Liquid crystal foam

C. Cruz[a,b], M. H. Godinho[c], A. J. Ferreira[c],
P. S. Kulkarni[d,e], C. A. M. Afonso[e] and P. I. C. Teixeira[f,g]

[a]Centro de Fisíca da Matéria Condensada, Universidade de Lisboa, Portugal
[b]Departamento de Física, Instituto Superior Técnico,
Universidade Técnica de Lisboa, Portugal
[c]Departamento de Ciência dos Materiais and CENIMAT/I3N,
Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Portugal
[d]REQUIMTE, Departamento de Química,
Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Portugal
[e]CQFM, Departamento de Engenharia Química e Biológica,
Instituto Superior Técnico, Universidade Técnica de Lisboa, Portugal
[f]Instituto Superior de Engenharia de Lisboa, Portugal
[g]Centro de Física Teórica e Computacional, Universidade de Lisboa, Portugal

Motivation

- Room-temperature ionic liquids are salts whose melting point is below 100°C.
- Typically they are made up of large polyatomic ions.
- They exhibit interesting properties leading to applications:
  - Green solvents;
  - conductive matrices for electrochemical devices.
- By careful molecular design they can be made to exhibit lamellar or columnar liquid crystalline (LC) phases at or near room temperature. These phases have enhanced ionic conductivity.

Sample preparation

- Solutions of n-alkylimidazolium salts in acetone were prepared at room temperature followed by stirring to allow homogenisation.

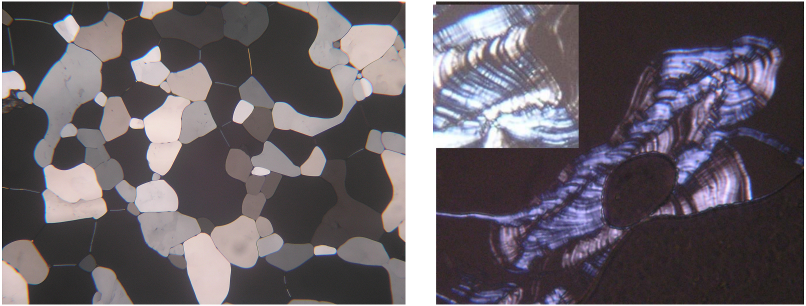
R= *n*-alkyl

1a: n=8
1b: n=10

- Films were cast and sheared simultaneously by moving a casting knife over a glass substrate at $v = 5$ mm/s. Film thickness after solvent evaporation was 10–20 μm. Films were then observed by polarised optical microscopy.

Some pretty pictures. . .

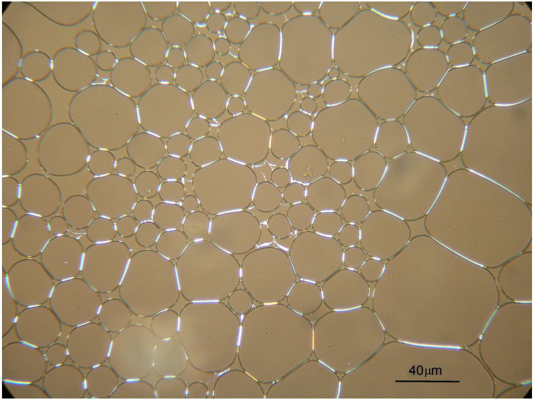
- Although these ionic LCs are solid at room temperature, shearing the sample between microscope slides made them go smectic:



- Left: mosaic texture (compound 1a); right: focal conics (compound 1b).

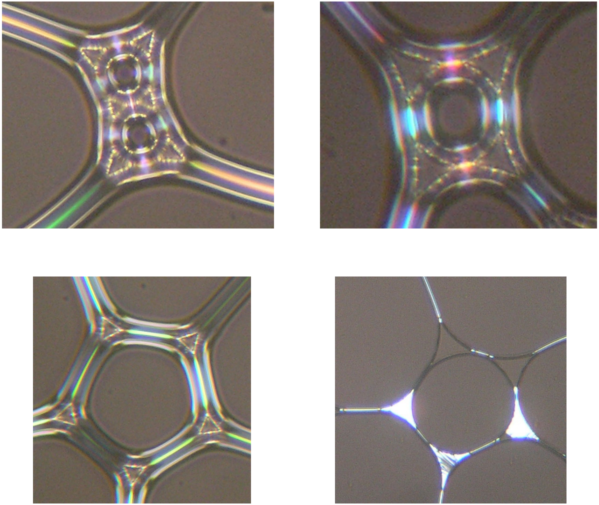
And now for something completely unexpected. . .

