Supplementary Information

1 Analysis of Scattering Data

We model our system as a set of strongly-interacting lamellar sheets that undergo thermal fluctuations in the structure factor, with the scattered intensity modulated by a form factor which accounts for the finite thickness of the lamellae. Whilst both paracrystalline and Caillé theories are apt for studying such systems [1], we apply the modified Caillé theory described by Nallet *et al* [2, 3], as has been used recently in a system similar to the one described in this paper [4]. Here the system is treated as a multilamellar sheet with a repeat distance, d, which undergoes thermally-induced fluctuations in the structure. This model gives the q-dependence of the scattered intensity of a sample containing randomly-oriented crystals of lamellae as:

$$I_{MCT}(q) = \frac{2\pi}{d} \frac{P(q)S(q)}{q^2} \qquad (1)$$

where $P(q)$ and $S(q)$ are, respectively, the form and structure factors of the lamellar system. It can be shown that in the region of a Bragg peak centred at q_0, thermal fluctuations give rise to a power-law divergence in the structure factor of the form [3]:

$$S(q) \propto |q - q_0|^{-1+\eta} . \qquad (2)$$

The scaling exponent of the scattered intensity in the region of the Bragg peak can be quantitatively related to the mechanical properties of the lamellae using the Caillé parameter, η, which is given by [2]:

$$\eta = \frac{q_0^2 k_B T}{8\pi \sqrt{KB}} \qquad (3)$$

where K and B are, respectively, the bending and bulk moduli of a bilayer. In our system, the scattering arises due to the contrast between the polar and non-polar region, in which the non-polar (i.e., the aliphatic tails) region has a length δ, and the polar region (containing the ammonium phosphate

group and any water) has a length $d - \delta$. The scattering length density of the repeat units of the lamellar system is modelled as a box function with a non-polar region of thickness δ centred at z = 0, i.e.,:

$$\rho(z) = \begin{cases} \Delta\rho : -\delta/2 < z < \delta/2 \\ 0 : \text{elsewhere} \end{cases} \tag{4}$$

where $\Delta\rho = \rho_{non-polar} - \rho_{polar}$. The square of the Fourier transform of this function yields the form factor [3]:

$$P(q) = \frac{4}{q^2} \ (\Delta\rho)^2 \ sin^2(q \ \delta/2). \tag{5}$$

as has been used elsewhere [4]. In addition to the scattering from the lamellar structure, thermal fluctuations in the aliphatic chains present in the dodecane and at the TAHP-dodecane interface lead to significant incoherent scattering at high-q. We model this thermally-induced behaviour as being diffusive, for which the appropriate structure factor is a Lorentzian of the form:

$$I_{bkg}(q) = \frac{I_\alpha}{1 + q^2 L^2} \tag{6}$$

where I_α is an arbitrary scaling factor, and L is a real-space length scale (typically on the order of 6Å). The scattering observed is thus the sum of equations 1 and 6. We do not attempt to extract any data from fits of the Lorentzian to the data, nor does it significantly impact the physics of the system in the region of the Bragg peaks.

Finally, we account for smearing of the scattering data due to the finite q-resolution of the experimental apparatus following the procedure described by Pedersen and Barker [5], in which the modelled scattering intensity at q_0 is convolved with a Gaussian smearing function $R(q, q_0)$, described by:

$$I(q_0) = \int_{q_{min}}^{q_{max}} R(q, q_0) \ I(q) \ dq \tag{7}$$

$$R(q, q_0) = \frac{1}{\Delta q \sqrt{2\pi}} \ \exp\left[- (q - \bar{q})^2 / 2(\Delta q)^2 \right] . \tag{8}$$

where $\bar{q}$ is the mean scattering vector and Δq is the q-resolution of the instrument.

