Lipid bilayers as potential ice nucleating agents

Electronic Supplementary Information

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The supplementary information contains the following: comparing water layer to theoretical orientational order parameter (θ) values for homogeneous water (section A, figure S1); system-by-system size distribution of largest icy clusters per frame (figure S2); filtering icy clusters by minimum size of 30 or 40 molecules (figure S3); comparing pure CHL bilayer to previous work on CHL crystals[1] and monolayers[2] (figure S4); RaLPS sugar distribution (figure S5).

A Theoretical orientation for homogeneous water

Figure S1 shows how a region of the water layer from the pure DPPC system compares to the theoretical distribution of water dipole moments θ for homogeneous bulk water. The theoretical probability density function for bulk water is:

$$f(\theta) = \frac{1}{2}\sin(\theta).$$

While there is a more clearly defined peak at $\theta = 90°$ in the DPPC water layer, θ values correspond well with the theoretical distribution, suggesting that this region of the water layer is behaving like homogeneous water, with respect to orientation.

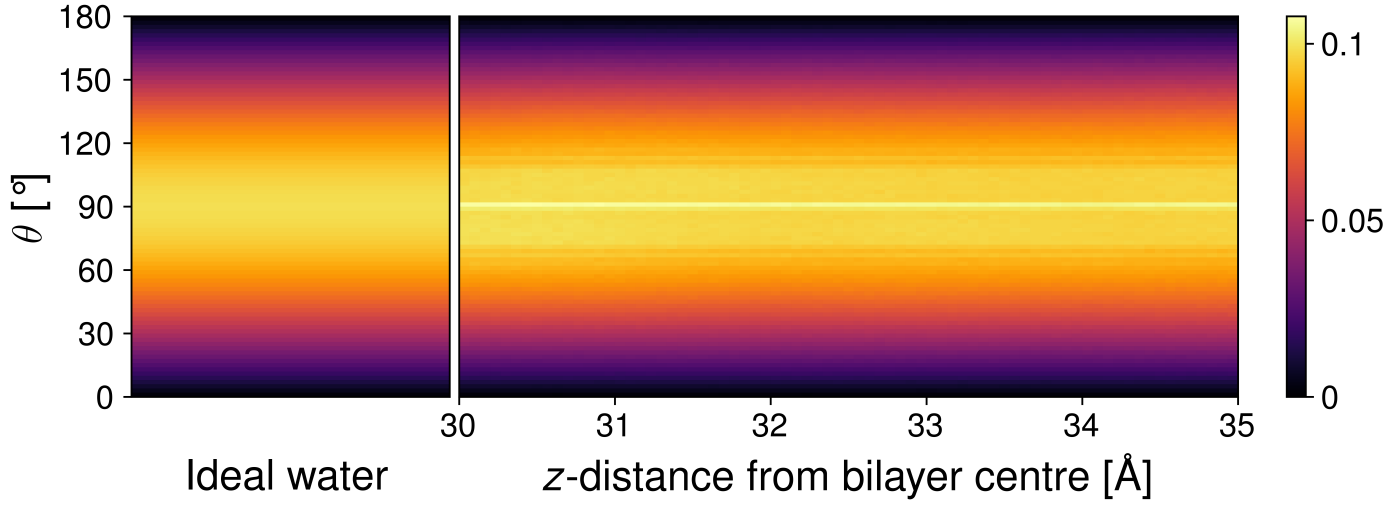

Figure S1: Orientational order parameter (θ) colour maps for theoretical homogeneous water (left) compared to a section of the water layer from the pure DPPC bilayer system (right). As in the main text, the scale for the colour map is count per frame per Å^3 per 180° (for pure DPPC). A value of $\theta = 0°$ corresponds to the dipole moment pointing away from the plane of the bilayer (along the normal) while a value of $\theta = 180°$ corresponds to the dipole moment pointing towards the plane of the bilayer.

