Neutron Reflectometry Yields Distance-Dependent Structures of Nanometric Polymer Brushes Interacting across Water

Supporting information

1.) Dry thicknesses of organic layers as obtained by ellipsometry

Tables S1 and S2 summarize the dry thicknesses D_{org} of various organic layers deposited on solid SiO₂ surfaces as determined by ellipsometry. Monolayers (MLs, Table S1) were deposited by LB at 35 mN/m onto non-functionalized hydrophilic surfaces. The organic layer thickness D_{org} therefore directly corresponds to the monolayer thickness d_{ML} . For a pure DSPC ML, the value obtained, $d_{DSPCML} = 25$ Å, is indicative of a dense ML. For DSPC incorporating 10 mol% PEG-lipid with polymerization degree (or monomer number) N = 114 the layer is significantly thicker, by 17 Å, owing to the additional PEG material. Double monolayers (DLs, Table S2) were transferred onto OTS-functionalized surfaces using the LS/LB transfer combination described in the main text. The DL thickness D_{DL} therefore follows from D_{org} as $D_{DL} = D_{org} - D_{OTS}$, where D_{OTS} was found to be highly reproducible ($D_{OTS} = 23 \pm 1$ Å). The obtained double layer thicknesses exhibit clearly systematic behavior and are consistent with the monolayer results in Table S1:

1.) Double monolayers are approximately twice as thick as single monolayers ($D_{DL} \approx 2D_{ML}$) when the same formulations are compared.

2.) D_{DSPCDL} is in good agreement with the period $d \approx 60$ Å of dehydrated DSPC multilayers at similar conditions ¹.

3.) The layer thickness increases systematically with the incorporated PEG amount. In fact, the PEG thickness D_{PEGDL} , which is obtained by subtracting D_{DSPCDL} from D_{DL} , scales approximately linearly with N. Finally, PEG thicknesses in ML and DL are found to be consistent, $D_{PEGDL} \approx 2D_{PEGML}$ for the same formulation.

In summary, all these observations demonstrate both effectiveness and reproducibility of the LS/LB sample preparation procedures used in the present work.

System	$D_{\rm org} = D_{\rm ML}$	$D_{\text{PEGML}} = D_{\text{ML}} - D_{\text{DSPCML}}$	2D _{PEGML}
pure DSPC Monolayer (ML)	D _{DSPCML} = 25 Å	-	-
DSPC with PEG-lipid ($f = 10\%$, $N = 114$)	42 Å	17 Å	34 Å

Table S1: Monolayer and sub-layer thicknesses as obtained by ellipsometry.

System	Dorg	$D_{\rm DL} = D_{\rm org} - D_{\rm OTS}$	$D_{\text{PEGDL}} = D_{\text{DL}} - D_{\text{DSPCDL}}$
OTS	<i>D</i> _{OTS} = 23 ± 1 Å	-	-
OTS + DSPC Double monolayer (DL)	79 Å	D _{DSPCDL} = 56 Å	-
OTS + DSPC DL with PEG-lipid ($f = 10\%$, $N = 22$)	87 Å	64 Å	8 Å
OTS + DSPC DL with PEG-lipid ($f = 10\%$, $N = 45$)	92 Å	69 Å	13 Å
OTS + DSPC DL with PEG-lipid ($f = 10\%$, $N = 114$)	114 Å	91 Å	35 Å

Table S1: Double monolayer and sub-layer thicknesses as obtained by ellipsometry.

2) Initial parameter values of the simultaneous fits

Initial values for all parameters concerning the layered structure of the functionalized solid surface and the proximal lipid layer, as well as for the uncompressed brush were taken from the bestmatching results obtained in reference ². For the interacting brushes under compression the packing density of the distal brush-decorated lipid monolayer was initially set identical to that of the proximal one. The surface separation *d* was initially adjusted manually to approximately match the overall sample thickness encoded in the hydration-dependent q_z -positions of the reflectivity minima (see Fig. 5 A). In Eq. 7, τ_H was initially set as $H_{PEG}^{\infty}/2$, { n_0 , τ_n } in Eq. 8 as {2, $H_{PEG}^{\infty}/2$ }, and { b_0 , b_1 , b_2 } in Eq. 9 as {5.0 Å, 0, 0}.

3) Details of the parameter fitting procedure

To simultaneously fit the adjustable parameters of the common model to a set of experimental reflectivity curves, we utilized the following procedure. Starting from initial parameter values specified in the supporting material, we first calculated the interfacial SLD profiles $\rho(z)$ corresponding to each condition, i.e. for each contrast fluid in case of single uncompressed brush and for each humidity level for the brushes under compression. In the next step, we calculated the reflectivity curves corresponding to the $\rho(z)$ profiles using dynamical reflection theory. To this end the profiles were discretized into hundreds of thin slabs of 1 Å thickness and of constant SLD. The q_z -dependent intensities were then calculated via application of Fresnel's reflection laws at each slab/slab interface using the iterative procedure of Parratt³. The procedure was implemented in a self-written fitting program based on the IDL software package (www.harrisgeospatial.com). To optimally constrain all parameters, we simultaneously fit all curves in a set by minimizing the chi-square deviation χ^2 between the entire sets of calculated and experimental reflectivity curves. The best parameter set, with minimal χ^2 was found iteratively using Powell's method⁴. The results were confirmed to be independent of the initial parameter values when they were taken from a physically plausible range. Estimates of the statistical parameter errors, corresponding to the 95% (two-sigma) confidence interval, were derived from the diagonal elements of the corresponding parameter covariance matrix⁵.

4) Reflectivity curves from interacting brushes prepared via double LB transfer

Fig. S1 compares reflectivity curves obtained at obtained at \approx 90 % relative humidity with the sample prepared by a combination of LS and LB transfers (as in the main text) and with a sample prepared via double LB transfer. It is seen that in the latter case the characteristic Kiessig fringes are (i) shifted to higher q_z values, indicating thinner layers and (ii) less pronounced, indicating a weaker SLD contrast. These two observations indicate a poorer transfer ratio and more structural disorder for the sample prepared via double LB transfer.



Figure S1: Neutron reflectivity curves obtained at \approx 90 % relative humidity from interacting brushes prepared by a combination of LS and LB transfers and via double LB transfer.

5) Best-matching roughness parameters ζ between the slabs describing the substrate and the proximal monolayer

a) Single brush

Si/SiO ₂	SiO ₂ / hydrocarbon chain	hydrocarbon chain/ lipid headgroup	lipid headgroup/ water
2 Å	5 Å	7 Å	12 Å

b) Interacting brushes

Si/SiO ₂	SiO ₂ / hydrocarbon chain	hydrocarbon chain/ lipid headgroup	lipid headgroup/ water
2 Å	7 Å	12 Å	10 Å

References:

- 1. L. J. Lis, M. McAlister, N. Fuller, R. P. Rand and V. A. Parsegian, *Biophysical journal*, 1982, **37**, 657.
- 2. E. Schneck, I. Berts, A. Halperin, J. Daillant and G. Fragneto, *Biomaterials*, 2015, **46**, 95-104.
- 3. L. G. Parratt, *Phys. Rev*, 1954, **95**, 359-369.
- 4. W. H. Press, S. A. Teukolsky, W. T. Vetterling and B. P. Flannery, *Numerical Recipes in C*, Cambridge University Press, Cambridge, New York, and Port Melbourne, 2 edn., 1992.
- 5. P. R. Bevington and D. K. Robinson, *Data Reduction and Error Analysis for the Physical Sciences*, Mcgraw-Hill, New York, 2003.