Electronic Supplementary Information (ESI) for "The impact of nanostructure on hygroscopicity and reactivity of fatty acid atmospheric aerosol proxies"

S1. Kinetic and hygroscopicity data

Observed pseudo-first order decay constants (k_{obs}) were measured in the same way as described in Milsom *et al*. – where the SAXS peak area was followed as a function of time.[1] Taking the natural log of each peak area normalised to the initial peak area, and plotting this against time, afforded a linear plot with the gradient being k_{obs}.

The key points are: (i) k_{obs} was measured at the fastest point of the reaction – where the decay was pseudo-first order (see Fig. 6 in the main text); (ii) these k_{obs} values are a measure of the rate of decay of oleic acid *in that nanostructure* – it is clear from the Raman decay (Fig. 6(f) in the main text) that oleic acid remains in the film after the destruction of the initially observed ordered phases.

Nanostructure	wt % fructose	k_{obs} / x 10^{-2} min^{-1}	k_{obs} (uncert.) / x 10^{-2} min^{-1}	Thickness / µm
Liquid	0	23	3	50
Inv. Mic.	20	31	7	95
Inv. Mic.	50	45	10	95
Ord. Inv. Mic.	33	18	2	83
Lam.	0	7	5	0.59
Lam.	0	0.64	0.01	73
Solid	0	0.04	0.01	50

Table S1. Kinetic data with measured pseudo-first order decay constants (k_{obs}) and corresponding nanostructure, composition and film thickness data. The "liquid" and "solid" nanostructures correspond to oleic acid and sodium oleate on their own, respectively – these were measured using Raman spectroscopy as described in Milsom *et al*..[1] All data with 0 wt % fructose are taken from Milsom *et al*..[1]

Nanostructure	wt % fructose	κ	κ (uncert.)	Thickness / µm
Inv. Mic.	20	0.342	0.02	39
Inv. Mic.	33	0.48	0.03	293
Inv. Mic.	50	0.35	0.05	34
Lam.	20	0.023	0.001	39
Hex.	33	0.048	0.002	293

Table S2. Hygroscopicity data for each phase measured from changes in nano-structural *d*-spacing with changes in humidity.

S2. The inverse micellar phase formed at high humidity without the addition of fructose
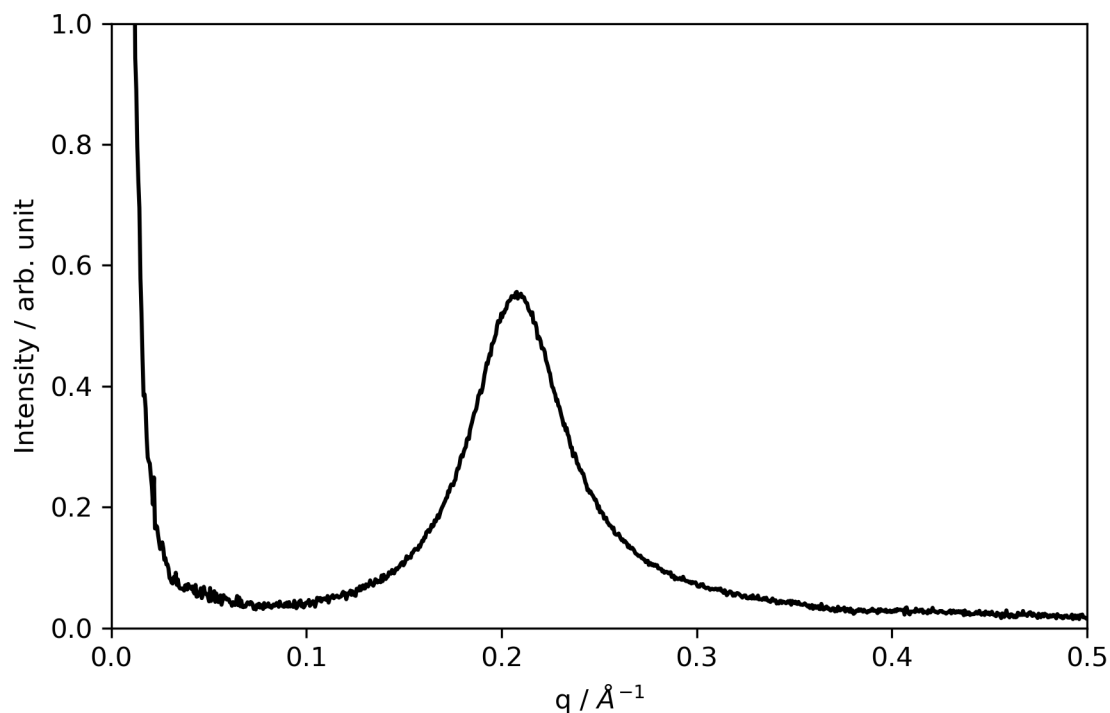

Figure S1. 1D SAXS pattern of a levitated particle of oleic acid:sodium oleate in a 1:1 wt held at 90 % RH for ~ 300 min. This peak corresponds to the inverse micellar phase with a *d*-spacing of 30.1 Å.