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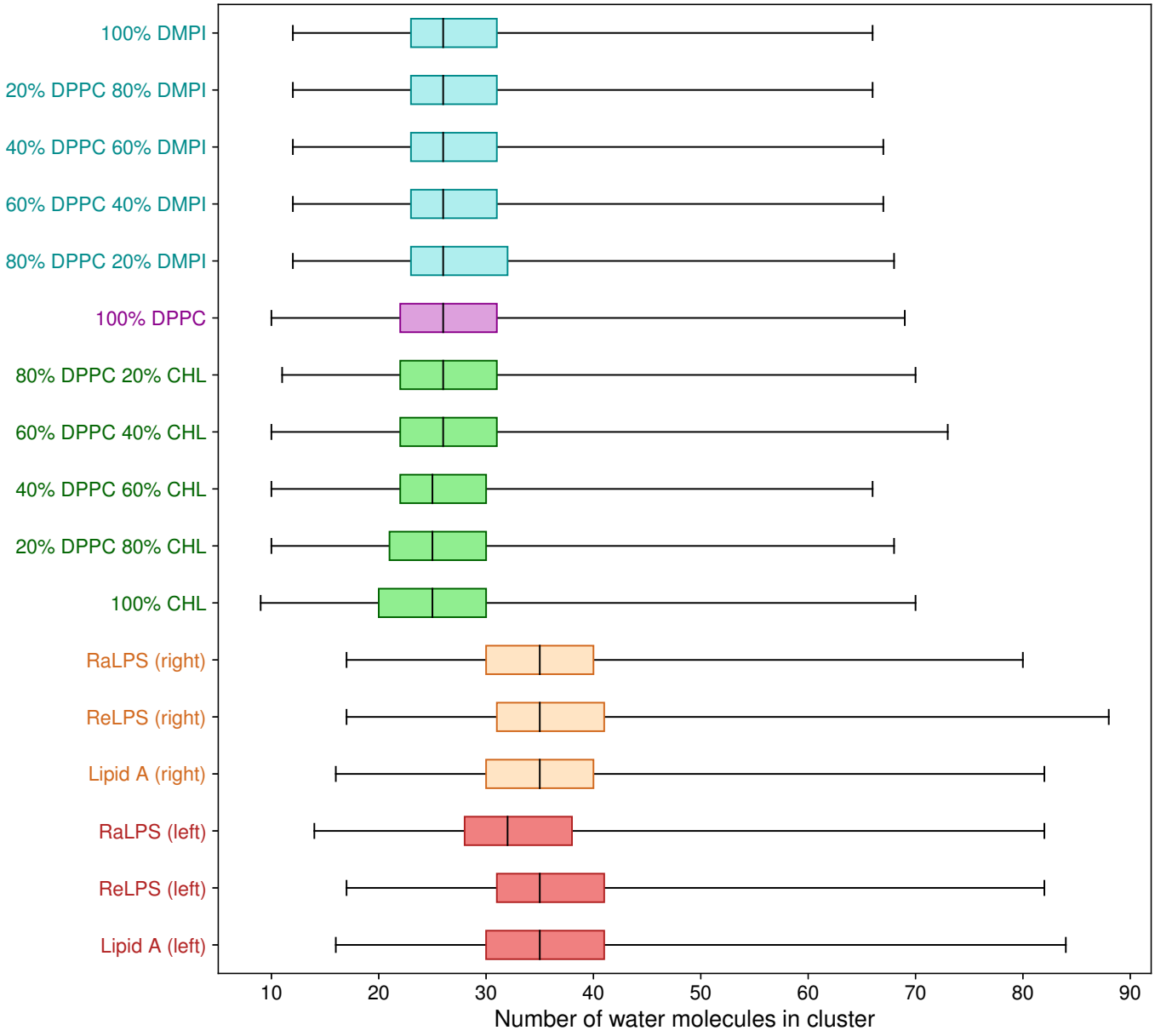

Figure S2: Box plots of the sizes of the largest icy cluster per frame for the various systems. The asymmetric LPS systems are split into "left": the side containing a mixture of phospholipids, and "right": the side containing Lipid A with (ReLPS, RaLPS) or without (Lipid A) lipopolysaccharide chains. The boxes extend from the upper to lower quartile, with a line at the median. The whiskers encase the entire range of values, excluding outliers; which are not plotted. Outliers are defined as being values falling above the 99.9th percentile.

