Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Shear-induced lamellar ionic liquid-crystal foam

A. J. Ferreira[a]; C. Cruz[ab]; M. H. Godinho[c]; P. S. Kulkarni[de]; C. A. M. Afonso[e]; P. I. C. Teixeira[fg]
[a] Centro de Fisíca da Matéria Condensada, Universidade de Lisboa, Avenida Professor Gama Pinto 2, Lisboa, Portugal [b] Departamento de Física, Instituto Superior Técnico, Universidade Técnica de Lisboa, Avenida Rovisco Pais, Lisboa, Portugal [c] Departamento de Ciência dos Materiais and CENIMAT/I3N, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica, Portugal [d] REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica, Portugal [e] CQFM - Centro de Química-Física Molecular and IN - Institute of Nanosciences and Nanotechnology, Instituto Superior Técnico, Universidade Técnica de Lisboa, Avenida Rovisco Pais, Lisboa, Portugal [f] Instituto Superior de Engenharia de Lisboa, Rua Conselheiro Emídio Navarro 1, Lisboa, Portugal [g] Centro de Física Teórica e Computacional, Universidade de Lisboa, Avenida Professor Gama Pinto 2, Lisboa, Portugal

To cite this Article Ferreira, A. J. , Cruz, C. , Godinho, M. H. , Kulkarni, P. S. , Afonso, C. A. M. and Teixeira, P. I. C.(2010) 'Shear-induced lamellar ionic liquid-crystal foam', Liquid Crystals, 37: 4, 377 — 382
To link to this Article: DOI: 10.1080/02678291003615673
URL: http://dx.doi.org/10.1080/02678291003615673

Liquid Crystals,
Vol. 37, No. 4, April 2010, 377–382

Shear-induced lamellar ionic liquid-crystal foam

A.J. Ferreira[a†], C. Cruz[a,b], M.H. Godinho[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, Avenida Professor Gama Pinto 2, P-1649-003 Lisboa, Portugal;* [b]*Departamento de Física, Instituto Superior Técnico, Universidade Técnica de Lisboa, Avenida Rovisco Pais, P-1040-001 Lisboa, Portugal;* [c]*Departamento de Ciência dos Materiais and CENIMAT/I3N, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, P-2829-516 Caparica, Portugal;* [d]*REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, P-2829-516 Caparica, Portugal;* [e]*CQFM – Centro de Química-Física Molecular and IN – Institute of Nanosciences and Nanotechnology, Instituto Superior Técnico, Universidade Técnica de Lisboa, Avenida Rovisco Pais, P-1040-001 Lisboa, Portugal;* [f]*Instituto Superior de Engenharia de Lisboa, Rua Conselheiro Emídio Navarro 1, P-1950-062 Lisboa, Portugal;* [g]*Centro de Fisica Teórica e Computacional, Universidade de Lisboa, Avenida Professor Gama Pinto 2, P-1649-003 Lisboa, Portugal*

(Received 17 November 2009; final version received 12 January 2010)

In a recent paper we reported an experimental study of two *N*-alkylimidazolium salts. These ionic compounds exhibit liquid crystalline behaviour with melting points above 50°C in bulk. However, if they are sheared, a (possibly non-equilibrium) lamellar phase forms at room temperature. Upon shearing a thin film of the material between microscope slides, textures were observed that are strikingly similar to liquid (wet) foams. The images obtained from polarising optical microscopy (POM) were found to share many of the known quantitative properties of a two-dimensional foam coarsening process. Here we report an experimental study of this foam using a shearing system coupled with POM. The structure and evolution of the foam are investigated through the image analysis of time sequences of micrographs obtained for well-controlled sets of physical parameters (sample thickness, shear rate and temperature). In particular, we find that there is a threshold shear rate below which no foam can form. Above this threshold, a steady-state foam pattern is obtained where the mean cell area generally decreases with increasing shear rate. Furthermore, the steady-state internal cell angles and distribution of the cell number of sides deviate from their equilibrium (i.e. zero-shear) values.

