Influence of ultrasonication on CNC photonic films:
Implications for the origins of CNC chiral self-assembly

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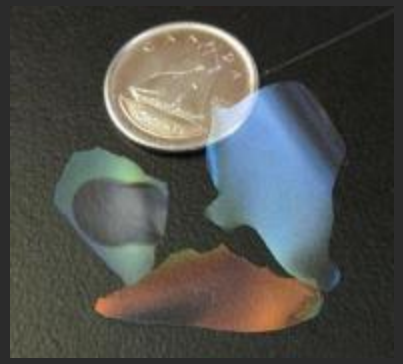
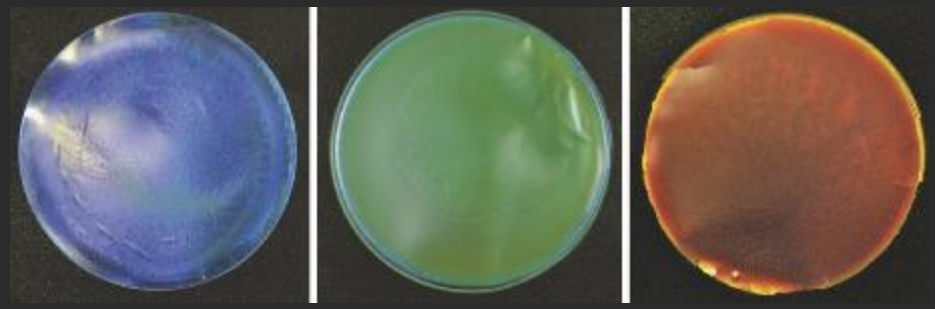
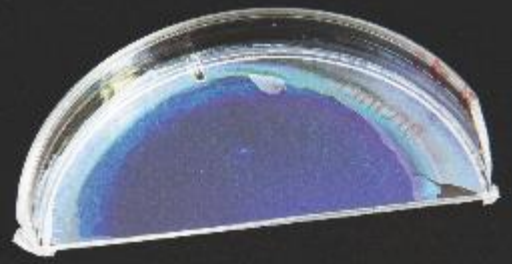
Photonic structures from cellulose nanocrystals



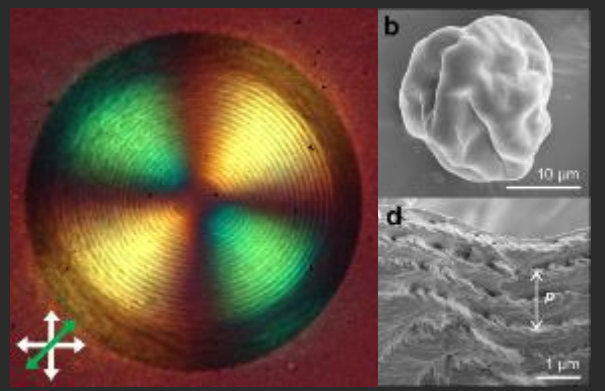
K. E. Shopsowitz *et al.*, *Nature* 468, 422–425 (2010)



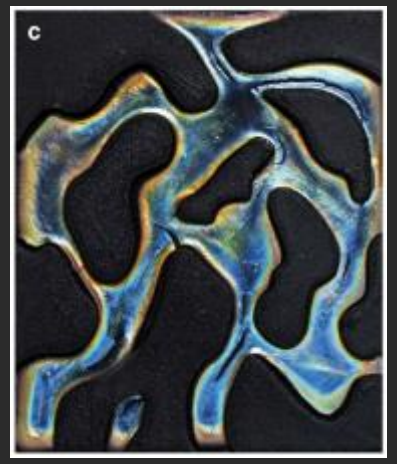
Yao et al., *Adv. Mat*. **29**, 1701323 (2017).



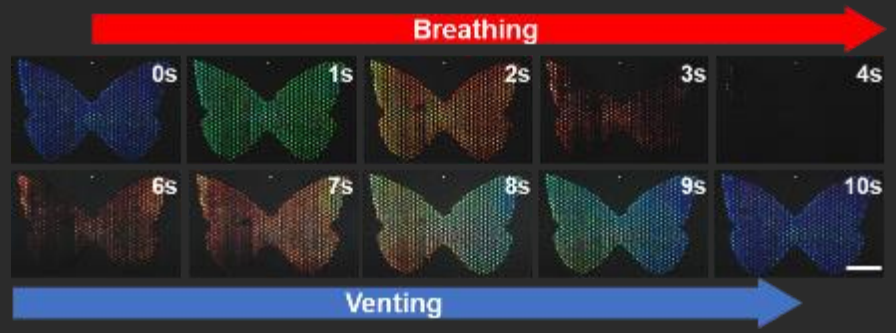
Dumanli *et al.*, *Advanced Optical Materials*. **2**, 646–650 (2014).



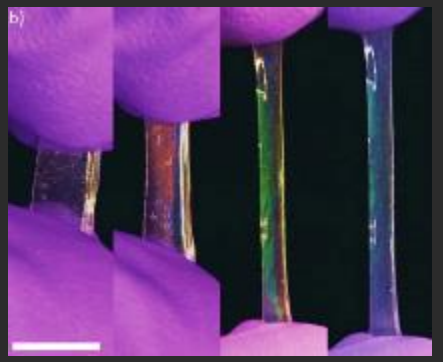
Parker *et al.*, *ACS Nano*. **10**, 8443–8449 (2016).