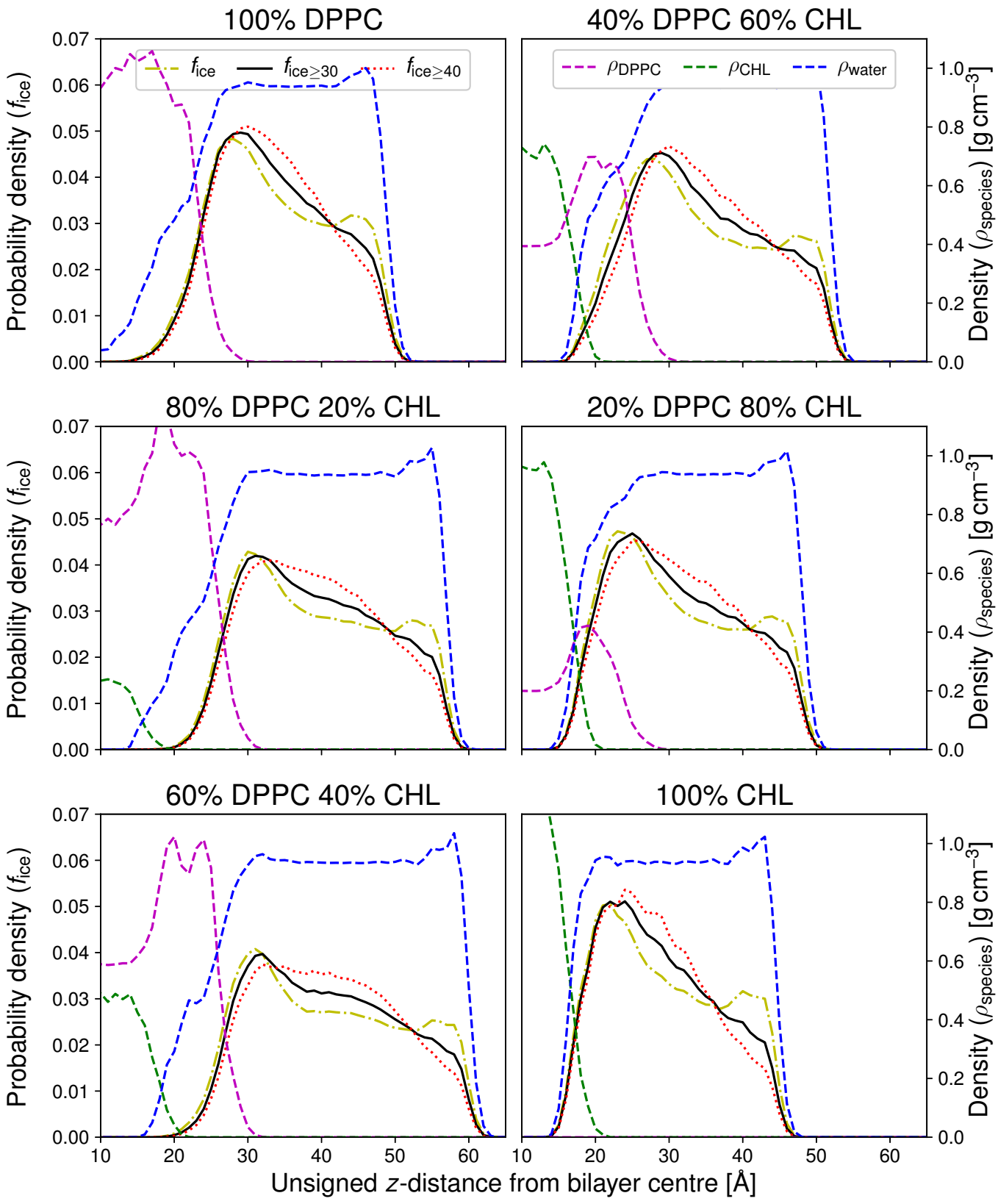

Figure S3: Probability density $f_{\mathrm{ice}}(z)$ (black, solid) for (unsigned) z-distance of water molecules, within a largest icy cluster, from the centre of mass of the bilayer. DPPC, CHL and water densities: $\rho_{\mathrm{DPPC}}(z)$, $\rho_{\mathrm{CHL}}(z)$ and $\rho_{\mathrm{water}}(z)$ are displayed with dashed magenta, green and blue lines, respectively. Corresponding PDFs only including clusters with minimum 30 or 40 molecules are shown by yellow and red dotted lines, respectively.