A sample of oleic acid-sodium oleate mixture (1:1 wt) was levitated and humidified to 90 % for ~ 300 min to afford the inverse micellar phase. The *d*-spacing observed for this system was 30.1 Å. There is a significant difference in *d*-spacing when compared with the *d*-spacings observed in our fructose-containing mixtures in the main text. The levitation-SAXS experiment is described in detail elsewhere.[2,3]

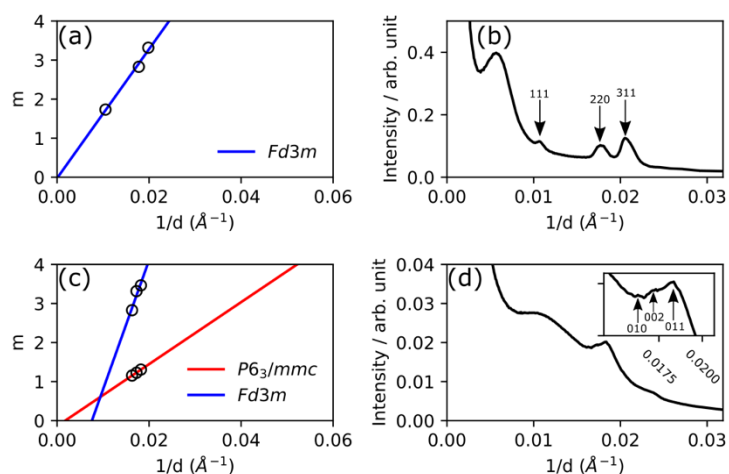**S3. Identifying the ordered inverse micellar phases observed in this study**

Figure S2. Indexing the inverse micellar cubic phases observed in this study. (a) - The *m* vs 1/*d* plot with linear fit for the Fd3m cubic phase symmetry observed at high RH and (b) - the corresponding SAXS pattern with the miller indices (*hkl*) of each scattered peak. (c) & (d) are the same plots for the P6$_3$/mmc symmetry observed during ozonolysis with an additional linear fit to the Fd3m symmetry, showing that the P6$_3$/mmc space group corresponds the best to the fitted peak positions.

In order to identify the cubic close-packed inverse micellar phases observed in this study, a relationship between the Miller indices (*hkl*) of each scattering plane and 1/*d* for each observed reflection. We define a parameter (*m*) which is unique to each cubic symmetry group observed here:

$$m = \sqrt{(h^2 + k^2 + l^2)} \quad \text{(Fd3m symmetry)}^4 \tag{1}$$

$$m = \sqrt{\frac{4}{3}(h^2 + k^2 + hk) + \frac{l^2}{R^2}} \quad \text{(P6}_3\text{/mmc symmetry)}^5 \tag{2}$$

R is the ratio of the cubic unit cell dimensions (*c/a*) for the hexagonal close-packing of spheres for the P6$_3$/mmc space group, with a theoretical value of 1.663.[5] A linear relationship between *m* and experimentally observed peak positions 1/*d* with an intercept at 0 would mean that the phase assignment is correct. This is the case for the Fd3m phase observed at high RH and with an organic composition of 50 wt % fructose (Fig. S2(a)). The cubic phase observed during ozonolysis of a 33 wt % fructose film is assigned to the P6$_3$/mmc arrangement, although the intercept was not quite 0. This may be due to the difficulty in fitting peaks which clearly have an overlapping scattering peak, affecting peak position determination (Fig. S2(c) & (d)). What is certain is that this set of peaks did not correspond to the Fd3m phase.

The slopes of these plots give the unit cell dimension (*a*) for each phase. These were 165 Å for the Fd3m phase and 79 Å for the P6$_3$/mmc phase. This corresponds to a micellar diameter of 117 Å for the Fd3m phase (where *a* = √2 x diameter) and 79 Å for the P6$_3$/mmc phase (where *a* = diameter). These values are higher than the 80 Å (Fd3m) and 76 Å (P6$_3$/mmc) indexed in a previous study on levitated particles of this system without fructose.[2]

This further corroborates what was discussed in the main text: the addition of fructose increases the size of inverse micelles formed.

References

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