Supplementary Information (SI) for Environmental Science: Atmospheres.

Appendix

Determining Reaction Progress from Total Neutron Counts

The value of reflectivity, *R*, at a given point of momentum transfer, *Q*, can be used to approximate the amount of material contained within a thin film at an interface between two bulk mediums with a scattering length density of zero. This is due to the proportional relationship between *R* and the intermediate material's thickness, δ, and scattering length density, *ρ*, under these conditions. Owing to the mathematical relationship $R = \frac{I}{I_0}$ where *I* is the intensity of the reflected beam and I_0 is the intensity of the incident beam, changes in *I* can be also be used to approximate changes in total film material at the null-reflecting interface. The proportional relationship between *R*, and thus *I*, and the amount of material at the interface, can be shown as follows.

The approximation of reflectivity for a single thin homogenous film of scattering length density ρ_1 between two bulk mediums of ρ_0 and ρ_2 can be described by the equation:

$$R(Q) \approx \frac{16\pi^2}{Q^4}\left[(\rho_1 - \rho)^2 + (\rho_2 - \rho_1)^2 + 2(\rho_1 - \rho_0)(\rho_2 - \rho_1)\cos(Q\delta)\right] \#(1)$$

In the instance where the scattering length density of these bulk mediums is zero then equation 1 can be simplified to:

$$R(Q) \approx \frac{16\pi^2(2\rho)^2}{Q^4}\left[sin^2\left(\frac{Q\delta}{2}\right)\right] \#(2)$$

In order to approximate the relationship between *R*, δ, and *ρ*, a Maclaurin expansion can be applied to $sin^2\left(\frac{Q\delta}{2}\right)$. The significance of the terms in the Maclaurin series were assessed by determining their proportion of $sin^2\left(\frac{Q\delta}{2}\right)$ for typical values from this experiment for *Q* (0.03) and δ (10). Terms 1, 2 and 3's proportion of the sin term were found to be 1.007, $3\text{x}10^{-5}$ and $1\text{x}10^{-9}$ respectively. Owing to the small contributions of terms beyond the first in approximations for *R*, only the first term is used. By substituting in the first term of the Maclaurin series expansion into equation 2 this produces the formula:

$$R(Q) \approx \frac{16\pi^2\rho^2\delta^2}{Q^2} \#(3)$$

Within this work, the reaction is monitored by the loss of material from the interface as a function of time. Taking equation 3 for a constant range of *Q*, then the change in *R* with respect to time is directly proportional to the amount of material contained at an interface [1] (ρδ):

$$R \propto \rho^2\delta^2 \#(4)$$

Hence, $\sqrt{I} \propto \sqrt{R} \propto \rho\delta$. The product of thickness and scattering length density can also be used as an approximation for surface excess, *Γ*.

The proportion of material at any given point in time relative to the starting amount of material is then calculated by

$$\frac{\Gamma_t}{\Gamma_{t=0}} \propto \sqrt{\frac{I_t}{I_{t=0}}} \#(5)$$

Thus to increase reliability in our result the full measured Q range is used, thus our kinetic variable is:

$$\int \sqrt{\frac{I(Q)_t}{I(Q)_{t=0}}} \#(6)$$

The ability for the model shown in equation 3 to predict reflectivity was considered over the ranges of neutron wavelengths used (~2-16Å), film thicknesses (1-30Å) and a single scattering length density of 1 x 10^{-6} Å^{-2}. This allowed constraints to be applied to data that would fall outside of the ability of this model to predict *R* accurately (within 5%). The results of this comparison can be seen in Fig 1, note that a vast majority of the expected λ and δ range for this experiment is beneath the 5% threshold. The capability of the models represented by equations 2 and 3 can be seen in Fig 2, which shows their comparison with real data from this work as well as predictions using the modelling software Refnx.