K.W. Klockars, O.J.Rojas *et al.*, *Cellulose* (2019) 26, 491

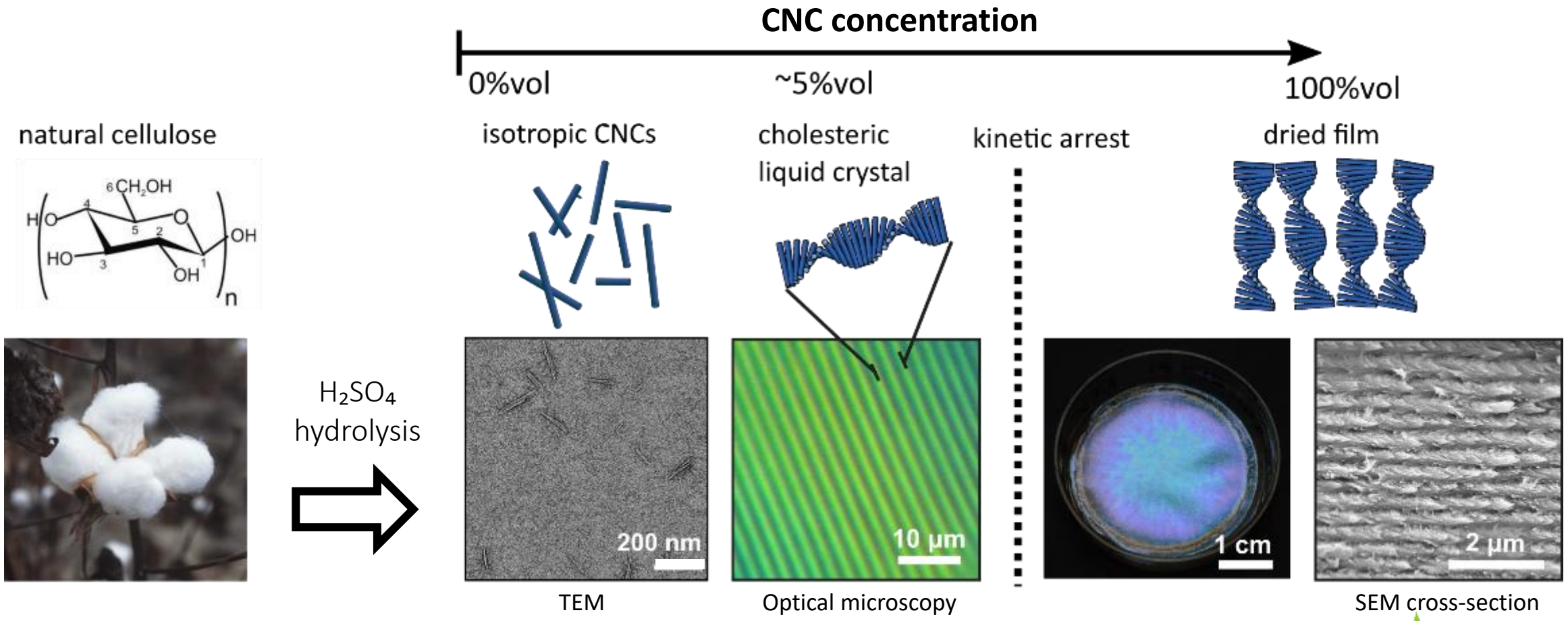


T. H. Zhao *et al.*, *Adv. Func. Mat.* **29**, 1804531 (2019).



C. E. Boott at al., *Angew. Chem. Int. Ed.* **59**, 226–231 (2020).

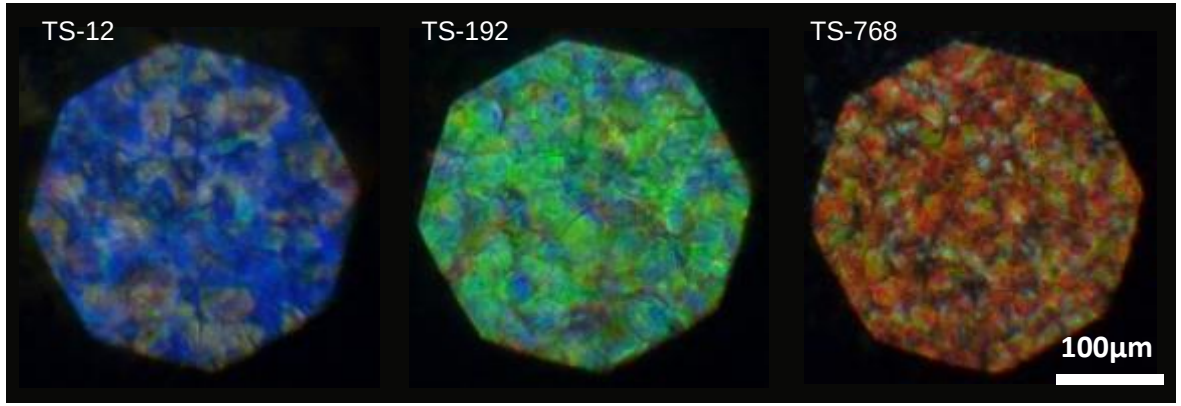
Self-assembly of cellulose nanocrystals

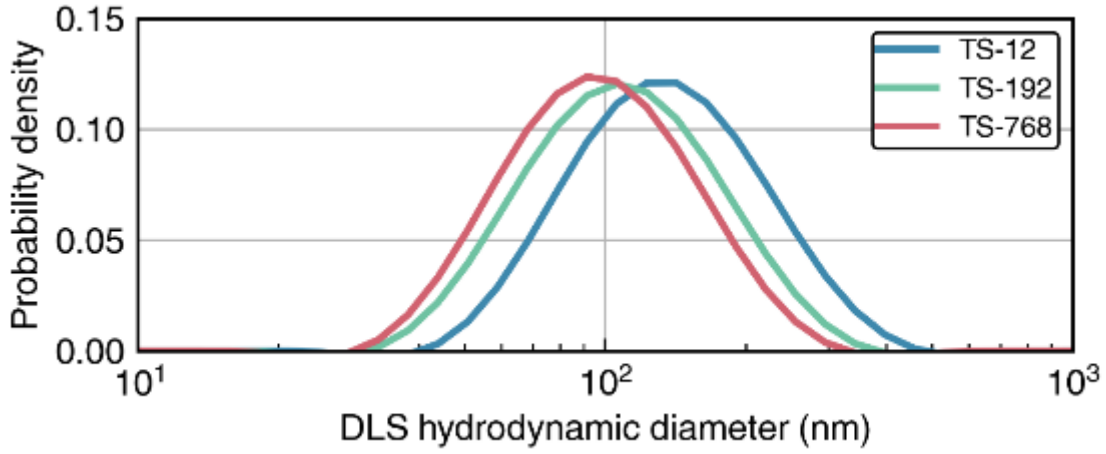


Parker *et al.*, *Advanced Materials*. **30**, 1704477 (2017).