- If the films are prepared from isotropic solutions and sheared, they exhibit a morphology typical of 2d soap foams:



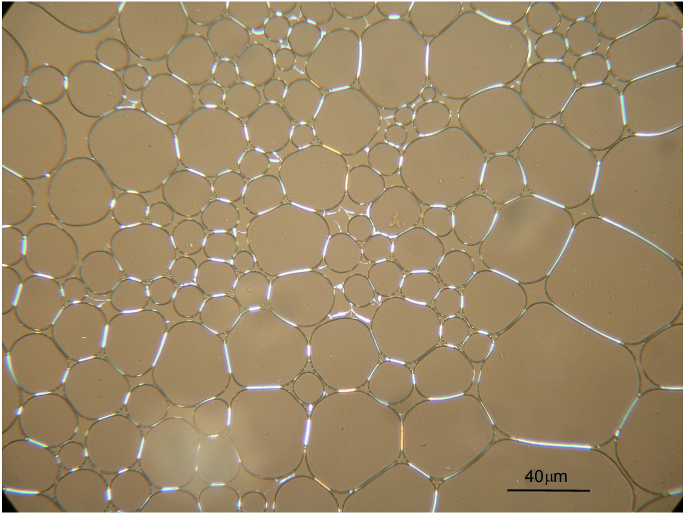
. . . but beautiful anyway

- The walls and vertices between cells have complex defect structures:



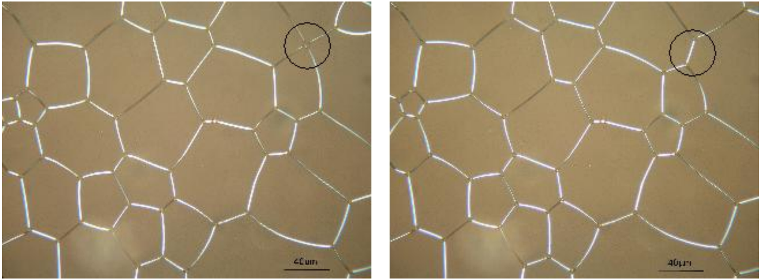
Time evolution of quiescent foam

- How does this foam coarsen?



T1 topological transformation in quiescent foam

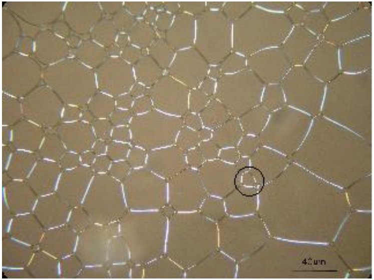
- In a T1 topological transformation, two neighbouring cells cease being neighbours and two previously non-neighbouring cells become neighbours, via an intermediate, unstable fourfold vertex.

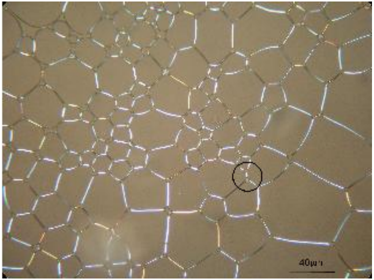


- The lifetime of the fourfold vertex is at most 10 minutes.

T2 topological transformation in quiescent foam

- In a T2 topological transformation, a cell shrinks and disappears.



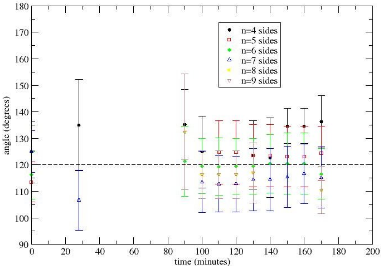


- The transformation took at most 10 minutes.

