Experimental report

24/02/2017

Proposal: 9-13-642 **Council:** 4/2016

Title: Using neutron reflectivity to understand the structural basis for therheology of molten chocolate

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: lecithin
sucrose coated silicon substrates with/without permalloy under layer
glyceryl trioctonoate
polyglycerylricinoleate (PGPR

Instrument	Requested days	Allocated days	From	To
D17	4	4	17/11/2016	21/11/2016

Abstract:

Molten chocolate is a semi-solid suspension of (mostly) sugar, but also cocoa and milk solids in oil. In order to allow the sugar grains to flow past each other, either when the chocolate is being made, or when it has melted in your mouth, it also contains surfactant additives. These are mostly naturally occuring products, such as lecithin, which comprises lipids which are found at surfaces in nature, but also some polymeric molecules such as PGPR. Rheology measurements suggest that the two additives behave cooperatively. Building on previous SANS measurements, we will use neutron reflectivity to determine how the two components are distributed at the oil/sucrose interface. This will allow us to test a model we have derived using polymer physics to explain how the additives lubricate the sugar grains. Understanding this would enable nicer, healthier and cheaper chocolate to be manufactured.

Using neutron reflectivity to understand the structural basis for the rheology of molten chocolate - Report

Experimental details

Neutron reflecitivity was measured from sucrose spin-coated silicon blocks mounted in a solid-liquid flow cell with an exchange volume of 1.2 mL. Pure triglyceride oils, Glyceryl Trioctanoate (GTO) and Glyceryl Trioleate (TO), followed by solutions of Lecithin, PGPR, or the binary mixture of the Lecithin/PGPR in oil were flowed through the cell and NR was measured. In addition to the Lecithin and PGPR samples, we also studied a POPC, a single component phospholipid, and PGPR binary mixture. The triglyceride oil allowed us to characterise the sucrose substrate for each sample and thereafter we can study the interfacial layer for each of the surfactant for the pre-characterised sucrose/oil interface. The sample matrix studies is detailed below

	TO	GTO
Lecithin	2.4%	2.4%
PGPR	-	2.4%
Lecithin + PGPR	1.2% + 1.2%,	1.2% + 1.2%
	1.8% + 0.6%	
	0.6% + 1.8%	
POPC + PGPR	0.6% + 1.2%	-

The concentration above are w/w percentage in oil and were chosen such as to mimic the molar concentrations of Lecithin and PGPR in chocolate. The POPC was used as a replacement for the polar lipid components of lecithin, which are ∼50% weight of lecithin. The rest of lecithin is oil which in our case is replaced by triglycerides.

Similarly spin coated samples have been previously characterised using Lab based X-ray reflectivity and fit to a sucrose layer of ∼55 nm.

Preliminary data analysis

The sucrose films can be fitted to layers between 50-60 nm, consistent with the XRR characterisation. For both the oils, the Lecithin data can be fit to a solvated multi-phospoholipid layer of ∼10 nm, the PGPR data to a solavted multi-layer of ∼30 nm layer and the binary mixture to a solvated layer of ∼100 nm layer. These fit use models comprising layers with high roughness (essentially a Gaussian distribution) to get an idea of the thickness of the layer, for comparison to our QCM-D and SANS data. The swelling trend is qualitatively consistent with the results we have from the other techniques.

Neutron Reflectivity from lecithin and PGPR layers in GTO

For GTO we used a 1:1 perdeuterated to hydrogenated mixture (d50-GTO) with SLD=$3.3*10^{-6}$ Å^{-2}, which gives us contrast against the Lecithin tails (SLD between -0.3 and $0.3*10^{-6}$ Å^{-2}) and PGPR (SLD=$0.4*10^{-6}$ Å^{-2})

As can be seen in Figure 1, there is a Bragg feature for lecithin (top left panel) and its binary mixture with PGPR (top right panel), which shows presence of lamellae. The lecithin data shows the Bragg feature at $q = 0.15$ Å^{-1} corresponding to a spacing of 41 Å.