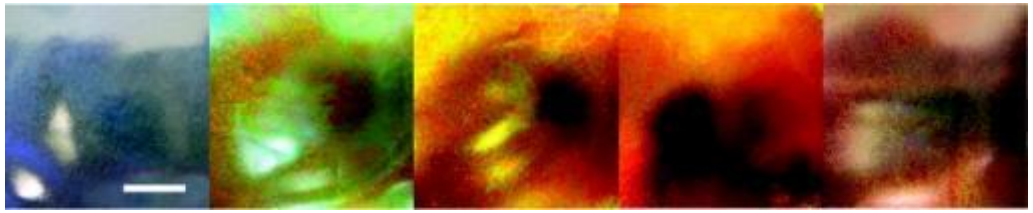
Ultrasonication as a tool to tune CNC size and film colour

Tip sonication (TS) dose





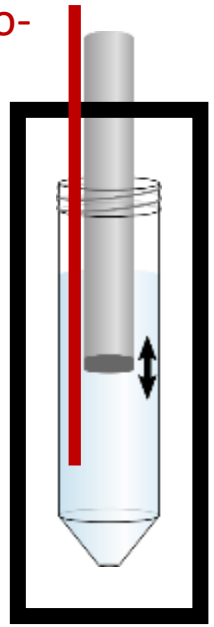
Tip sonication dose



Beck et al, *Biomacromolecules* **12**, 167–172 (2011).

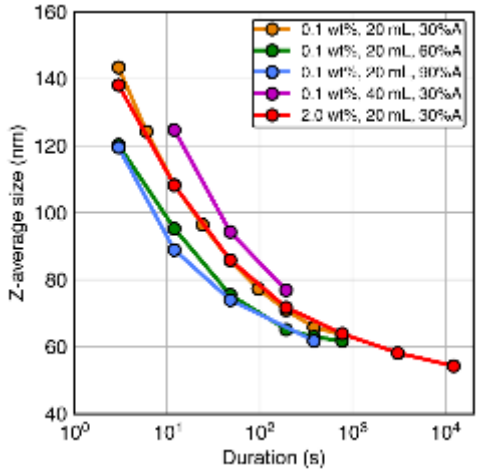
How does CNC size influence self-assembly?