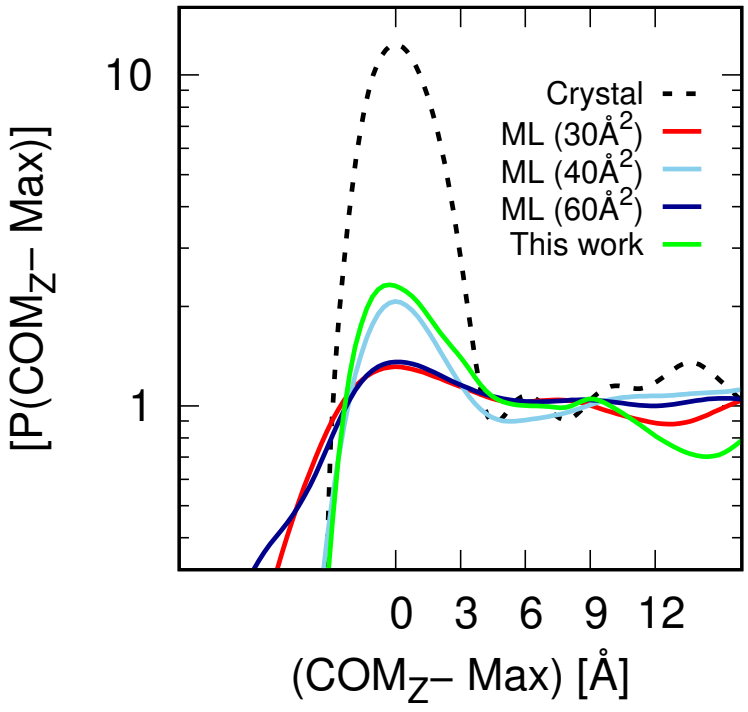

Figure S4: A comparison of the distribution of icy clusters for the pure CHL bilayer with previous values from CHL crystals[1] and monolayers.[2] Unlike the other plots, the distribution of cluster centres of mass are used rather than every molecules within each cluster. As with before, only clusters of at least 30 molecules are used.

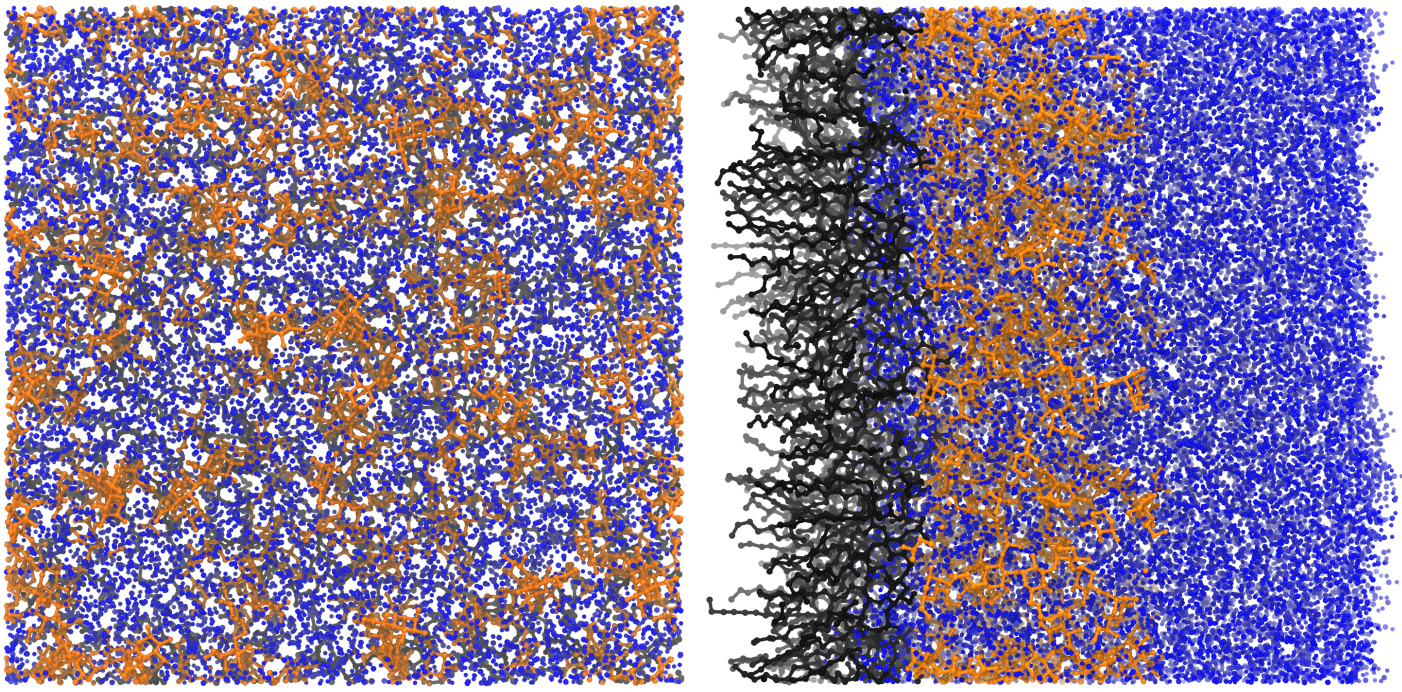

Figure S5: Distribution of sugars in the RaLPS system. Left panel shows xy-plane cross section. Right panel shows the system across the z-axis. Lipid A is coloured black, sugars are coloured orange, water molecules are coloured blue. Hydrogen atoms are not drawn for Lipid A and sugars.

References

[1] G. C. Sosso, T. F. Whale, M. A. Holden, P. Pedevilla, B. J. Murray and A. Michaelides, *Chem. Sci.*, 2018, **9**, 8077–8088.

[2] G. C. Sosso, P. Sudera, A. T. Kunert, T. F. Whale, J. Fröhlich-Nowoisky, M. Bonn, A. Michaelides and E. H. G. Backus, *Chem. Sci.*, submitted.