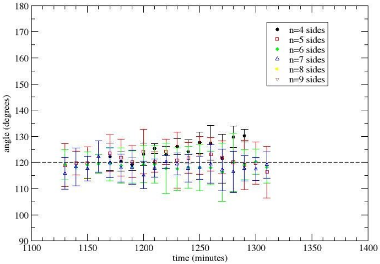
Internal cell angles in quiescent foam

- In an ordinary liquid foam at equilibrium, internal cell angles are 120°.

(a)

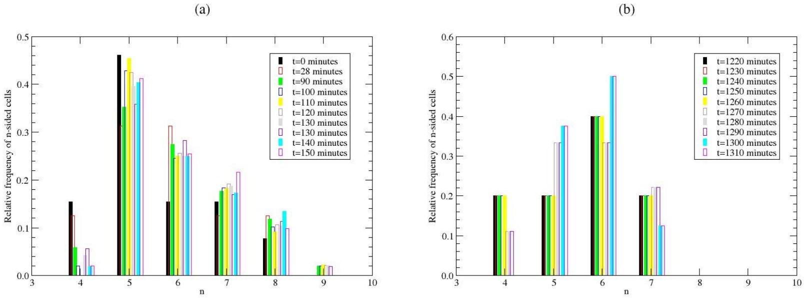


(b)



- Both at early and late times, internal cell angles (when they can be defined) are clustered around 120°, which is indicative of a quasi-static process and uniform surface tension.

Distribution of cell sides in quiescent foam



- Cells with fewest (4) or most (8 and 9) sides tend to disappear. Many 5-sided cells survive until relatively late.
- Distribution of cell sides becomes peaked at $n = 6$: $\langle n \rangle \approx 6.0 \pm 0.2$ (early times) and $\langle n \rangle \approx 5.6 \pm 0.3$ (late times).
- Overall shape of distribution and peak position agree generally with those for ordinary liquid foams.

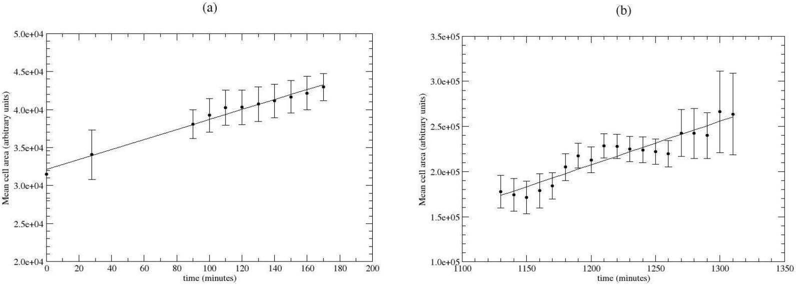
Growth law in quiescent foam

- In ordinary 2d liquid foams, the mean cell area grows linearly with time:

$$\langle A \rangle \sim t^1$$

- In LC foams the growth exponent might be smaller, due to defects:

$$\langle A \rangle \sim t^{0.4}$$

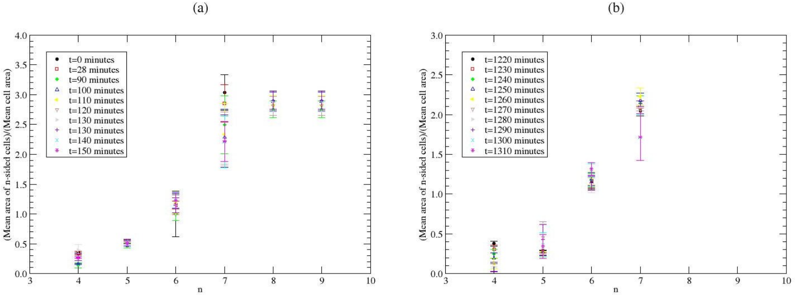


- Our data are not incompatible with a linear increase.