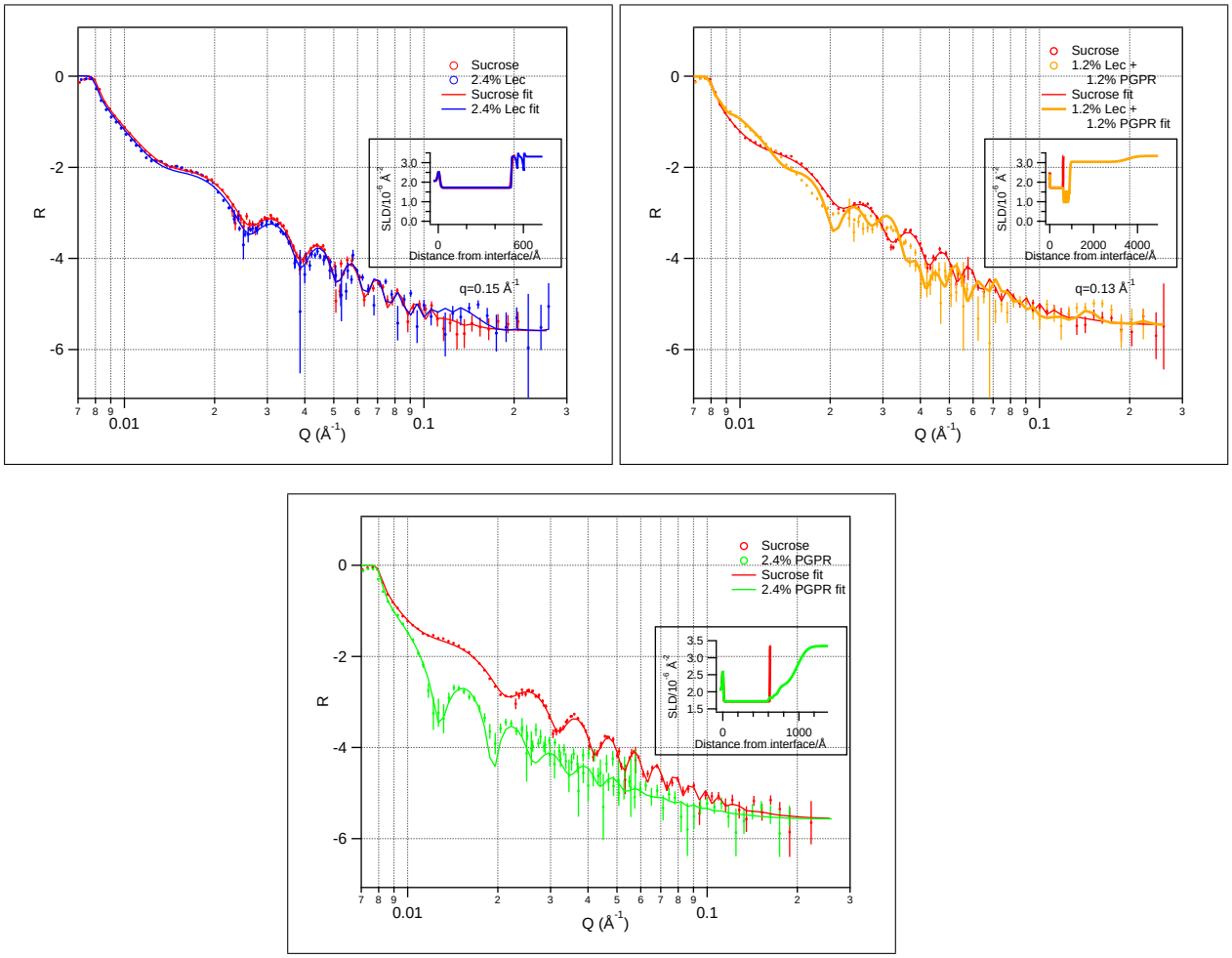

Figure 1: Neutron Reflectiivty from thin films comprising Lecithin (top left panel), a 50:50 Lecithin/PGPR mixture (top right panel) and PGPR (bottom panel) in d50-GTO. The inset shows the SLD profile of the preliminary fits.

In the presence of PGPR this shifts to $q = 0.13$ Å^{-1} corresponding to a spacing of 48 Å. The total structure for Lecithin extends to 11 nm (5 phospholipid layers) and 150 nm for Lecithin+PGPR (7 phospholipid swollen layers followed by a diffused layer). For PGPR only (bottom panel in Figure 1), we have a solvated multilayer of 40 nm with no Bragg feature showing an absence of order in the PGPR layer.

Neutron Reflectivity from lecithin and PGPR layers in TO

For TO we used pure hydrogenated oil (h-TO) with SLD=$0.2 * 10^{-6}$ Å^{-2}, which gives us contrast against the Lecithin head (SLD=$1.84 * 10^{-6}$ Å^{-2}). Given, we have no contrast against the PGPR (SLD=$0.4 * 10^{-6}$ Å^{-2}), we did not study PGPR by itself for h-TO oil subphase.

As can be seen in Figure 2, the lecithin data can be fit to 5 phospholipid layers structure of 12 nm (left panel) and the lecithin+PGPR data can be fitted to a 7 phospholipid swollen layers followed by a diffused structure extending to 50 nm (right panel). The structure can be more extended with PGPR/oil layers but we have no information about this as we have no contrast against PGPR.