References

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[5] J. G. Barker and J. S. Pedersen. Instrumental Smearing Effects in Radially Symmetric Small-Angle Neutron Scattering by Numerical and Analytical Methods. *J. Appl. Crystallogr.*, 28:105–114, 1995.
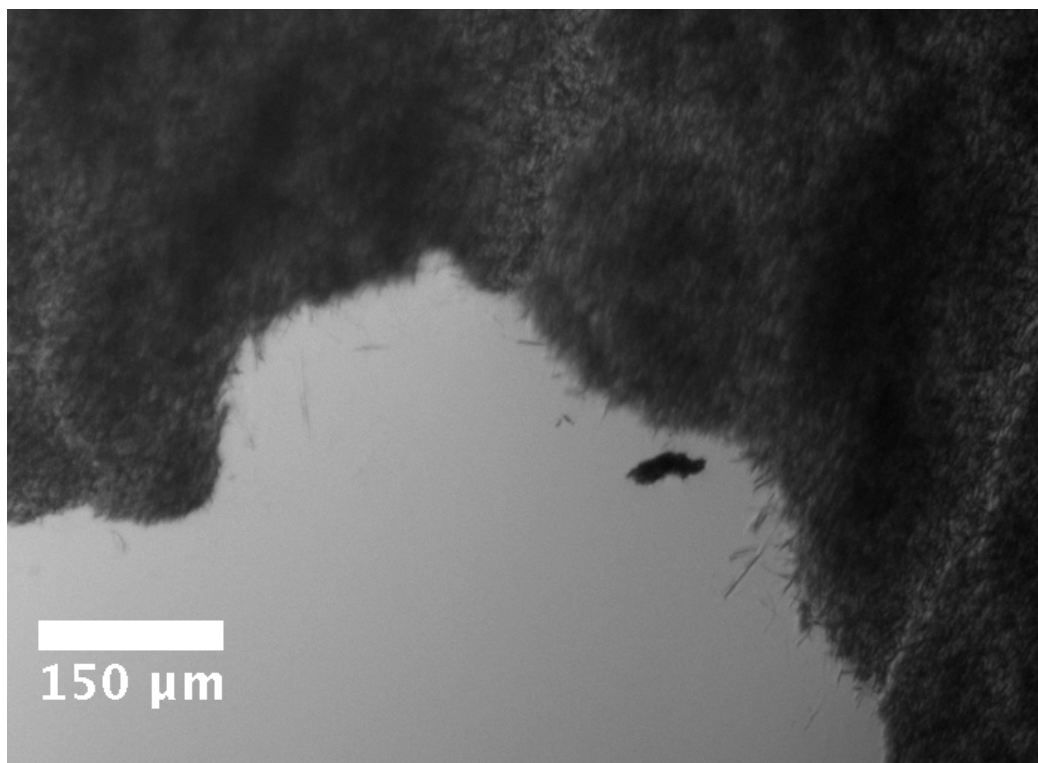
2 Supplementary Figures