Correlating tip sonication dose and CNC size

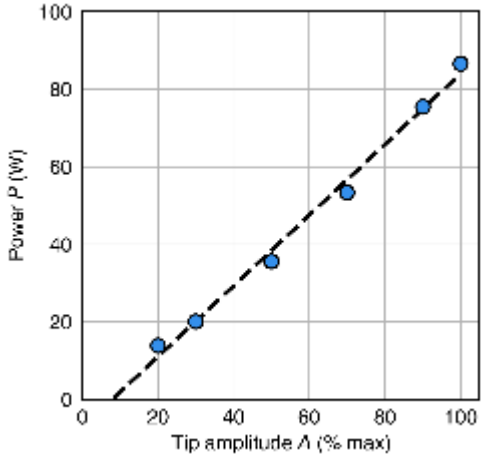


TS parameters

- Suspension volume
- CNC concentration
- Tip amplitude



Sonic

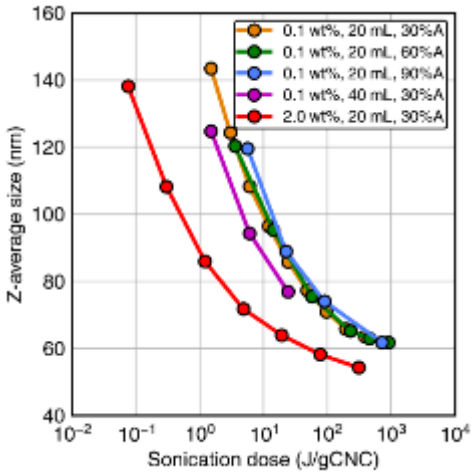


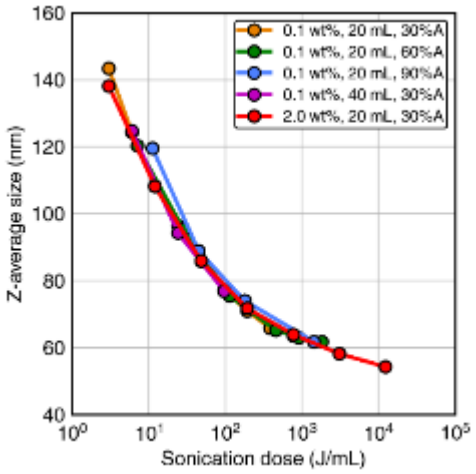
expressed as

ime

J/gCNC

J/mL

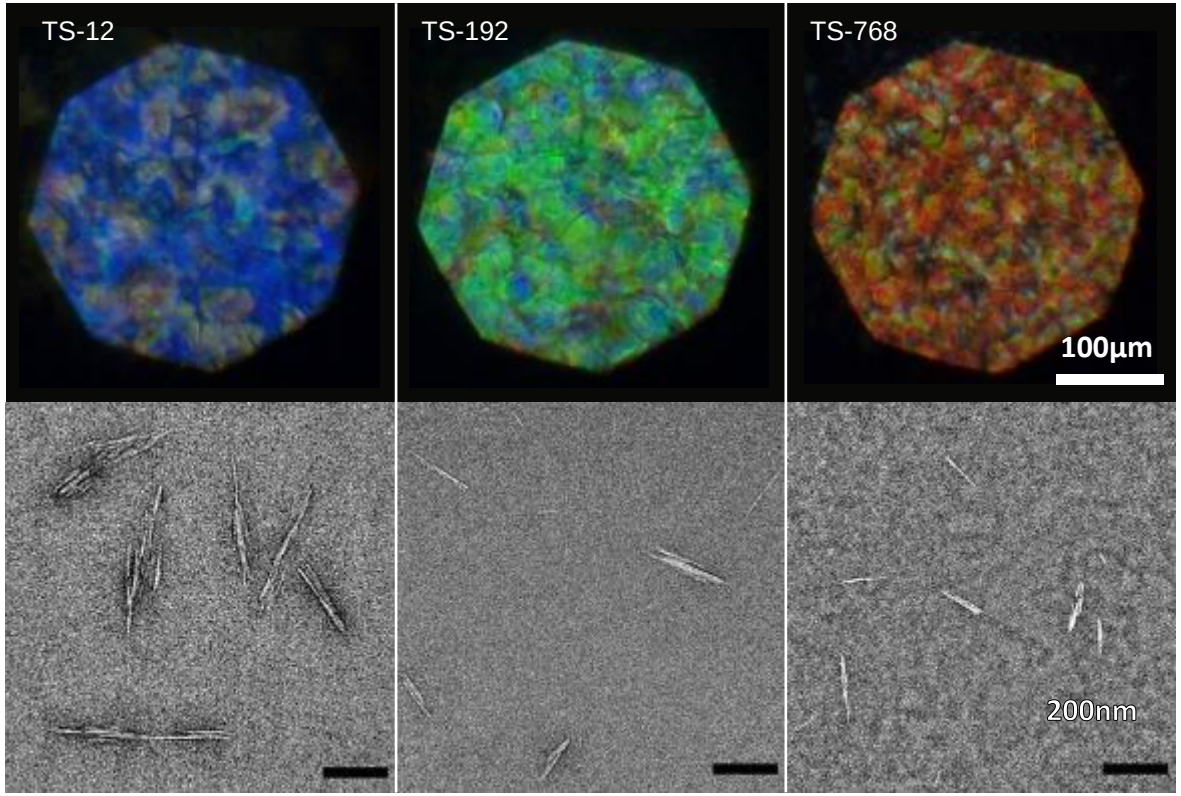




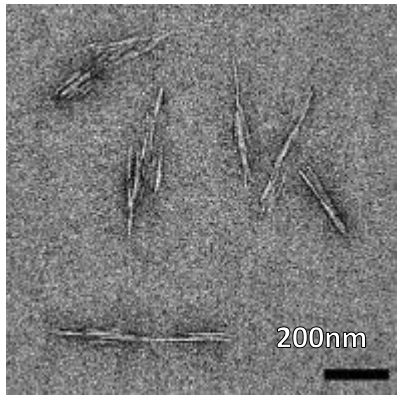
Calibrate tip amplitude to output power using calorimetry

Tracking size and shape changes using TEM images

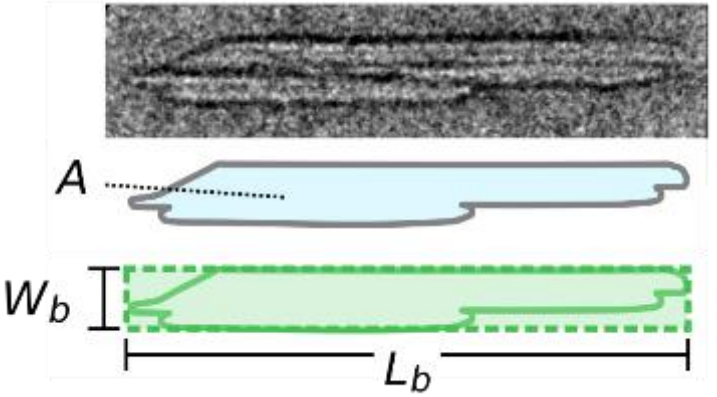
Tip sonication (TS) dose



Decreasing “bundled-ness” of CNCs



Trace outlines



- Box length
- Box width
- **Area, perimeter, …**

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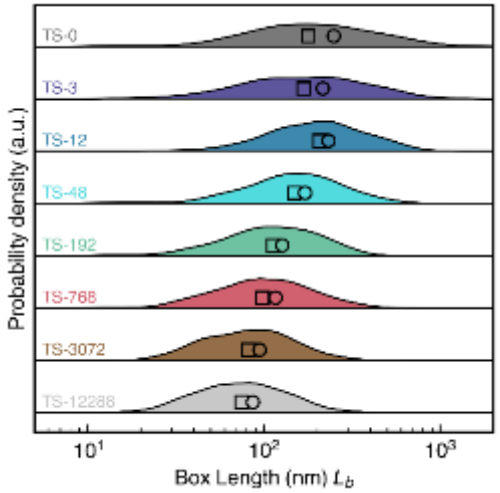
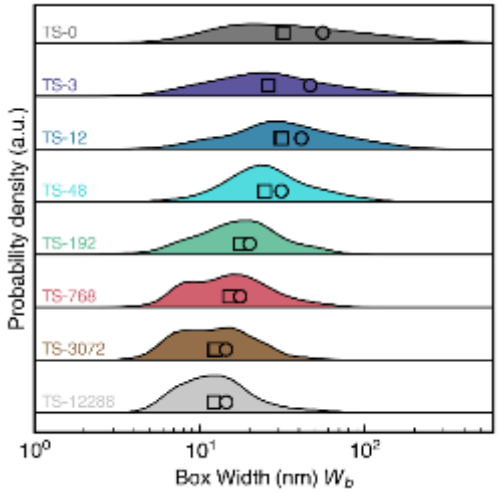
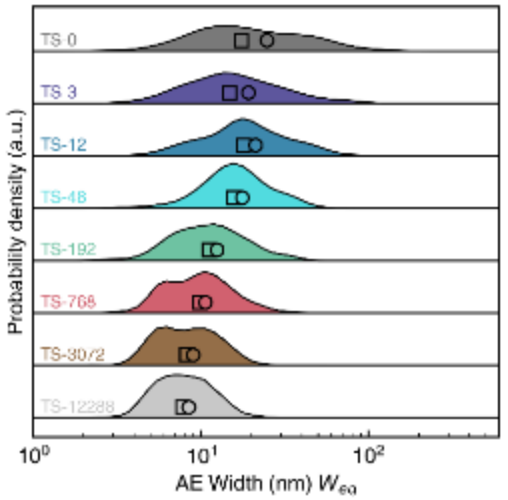
Sonication produces smaller and more rectangular CNCs

