Supplementary Data

1.Neutron Reflectometry Model to Experimental Data Fitting

Three isotopic contrasts of neutron reflectivity profiles were collected using collected for the equilibrium adsorption of Pin-a and β-Pth to condensed phase DPPG monolayers. Fitting of these contrasts allowed the contribution and location of the phospholipid and protein components of the interfacial structure to be determined. Data was obtained using lipid samples with hydrogenated and with deuterated acyl chain regions, to provide isotopic contrast between the proteins and the lipids at the interface. Experiments were carried out with non reflective water solutions (NRW: 8% D_2O, 92 % H_2O) on which the reflectivity profile is only sensitive to the interfacial region and D_2O on which reflection is sensitive to hydrogenous material. This combination of isotopic contrasts has been previously used to quantitatively determine the structure of interfacial films (*1*)(*2*)(*3*)(*4*)(*5*).

Table 1: Summary of known scattering lengths, scattering length densities and molecular weights of the lipid and protein components studied.

Lipid / Protein / Solvent	Scattering length ($\sum b$)/ 10^{-3} Å	Scattering length density/10^{-6} Å^{-2}	Molecular weight/g mol^{-1}
h-DPPG	0.39	0.36	721
tail d-DPPG	6.84	6.24	783
DPPG head group	6.13	2.52	299
h-DPPG tail	-0.32	-0.398	422
d-DPPG tail	0.71	7.54	484
Pin-a in NRW	31.13	1.97	12920
Pin-a in D_2O	51.34	3.22	13102
β-Pth in NRW	11.19	1.86	4953
β-Pth in D_2O	19.72	3.21	5033
NRW	-	0	18.16
D_2O	-	6.35	20

1.1 Equilibrium Pin-a adsorbed Condensed phase DPPG monolayer

Abeles layer model fitting of the experimental reflectometry profiles for the protein/lipid interfaces were carried out using methods previously described by Clifton *et al*(*1*). Briefly, in this approach the experimental reflectivity data is fitted to the simplest model possible that is able to describe the interfacial region. The model is increased in complexity (i.e. the number of fitted layers) until a satisfactory fit to the data is obtained. For example, as the simpliest possible layer structure a single layer model is used initially in data fitting. This interfacial structure would suggest a homogenous protein/phospholipid film at the air/liquid interface. For the data described in this paper, simultaneous fitting of the three reflectivity profiles to this structure resulted in poor model-to-data fits of the experimental reflectivity profiles (see Figure 1 (A)), it was therefore determined that the protein/lipid layer structure for Pin-a binding to a DPPG monolayer was not a homogeneous layer.

Using a two layer model resulted in an upper layer of lipid at high volume fraction and a lower layer containing lipid head group and protein. The best two layer model did not fit to the data satisfactorily, as shown in Figure 2, since the fringes in the NR profiles were not well represented by the model. Therefore, a more complex three layer model was used to describe our data as discussed in the text of the main article and explained below.

A three layer model of the interfacial structure was used to fit the NR profiles for Pin-a adsorption to DPPG (Figure 3). In this model, the lipid acyl chain region, head group region and an adsorbed protein region below the lipid layer are treated as separate layers. Simultaneous fitting to the three experimental data sets with this model of the interfacial structure were good. It was therefore determined that this model was the simplest structure that best describes the interfacial structure of the Pin-a/DPPG interface. The thicknesses of the layers found in this structure match well with previously described lipid monolayer structures both with and without adsorbed protein and therefore the conclusion that layers 1 and 2 of this structure contains the lipid acyl chain and head group regions of the monolayer and the third layer is composed solely of an adsorbed protein layer. Error and quantitative analysis of the model to data fits was then conducted (see main article).

