sealed chamber providing an inert atmosphere. We will focus on the results and implications from measurements of domain size distribution and area fraction for four different mixed acyl phospholipid species with varying degrees of unsaturation in the acyl chain (1, 2, 4, 6). We have applied a recently developed technique to measure the line tension of these systems using the size distribution [1]. This experimental approach allows us to investigate the relationship between the miscibility phase transition, line tension, and degree of unsaturation even for systems with small domains not otherwise amenable to line tension

studies. Experiments described above were combined with more traditional Langmuir film-balance techniques including pressure-area isotherms.

[1] Lee et al., Relating Domain Size Distribution to Line Tension and Molecular Dipole Density in Model Cytoplasmic Myelin Lipid Monolayers. PNAS 108, 9425-9430.

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Effects of Oleic Acid on Stratum Corneum Lipids in Langmuir Monolayers

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The mechanism of oleic acid (OA) as a transdermal permeation enhancer has long been debated. In this study, the interaction between OA and stratum corneum (SC) lipids was investigated with an aqueous monolayer of model SC lipids. Different amount of OA was cospread with equal molar mixture of ceramide, cholesterol and palmitic acid at the air/water interface. The monolayer phase behavior was monitored through surface pressure-molecular area isotherms (π -A isotherms). With increasing OA concentration in the monolayer, the resultant films became more fluid and more compressible. OA also modified the domain structure in SC monolayers as visualized through Brewster Angle Microscope (BAM). The miscibility curve derived from π -A isotherms demonstrated the preferential interaction between OA and SC lipids. IRRAS measurements showed that OA mixed with ceramide and disordered its acyl chains. The acyl chain order of palmitic acid was also lowered by OA but to a lesser extent.

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Comparison of Cholesterol and 25-Hydroxycholesterol in Phase Separated Phospholipid Monolayers

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Experimental studies of the phase separation of coexisting liquid phases in mixed phospholipid/sterol monolayer systems have contributed significantly to our understanding of the unique role that cholesterol plays within lipid membranes. Cholesterol is not unique in its ability to promote phase separation in these model systems. Several cholesterol analogs display similar liquid-liquid phase coexistence in monolayer and bilayer systems. One particularly interesting example of this is 25-hydroxycholesterol (25OH), which has been previously noted to have a kink in its monolayer pressure-area isotherm corresponding to the miscibility phase transition as well as for its pathological effect on the plasma cell membrane. We present the results of experiments using traditional Langmuir film-balance techniques (pressure-area isotherms) and surface potential measurements to identify changes in molecular orientation during monolayer compression. Fluorescence microscopy experiments complement these studies with comparisons of domain size distributions, area fraction, and line tension measurements. From our preliminary work it is clear that there are many similarities between the phase behavior of these two systems as well as many significant differences.

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Physical Properties of an Asymmetric Nanobio Lipid Membrane

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Presence of additional phospholipids in one of alive cell's lipid membrane monolayers is one of the interesting phenomena. A very important part of living cells of biological systems is lipid membrane, and the mechanical properties of this membrane plays an important role in biophysical investigations. It is interesting to evaluate the effect of additional phospholipids insertion in one leaflet of a bilayer on the physical properties of obtained asymmetric lipid membrane. In the present work a coarse-grained molecular dynamics simulation is carried out to compute the physical properties of each leaflet of such a bilayer. Our simulations reveal that the insertion of additional phospholipids into one monolayer results in an asymmetrical change in the lateral pressure of the individual bilayer leaflets. The relative variation in the lateral pressure of the two leaflets as a result of a change in the contribution of the various intermolecular forces may potentially be expressed morphologically.

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Interactions of Cymal-6 and Lipid Vesicles

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The solubilization of biological or liposomal membranes, induced by detergents and detergent-like biomolecules, is important to many technical applications and biological phenomena. In fact, the interactions of classical detergents