TS dose

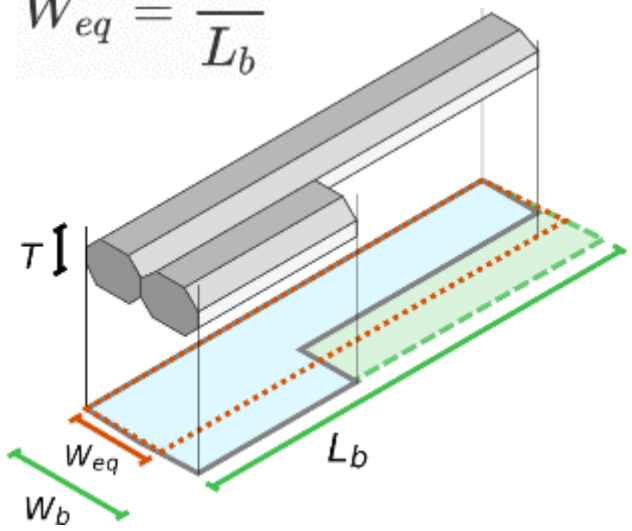






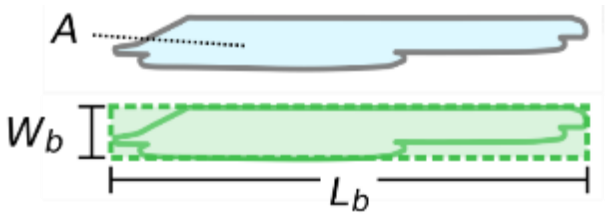
Area-equivalent (AE) width

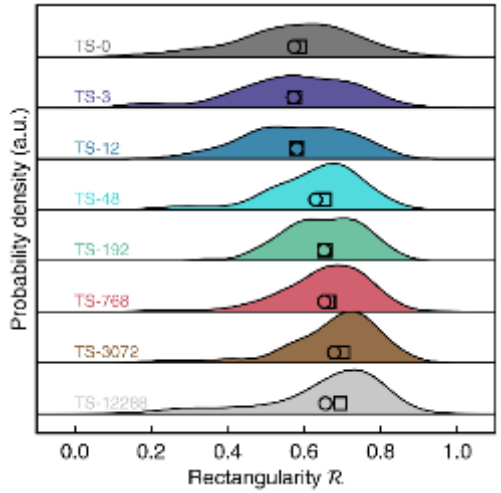
$$W_{eq} = \frac{A}{L_b}$$

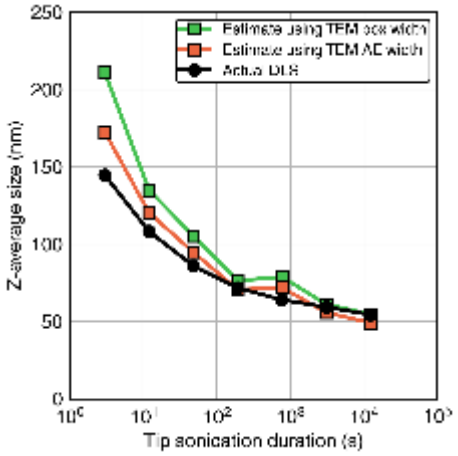


Rectangularity

$$\mathcal{R} = \frac{A}{L_b W_b}$$

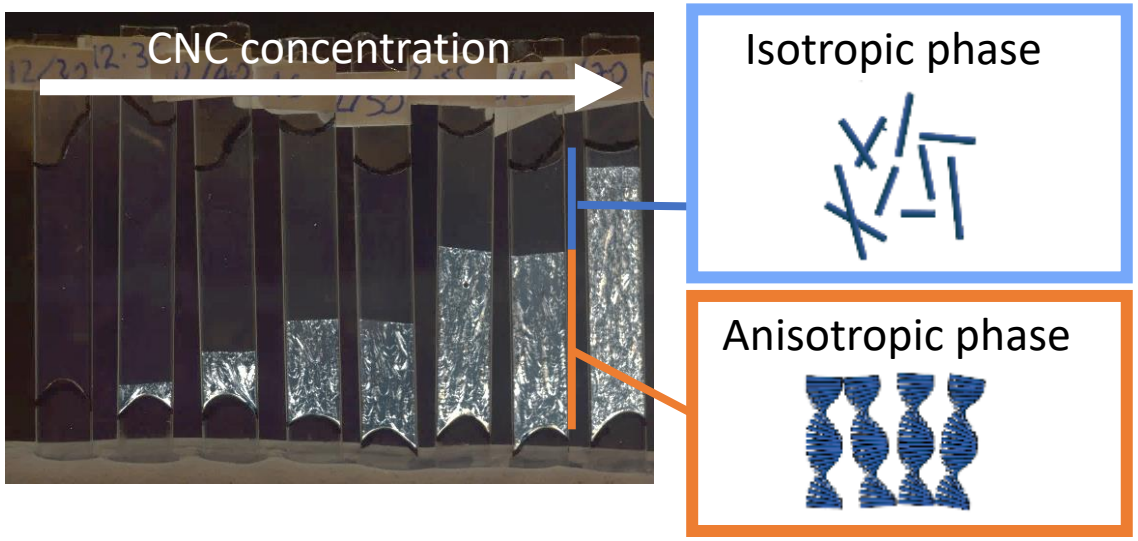




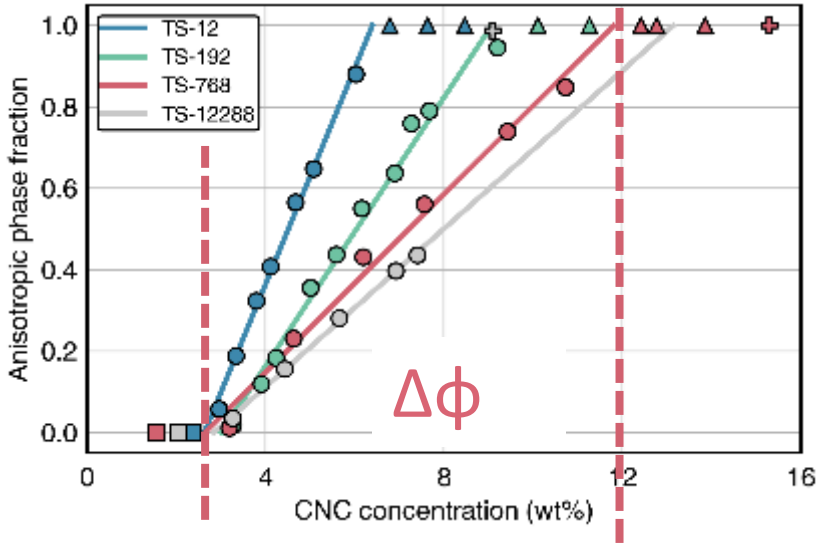


AE width predicts DLS size better than box width

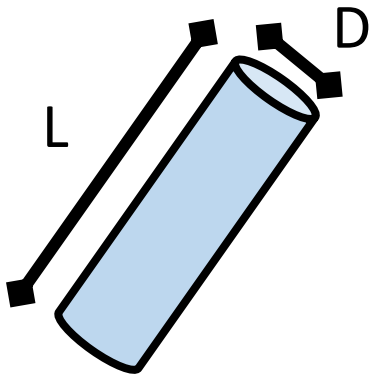
Sonication changes CNC phase separation behaviour



Sonication widens the biphasic region (Δϕ)