Lewis' law in quiescent foam

- The mean area of *n*-sided cells is linear in *n* – bigger bubbles tend to have more sides:

$$\langle A(n)\rangle = \langle A\rangle\,[1 + c\,(n-6)]$$

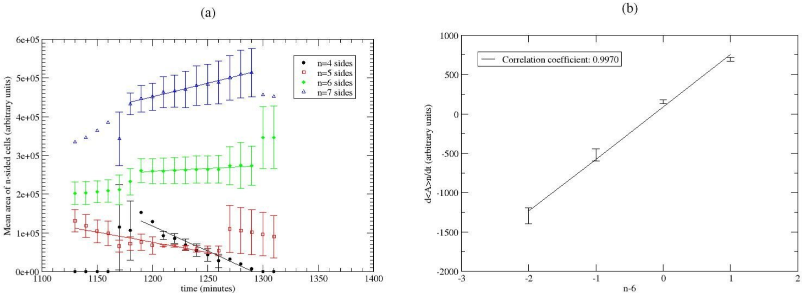


- At late enough times the mean cell area is an increasing function of *n* with an upward concave shape.

Von Neumann's law in quiescent foam

- In 2d foams, cells with more than 6 sides grow, cells with fewer than 6 sides shrink.:

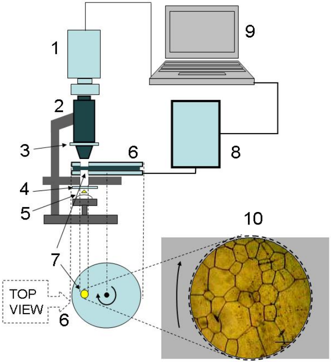
$$\frac{d\langle A(n)\rangle}{dt} = C\,(n-6)$$



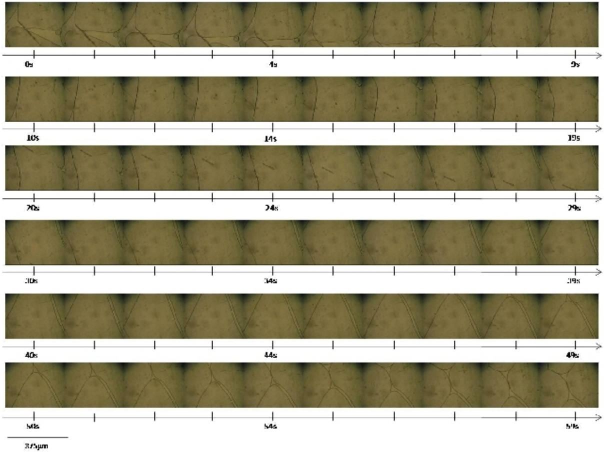
- At late times, $d\langle A(n)\rangle/dt$ is indeed approximately linear in n.

Time evolution of foam under shear

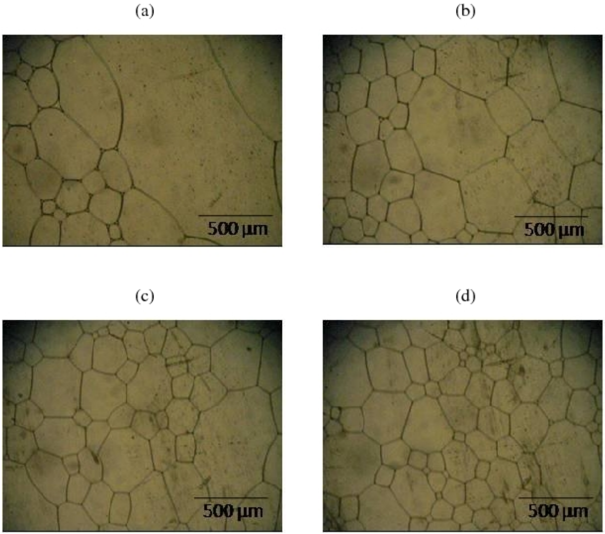
- What now if we subject our foam to a controlled shear? And keep the film thickness constant, keep moisture out?
- So, the development of the foam textures was observed by polarising optical microscopy, at room temperature (24°C) and well-defined shear rates. Sample thickness was 5 μm.
- Textures form only for shear rates above a threshold that is between 30 and 40 s^{-1}.