Keywords: liquid foams; ionic liquid crystals; shear

1. Introduction

Ionic liquids are liquids that consist solely of cations and anions, and whose melting points are below 100°C. This sets them apart from molten salts such as sodium chloride, which are liquid only far above room temperature. Typically, ionic liquids consist of polyatomic, organic cations and anions. By linking long alkyl chains to either ion, they can be made amphiphilic, and the resulting compounds may exhibit anisotropic, liquid-crystal (LC) phases. The resulting LCs are amphotropic, in that orientational order can be driven by either temperature (as in thermotropic LCs) or concentration (as in lyotropic LCs) changes (see, e.g., [1] for a review). Their study may therefore be relevant to living systems, where ions and long-chain molecules coexist in an aqueous environment and orientationally ordered phases are also present, e.g., in cell membranes [2]. Furthermore, the ionic nature of these materials combined with their self-organising properties allows the optimisation of functional characteristics including conductivity [3]. Applications to date include green solvents and ion-conductive matrices for electrochemical devices [4].

In an earlier paper [5] we reported the characterisation, by polarising optical microscopy (POM), differential scanning calorimetry and X-ray diffraction, of two *N*-alkylimidazolium salts that exhibit lamellar mesophases at temperatures above 50°C. Surprisingly, we found that shearing the crystalline sample between microscope slides induces LC behaviour at room temperature, which was stable over a timescale of at least several days. Even more surprising was that the film morphologies bear a very strong resemblance to those of two-dimensional (2d) foams: when observed between cross polarisers, the material is seen to partition into dark domains (henceforth referred to as 'cells' or 'bubbles') separated by brighter, birefringent walls that are approximately arcs of circle and meet at vertices ('Plateau borders') with three or more sides. The system is clearly fluid: the walls, which we conjecture might be regions of high concentration of

---

†Present address: Department of Chemistry, University of Hull, Cottingham Road, Kingston upon Hull HU6 7RX, UK.
*Corresponding author. Email: piteixeira@cii.fc.ul.pt.

ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678291003615673
http://www.informaworld.com

defects, respond to pressure applied to the microscope slide as fast as the human eye can follow, i.e. in less than about 100 ms for a film thickness below 10 μm. The cells are filled with air, as imperfections on the bottom glass slide can be seen through them. These may have been air bubbles trapped between the irregular surface of the solid film and the top glass slide. This introduces new interesting problems concerning the molecular organization within the cell walls and Plateau borders of the foam, and also the forces that determine the observed foam-like behaviour.

We then set out to investigate whether our system satisfies known quantitative results for foams [6], and found that indeed [7]: (i) where three walls meet, they do so at approximately 120° angles, for all times studied; (ii) Lewis's law of linear relation between the cell area and number of sides is approximately satisfied at late times; (iii) the morphological patterns coarsen in time, both T1 (neighbour switching) and T2 (cell disappearance) processes are observed and, at late times, evolution is consistent with von Neumann's law (cells with more than six sides grow, whereas those with fewer than six sides shrink); and (iv) relatively large numbers of five-sided cells survive up to fairly late times. Results (i) and (iii) suggest that surface tension may play a key role in determining the physics of this system, as it does in low-viscosity liquid foams.

Clearly our understanding is very incomplete. Our original observations, as presented in [7], were performed on a film of ionic LC sandwiched between glass slides after application of an uncontrolled shear. Also no attempt was made to keep the film thickness constant throughout the experiment. In this paper we report on a POM study of films of constant thickness under shear, at room temperature. Their morphological properties were determined and correlated with the shear rate, as well as compared with those of equilibrium liquid foams.

2. Experimental details

As in our earlier work [5, 7], we used the ionic LC 1-*n*-octyl-3-methylimidazolium *p*-toluenesulfonate. The synthesis and characterisation of this compound have been described in detail in [5, 8]. Solutions in acetone (64% w/w) were prepared at room temperature, followed by stirring to allow homogenisation. Films were cast and sheared simultaneously by moving a casting knife over a glass substrate at a controlled shear rate determined by $v = 5$ mm s^{-1}. Film thickness after evaporation of the solvent was estimated using a Mitutoyo digital micrometer; films of 5-μm thickness were empirically selected as the most adequate for the formation of the patterns reported previously.