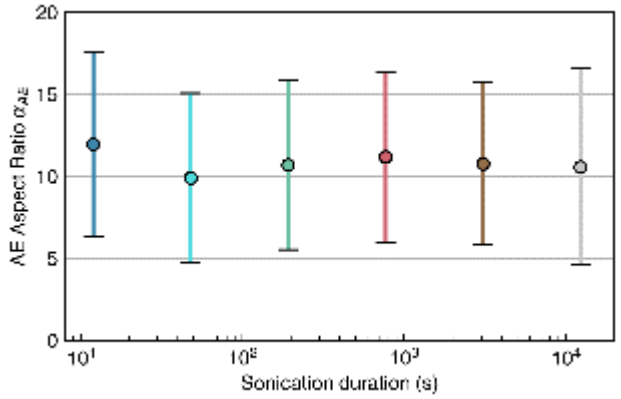
Onsager theory (cylinders):



Expect:

$$\Delta\phi \propto \frac{D}{L}$$

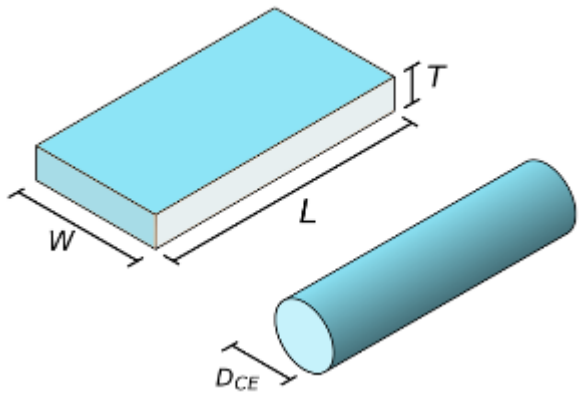
But… no clear trend for length/width aspect ratio (?)



Onsager, L. (1949). Annals New York Academy of Sciences. **51**, 627–659 (1949).

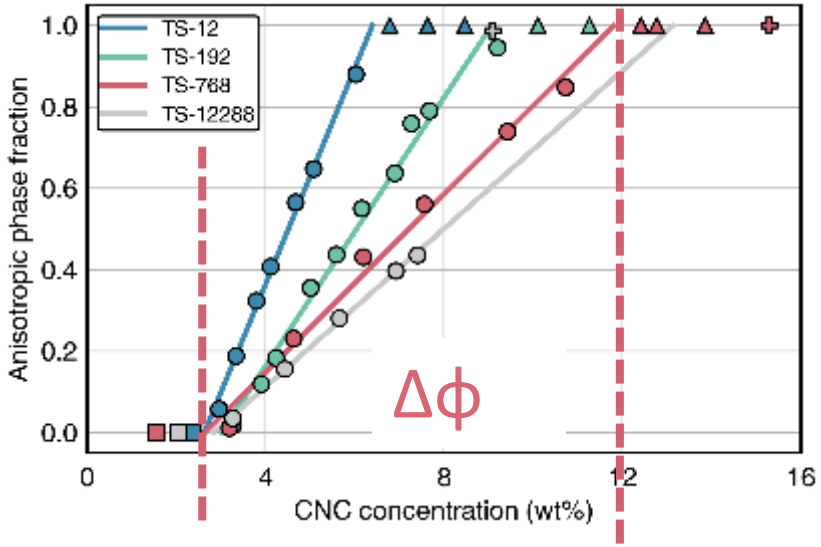
Correlating 3D shape changes with nematic assembly

CNCs are not cylinders

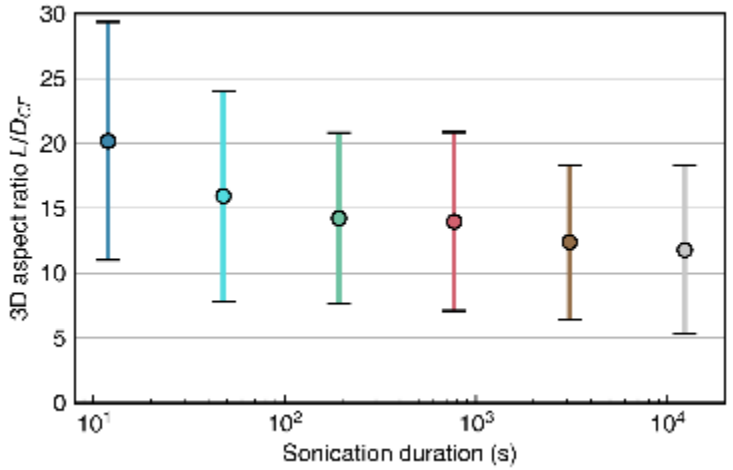


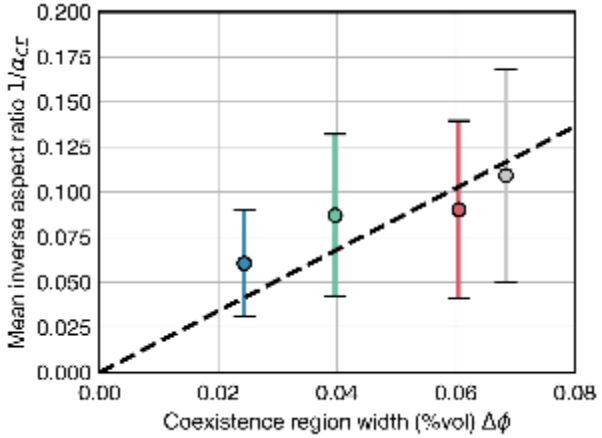
Circle-equivalent (CE) diameter

$$\frac{\pi}{4} D_{CE}^2 = WT$$



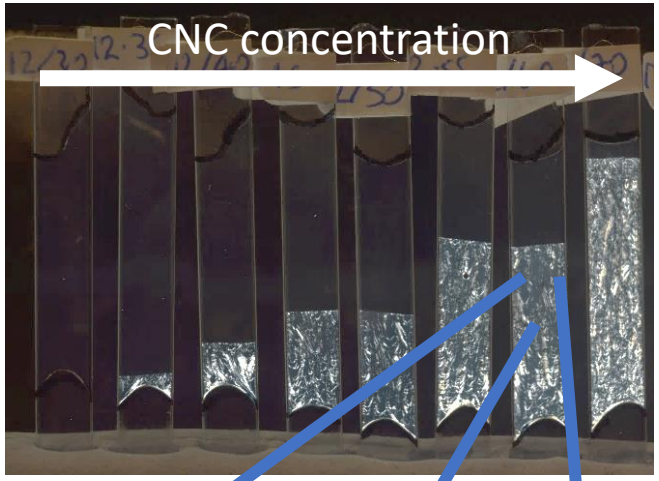
"Cylinder" aspect ratio (L/D_{CE}) **decreases** with sonication