1 – Camera
2 – Microscope
3 – Analizer
4 – Polarizer
5 – Light source
6 – Parallel plates shearing system with sample
7 – Window in parallel plates shearing system for sample observation
8 – Shearing system controller
9 – Computer
10 – Sample observed through window between crossed polarizers

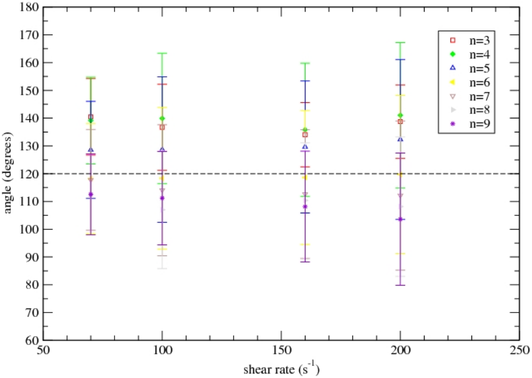


- Time evolution of LC foam structure for a shear rate of 20 s^{-1}. Cells are typically elongated and larger that the micropscope's field of view. Shear is applied along the vertical direction.



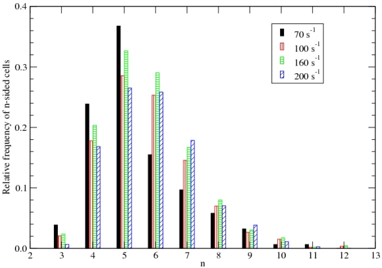
- Sheared ionic LC between polarisers, for shear rates (a) 70 s^{-1}, (b) 100 s^{-1}, (c) 160 s^{-1} and (d) 200 s^{-1}. Shear is applied along the vertical direction.

Internal cell angles in foam under shear



- Cells with fewer than 6 sides tend to have larger internal angles, whereas those with more than 6 sides tend to have smaller internal angles. This happens for all shear rates. Maybe smaller and larger cells are, respectively, compressed and stretched in the direction of shear.

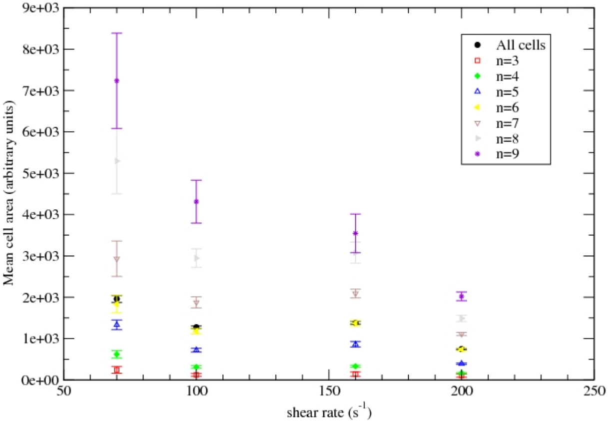
Distribution of cell sides in foam under shear



Shear rate (s^{-1})	$\langle n \rangle$	Standard deviation
70	5.4	1.5
100	5.7	1.5
160	5.7	1.5
200	5.9	1.4

- $\langle n \rangle$ approaches 6 from below with increasing shear rate.
- The standard deviations are quite large.

Mean cell area *vs* shear rate



- There is a clear trend towards smaller cells at higher shear rates.
- This appears to be slightly non-monotonic for all cells except those with nine or more sides.

Summary

- We have attempted to quantify the morphology of our non-equilibrium LC foam, both quiescent and under controlled shear.
- Our results suggest that surface tension may play a key role in determining the physics of this system, as it does in low-viscosity liquid foams, despite the fact that our LC is in fact rather viscous.
- There appears to be a threshold shear rate below which the foam-like patterns do not form.
- Above this threshold, larger shear rates produce smaller cells.
- The internal cell angles and cell side distributions deviate from those of an equilibrium foam, especially at the lower shear rates.
- We do not know what role liquid crystallinity plays in this system, except that it probably behaves like a soap because it is a smectic.
- Some outstanding questions:
    - What is the effect of temperature?
    - What is the effect of film thickness?
    - What is the effect of water? (Residual, atmospheric moisture. . .)
    - What is the long-time dynamics, in particular the growth exponent?
    - Can we stabilise the foam, e.g., by adding solid particles?

References

- M. H. Godinho *et al.*. Liq. Cryst. **35**, 103–107 (2008).
- C. Cruz *et al.*. Phil. Mag. Lett. **88**, 741–747 (2008).
- A. J. Ferreira *et al.*. Liq. Cryst. **37**, 377–382 (2010).

Acknowledgements

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One last pretty picture. . .