Figure S1: Light micrograph of the TAHP film formed at pH 7, shown in Fig. 2 (main article), after the film was ruptured using a glass pipette. The dark regions are the TAHP film. Note the needle-like crystallites clearly seen at the edges of the film.
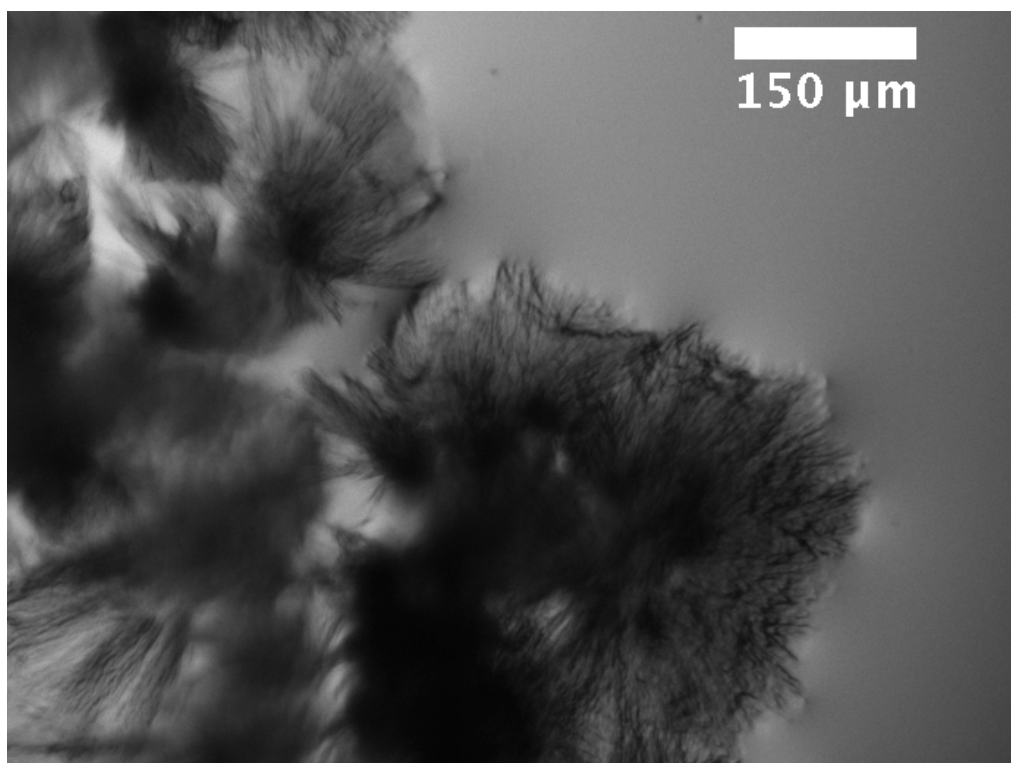
Figure S2: Light micrograph of the TAHP film formed at pH 8, shown in Fig. 2 (main article). Note the significant deformation of the oil-water interface due to the presence of the TAHP crystallites.
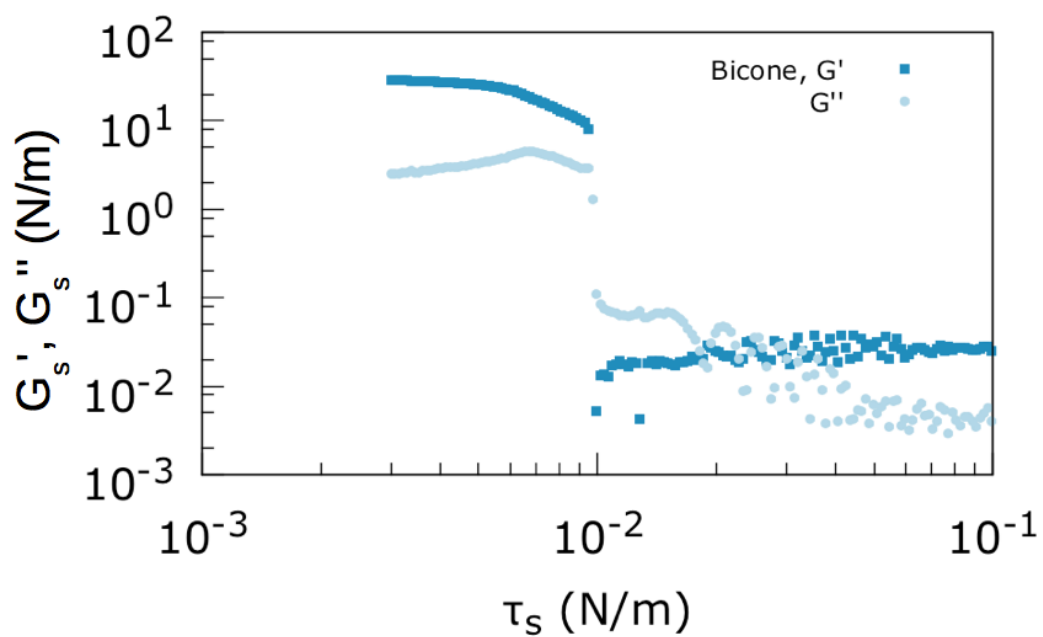
Figure S3: Surface shear rheological moduli against interfacial stress obtained using a stainless steel bicone geometry and an AR-G2 rheometer operated in controlled stress mode. [TDA] = 2.5mM, pH 5, 0.5Hz.