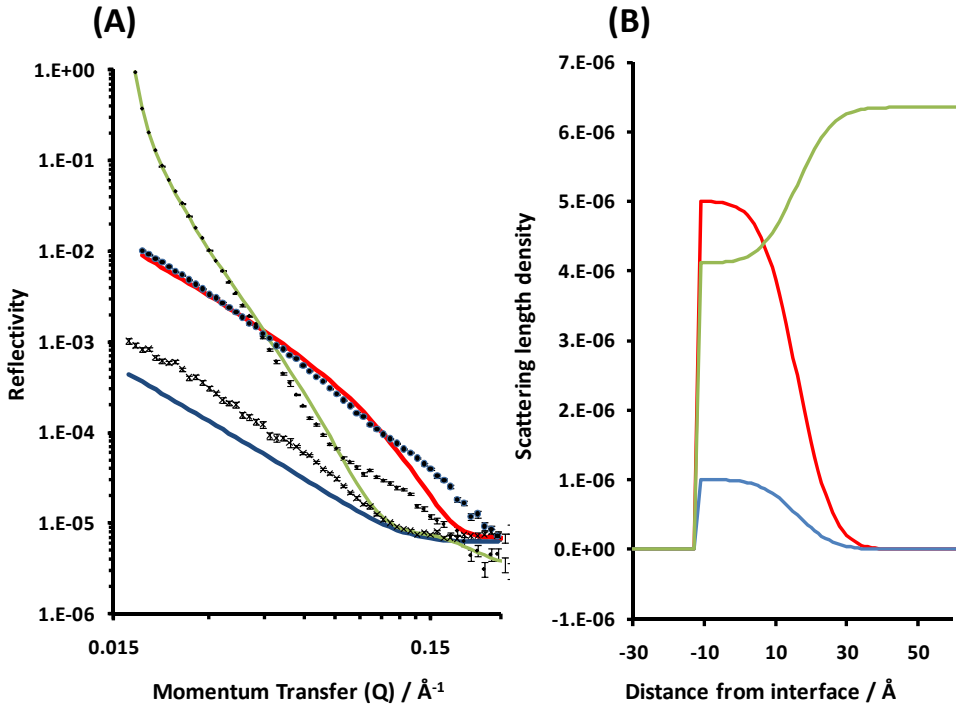

Figure 1, Neutron reflectometry profiles and best one layer model data fits for Pin-a adsorbed to a condensed phase DPPG monolayer (A) and the scattering length density profiles that these fits describe (B), The isotopic contrasts shown are Pin-a/d-DPPG on NRW (red line for the model, • for the experimental data), Pin-a/h-DPPG on NRW (blue line for the model, × for the experimental data) and Pin-a/h-DPPG on D_2O (green line for the model, ◊ for the experimental data).

Table 2: Parameters obtained from the best single-layer model fits of equilibrium Pin-a adsorbed DPPG monolayers.

Layer + H/D contrast	Fit parameters		φ_{lipid}	$\varphi_{protein}$	$A_{lipid}/Å^2$	Γ_{prot} / mg m^{-2}
	τ/Å	ρ/10^{-6} Å^{-2}				
Layer 1						
h-DPPG on NRW	28	1.1	0.64	0.44	60.57	1.67
d-DPPG on NRW	28	4.9				
h-DPPG on D_2O	28	4.11				

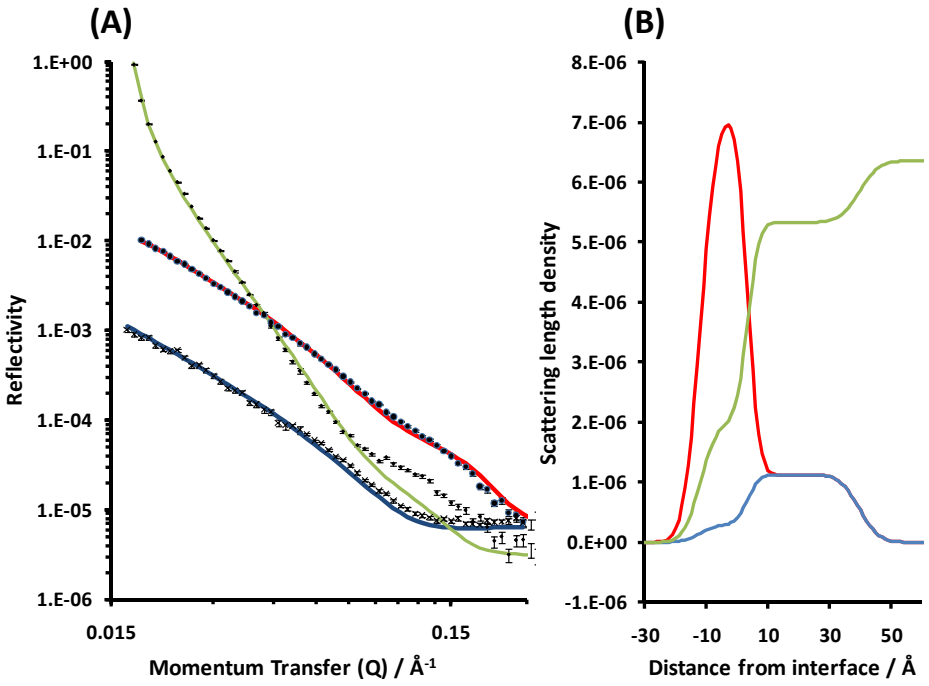

Figure 2, Neutron reflectometry profiles and best two layer model data fits for Pin-a adsorbed to a condensed phase DPPG monolayer (A) and the scattering length density profiles that these fits describe (B), The isotopic contrasts shown are Pin-a/d-DPPG on NRW (red line for the model, • for the experimental data), Pin-a/h-DPPG on NRW (blue line for the model, × for the experimental data) and Pin-a/h-DPPG on D_2O (green line for the model, ◊ for the experimental data).