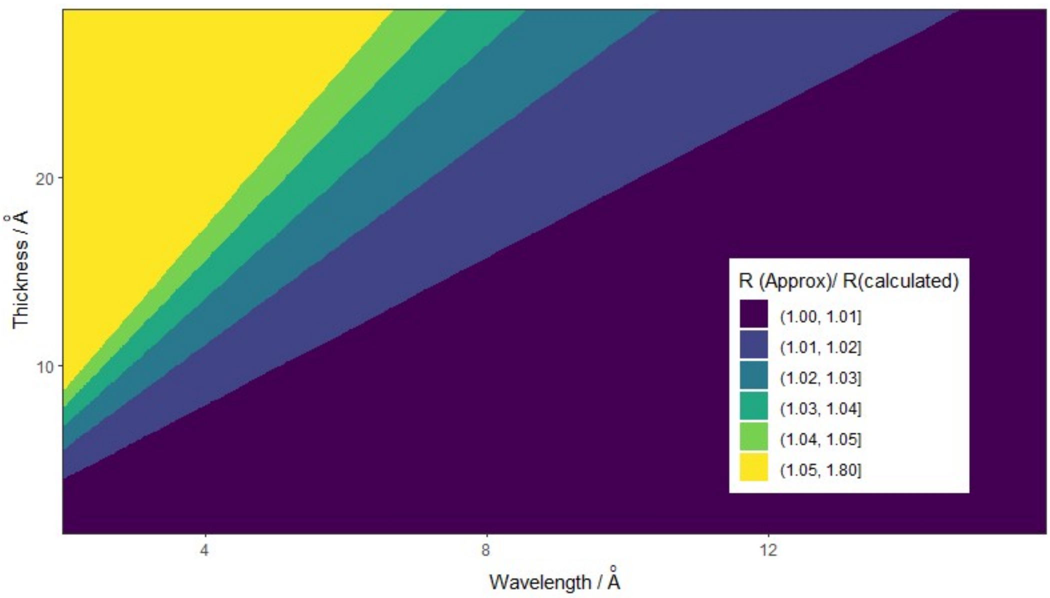

Fig 1. The accuracy of a simplified approximation of Neutron Reflectivity (Equation 3) in comparison to a standard approximation formula (equation 2) of a single thin film between two bulk mediums with scattering length densities of zero. Reflectivity was approximated over ranges relevant to the values of momentum transfer and film thickness observed in this work.

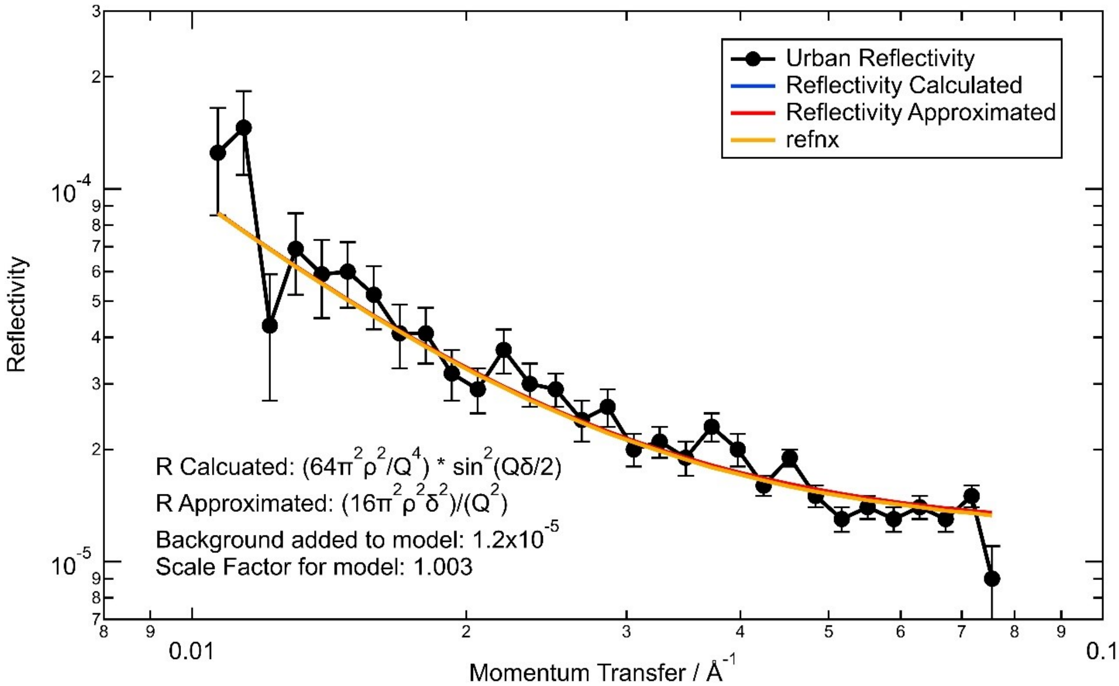

Fig 2. A comparison of neutron reflectometry data of a thin film of urban atmosphere-extracted material at the air-water interface with approximations of Reflectivity through equations 2 (blue) and 6 (red), and fitting procedures in Refnx (orange) as typically used elsewhere in this work. Note that the values determined through equations 2 and 6 are so similar the reflectivity values produced through equation 2 are hidden beneath the results from equation 6.

References:

1 E. Staples, L. Thompson, I. Tucker, J. Penfold, R. K. Thomas and J. R. Lu, Surface composition of mixed surfactant monolayers at concentrations well in excess of the critical micelle concentration. A neutron scattering study, *Langmuir*, 1993, **9**, 1651–1656.