SUPPLEMENTARY MATERIAL

Point charge of the hydroxyl moiety of Gb_3

4 model compounds, 1) CH2=CH-CH2-OH, 2) CH3-CH2-CH2-OH, 3) CH3-CH=CH-CH3 and 4) CH3-CH=CH-CH2-OH were considered. That is, most of the proposed point charges depend weakly on the particular structure. All model compounds suggest essentially the same charge on the hydroxyl oxygen atom, -0.72 e (1), -0.71 e (2), -0.70 e (4). Neither double bond nor additional methyl group perturbs this value significantly. We, therefore, assign -0.7 e to oxygen atom. For hydroxyl hydrogen, model compounds suggest +0.40 e (1), +0.42 e (2), +0.40 e (3). We assign +0.4 e charge. Since hydroxyl group is charged and α-carbon should be also charged to preserve electrical neutrality of the moiety. The charges on α-carbon depend on the compound, +0.57 e (1), +0.29 e (2), +0.51 e (4). The double bond of β-carbon plays a principal role. The impact of terminal CH3 group is also important, but is not drastic. Considering the particular structure of our moiety (Green segment of Fig.**??** *A*) the charge of +0.5 e is proposed. The observation is qualitatively similar for β-carbon, -0.14 e (1), +0.18 e (2), -0.20 e (3), -0.33 e (4). Note that the sum of point charges located on O-H-CH2-CH= moiety is close to zero in all test cases. Therefore, this moiety can be considered neutral, while the charges can be seamlessly transferable to other lipids containing this moiety. The double bond does not influence charges of OH group, but OH group influences charges of -CH=. We assign -0.3 e to -CH= carbon. In turn, the charges on hydrogen atoms are notably small, less than $\pm$0.1e. It is convenient to pick up small hydrogen charges to neutralize the moiety. γ-carbon, =CH- in (1), (2), (4), is nearly neutral. We set +0.1 e on carbon and -0.1 e on its hydrogen. The average charge on the β-carbon's, -CH=, hydrogen is +0.1 e. If the charge on α-CH2 hydrogen atoms were zero, the fragment would be neutral. However, in the fitted ESP these charges are around -0.05 e. We add +0.1 e to α-carbon and set -0.05 e to each of hydrogen atoms bonded to this atom. Thus, we get +0.6 e on α-carbon and -0.05 e on hydrogen atoms. Van der Waals and bonded parameters for O, H and C have been taken from the CHARMM36 FF. The described procedure of ESP charges assignment evidences that OH group and α-carbon belong to the hydrophilic moiety, whereas other atoms are hydrophobic and will contribute to the hydrophobic core of the bilayer. The arrangement of the latter is determined primarily by weaker van der Waals forces. Since we used essentially the same procedure as documented in the CHARMM36 FF for biomolecules, the obtained parameters are well compatible with each other.

Voroni tessellation graph

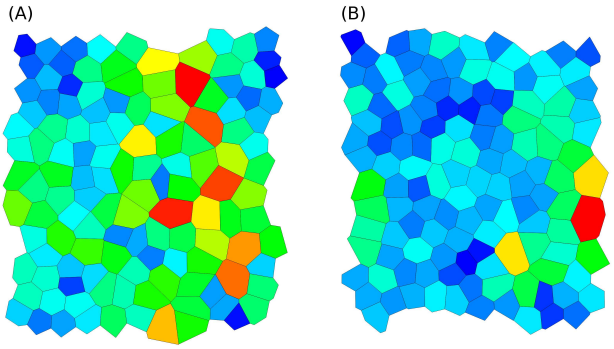

Fig. 1 Voroni tessellation of the hydrophobic chains for 50 % S-Gb_3. A) Disordered phase, beginning of the simulation B) Ordered phase, end of the simulation . Dark blue shows the smallest area per lipid and red show the largest area per lipid.