Table 3. Parameters obtained from the best two-layer model-to-data fits for Pin-a adsorbed to DPPG monolayers at equilibrium.

Layer + H/D contrast	Fit parameters		φ_{lipid}	$\varphi_{protein}$	$A_{lipid}/Å^2$	Γ_{prot} / mg m^{-2}
	τ/Å	ρ/10^{-6} Å^{-2}				
Layer 1						
h-DPPG on NRW	15	0.28	0.87	0.32	84	0.65
d-DPPG on NRW	15	7.2				
h-DPPG on D_2O	15	2				
Layer 2						
h-DPPG on NRW	35	1.16	0.1	0.44	84	2.1
d-DPPG on NRW	35	1.16				
h-DPPG on D_2O	35	5.3				

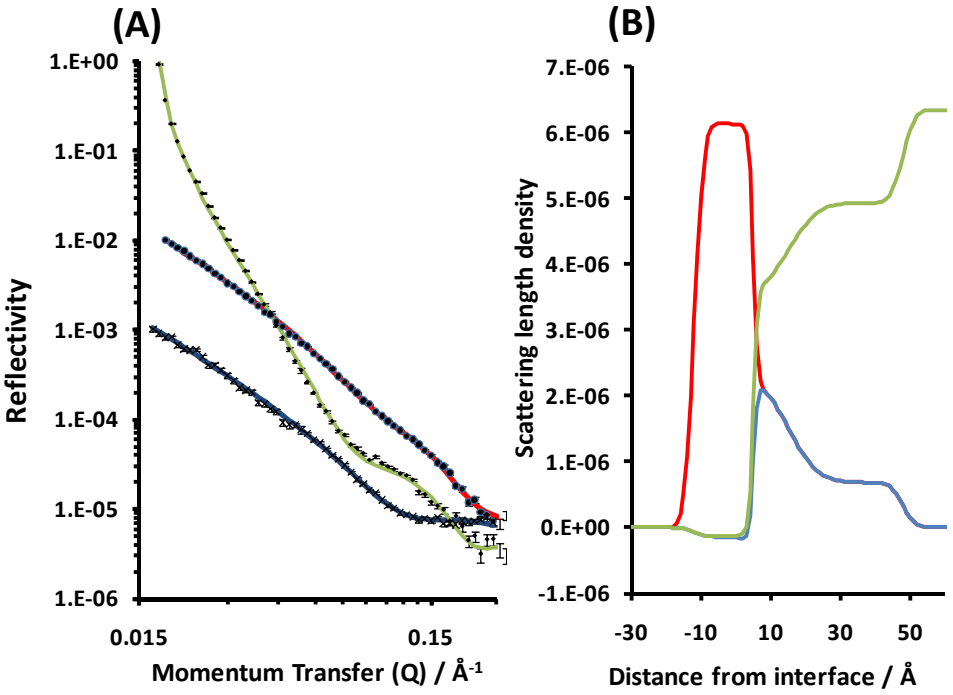

Figure 3, Neutron reflectometry profiles and best three layer model data fits for Pin-a adsorbed to a condensed phase DPPG monolayer (A) and the scattering length density profiles that these fits describe (B), The isotopic contrasts shown are Pin-a/d-DPPG on NRW (red line for the model, • for the experimental data), Pin-a/h-DPPG on NRW (blue line for the model, × for the experimental data) and Pin-a/h-DPPG on D_2O (green line for the model, ◊ for the experimental data).

Table 4. Parameters obtained from the best three-layer model-to-data fits for Pin-a adsorbed to DPPG with associated fitting errors

Layer + H/D contrast	Fit parameters		φ_{lipid}	$\varphi_{protein}$	A_{lipid}/Å^2	Γ_{prot} / mg m^{-2}
	τ/Å	$\rho/10^{-6}$ Å^{-2}				
Layer 1						
h-DPPG on NRW	16.8±0.69	0.1 ± 0.19	0.75± 0.028	0.22±0.048	64±2.4	0.6±0.05
d-DPPG on NRW	16.8±0.69	6.11 ± 0.13				
h-DPPG on D_2O	16.8±0.69	0.14± 0.3				
Layer 2						
h-DPPG on NRW	7.9±0.85	1.85 ± 0.16	0.56± 0.09	0.24±0.12	64±10.4	0.31±0.07
d-DPPG on NRW	7.9±0.85	1.85± 0.16				
h-DPPG on D_2O	7.9±0.85	3.86±0.5				
Layer 3						
h-DPPG on NRW	9.3±4	0.61±0.14	-	0.23±0.075	-	0.36±0.12
d-DPPG on NRW	9.3±4	0.61±0.14				
h-DPPG on D_2O	9.3±4	5.4± 0.3				

References

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