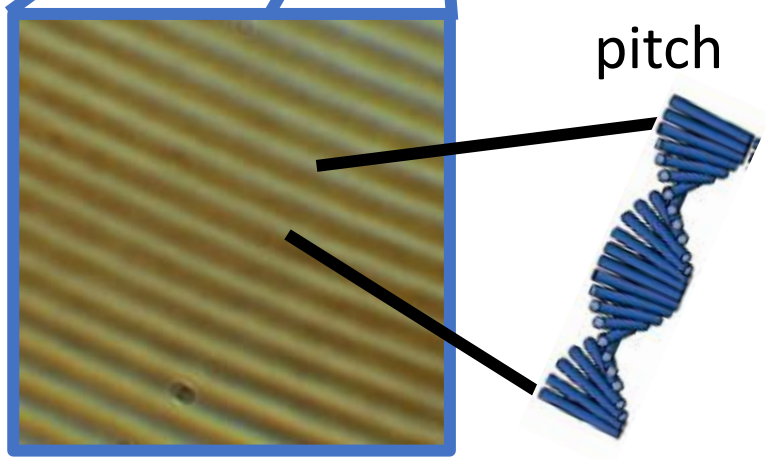




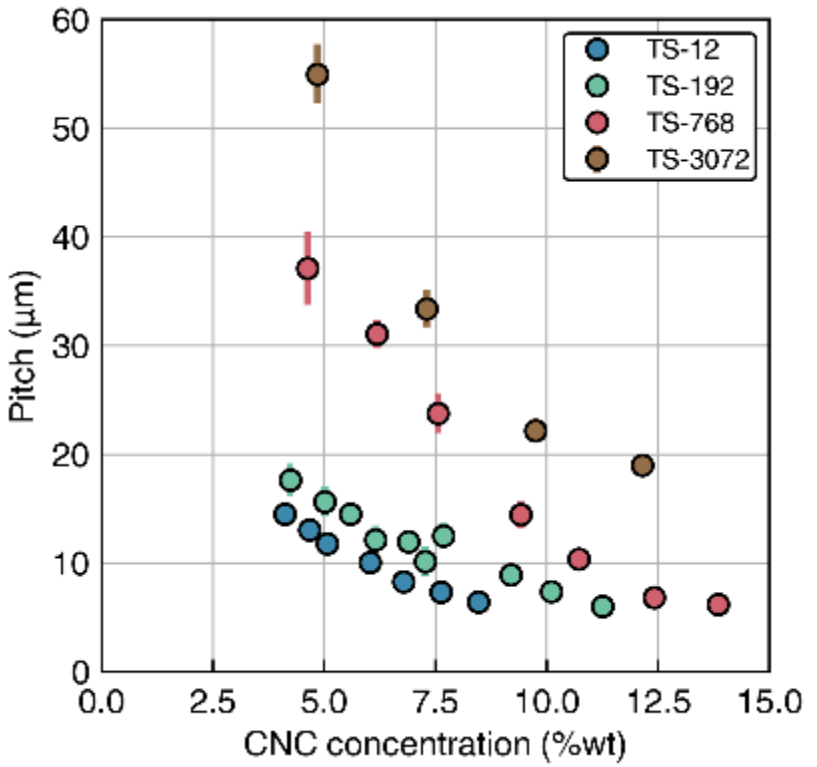
$$\Delta\phi \propto \frac{D}{L}$$

Sonication causes a red-shift by increasing the cholesteric pitch

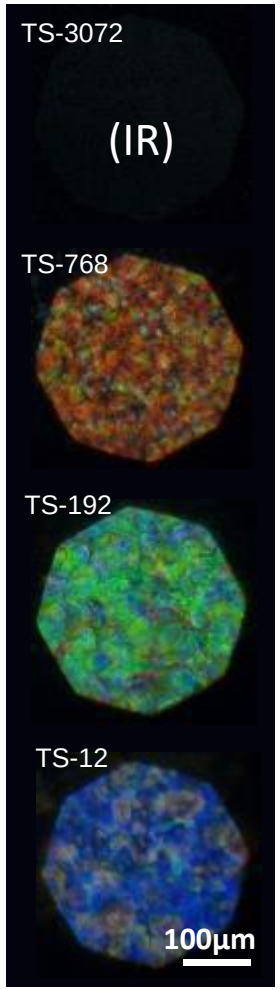




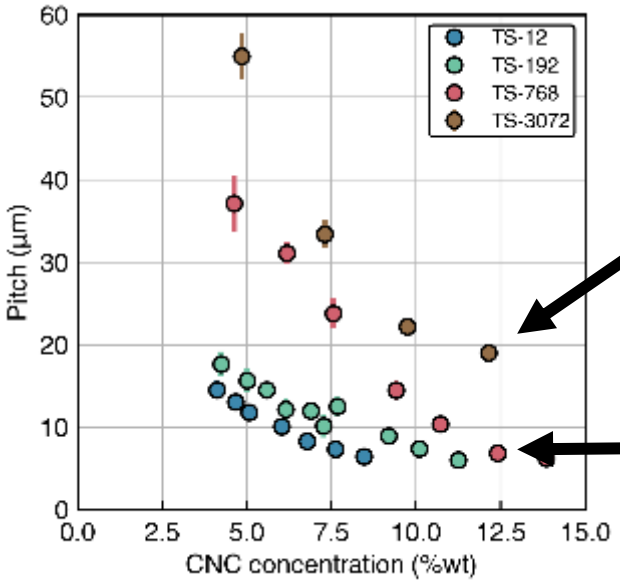
Optical microscopy



TS dose



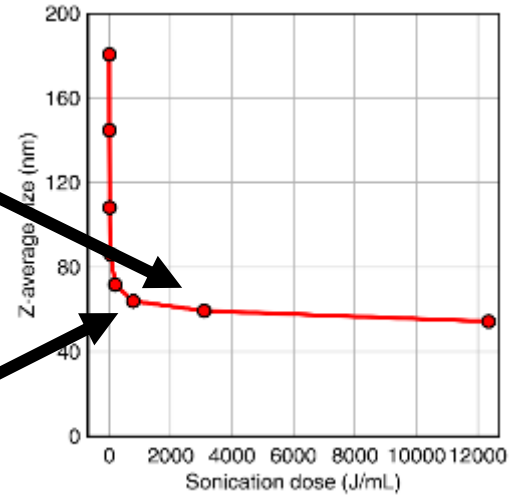
Evidence of chiral bundles as the origin of CNC mesophase chirality

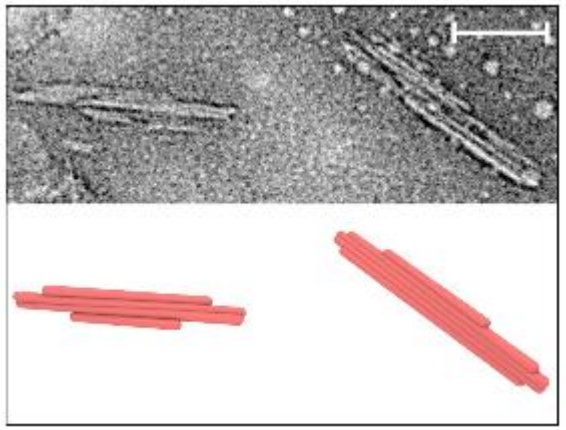


TS-3072

vs.