As can be seen in Figure 3, there is a Bragg feature for lecithin and its binary mixture

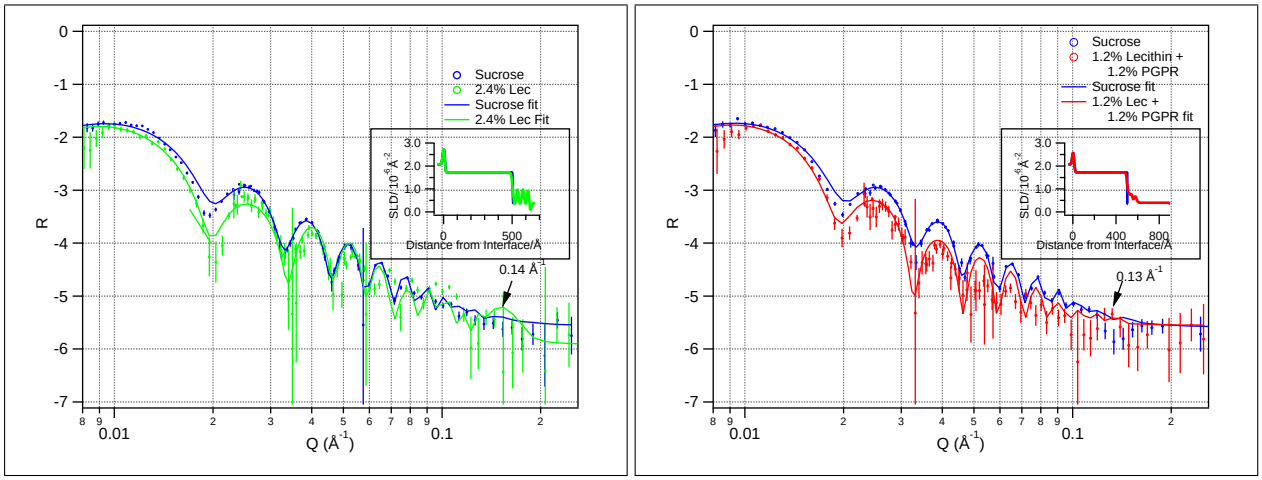

Figure 2: Neutron Reflectiivty from thin films comprising Lecithin (left panel) and 50:50 binary mixture of Lecithin & PGPR (right panel) in TO. The inset shows the SLD profile of the preliminary fits.

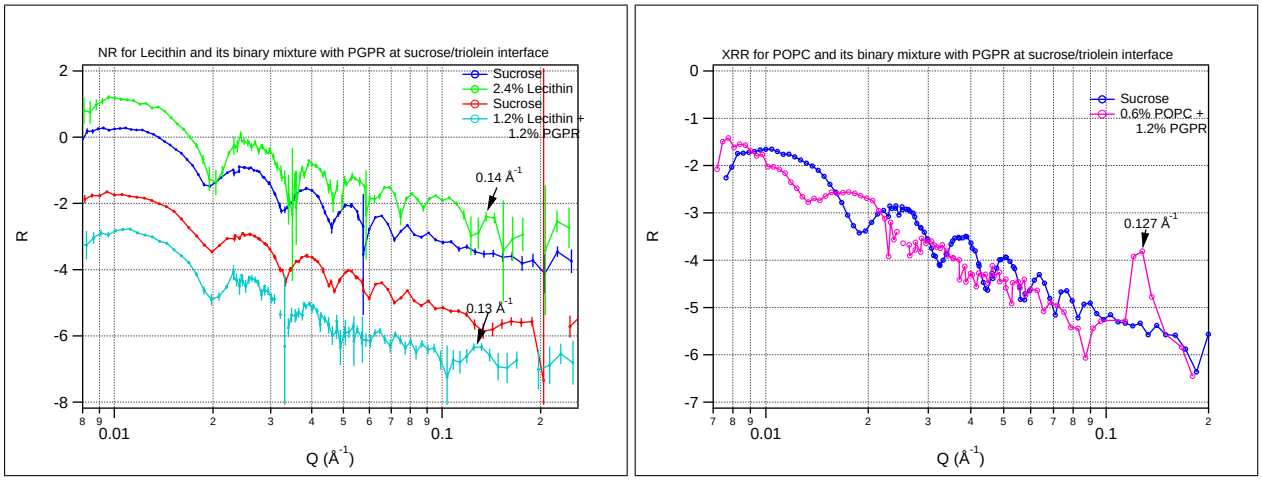

Figure 3: Neutron Reflectiivty from thin films comprising Lecithin and 50:50 Lecithin & PGPR (left panel) and POPC & PGPR (right panel) in TO. This shows the presence of a Bragg like features associated with lamellae.

with PGPR (left panel), showing presence of lamellae similar to the GTO data. The lecithin data shows the Bragg feature at $q = 0.14$ Å^{-1} corresponding to a spacing of 44 Å. In the presence of PGPR this shifts to $q = 0.13$ Å^{-1} corresponding to a spacing of 48 Å. In addition to the Lecithin and PGPR data, we also did a measurement with d31-POPC+PGPR to enhance the contrast of POPC against TO and confirm the presence of lamellae. As can be seen in the right panel in Figure 3, the POPC+PGPR mixture gives a Bragg peak at $q = 0.127$ Å^{-1} corresponding to a spacing of 50 Å.

The fitting will be refined by using detailed models incorporating more realistic distribution like a swollen polymer layer for PGPR, and patchy multiple head-size phospholipid layers for the lecithin, representing the multi-component nature of lecithin, and combining both these structural elements for the binary mixture. This is ongoing.