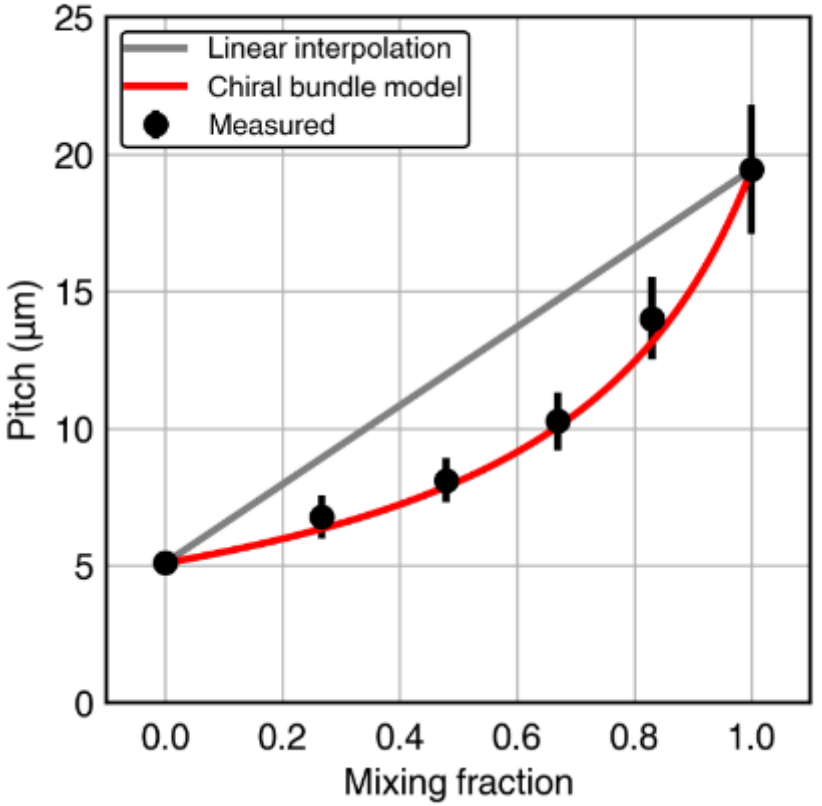
TS-768





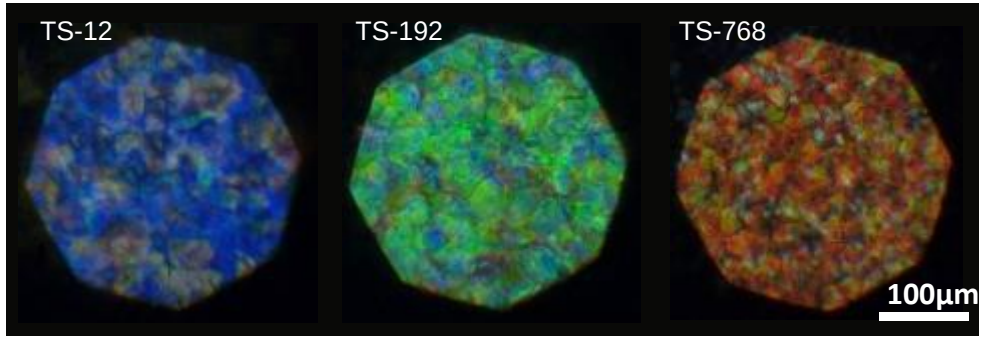
"Bundles" of crystallites act as **chiral dopants**

$$\frac{1}{P} = \beta\, c_{dopant}$$

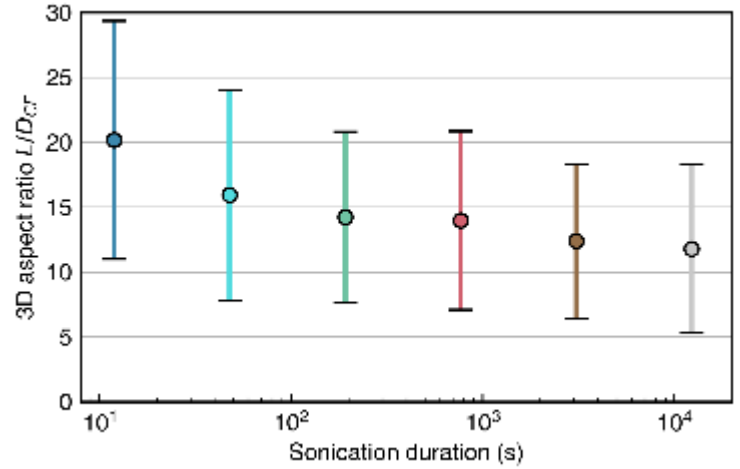


Conclusions

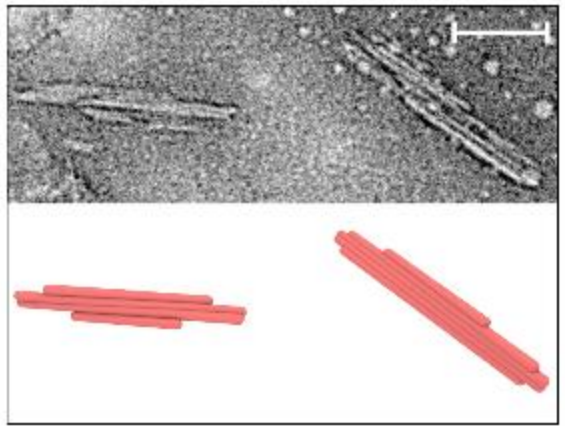
- Sonication dose must be expressed as **energy per volume**



- Sonication decreases the 3D aspect ratio



- Evidence that cholesteric pitch arises from chiral bundles broken by sonication



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