Development of the foam textures was observed at room temperature (24°C) by POM, under controlled conditions, using an Olympus BH microscope coupled with an Olympus Camedia C-5060 camera and a Linkam CSS 450 Cambridge shearing system. Our experimental setup is shown schematically in Figure 1. The shearing system is a sealed, watertight unit, therefore there was no change in the water content of the ionic liquid in the course of our measurements

3. Results

Foam-like textures were seen to form only for shear rates above a threshold that is between 30 and 40 s^{-1}. For shear rates around this threshold, we observe what looks like a dispersion of very large cells/bubbles (linear size $l \sim 1$ mm, whereas for higher shear rates $l \sim 200$ μm), each bounded by a single, mostly convex wall (approximately circular or elliptical), and separated from one another by an apparently continuous liquid medium (see Figure 2). For higher shear rates, the patterns become increasingly similar to (dryer) liquid foams with cells of well-defined sides separated by walls of an approximately uniform thickness of about 1.5 μm. As confirmed by image analysis, these walls are approximately arcs of circles, meeting in three-fold vertices at angles of approximately 120°, as described in the following.

Four different shear rates (70, 100, 160 and 200 s^{-1}, all well above the threshold shear rate) were considered. The observation time was 5 minutes, much shorter than typical LC foam coarsening times of hours [7]: this is a 'fresh-made' foam, therefore we do *not* expect it to be in the asymptotic scaling regime.

Textures, of which typical examples are shown in Figure 3, were observed between polarisers at an angle of 70–80° for optimal brightness and were recorded during shearing using the digital camera. This was done separately for each shear rate, always starting from the uniform film; we did not switch between shear rates in the course of a data-collection run. Images were analysed by extracting a number of frames from the movie, corresponding to non-overlapping regions of the sample. This was done by taking into account the rotation of the shearing system's disc and the image sampling rate of the movie. The largest area that can be observed is a ring of mean radius equal to the observation radius of the shearing system (7.5 mm) and a maximum width given by the width of the field of view of the microscope. This yielded a set of about 20 images for each shear rate investigated, where the time gap between consecutive images depends on the shear rate. The first image of each set was taken after an initial (empirically determined)

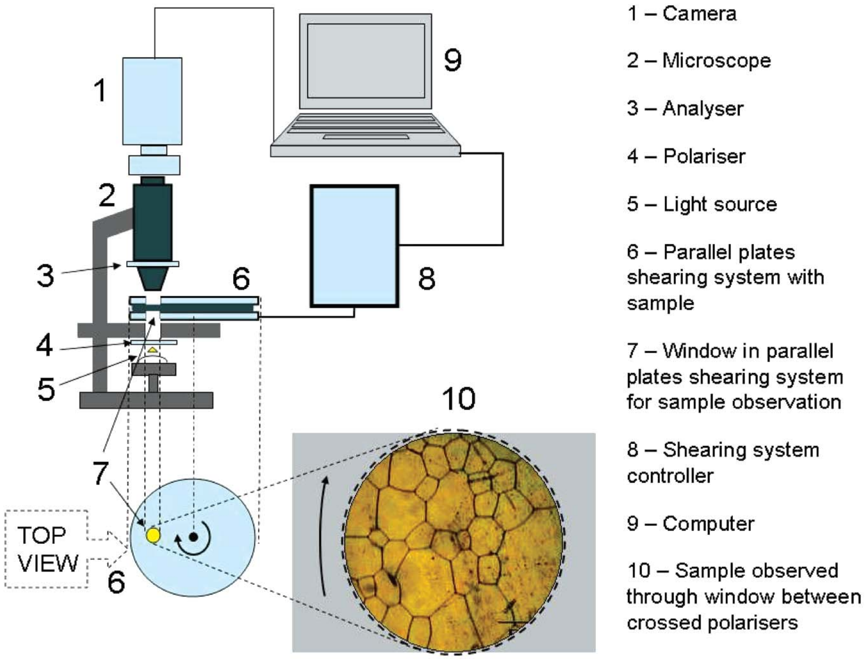

Figure 1. Schematics of our controlled shearing and image collection system.

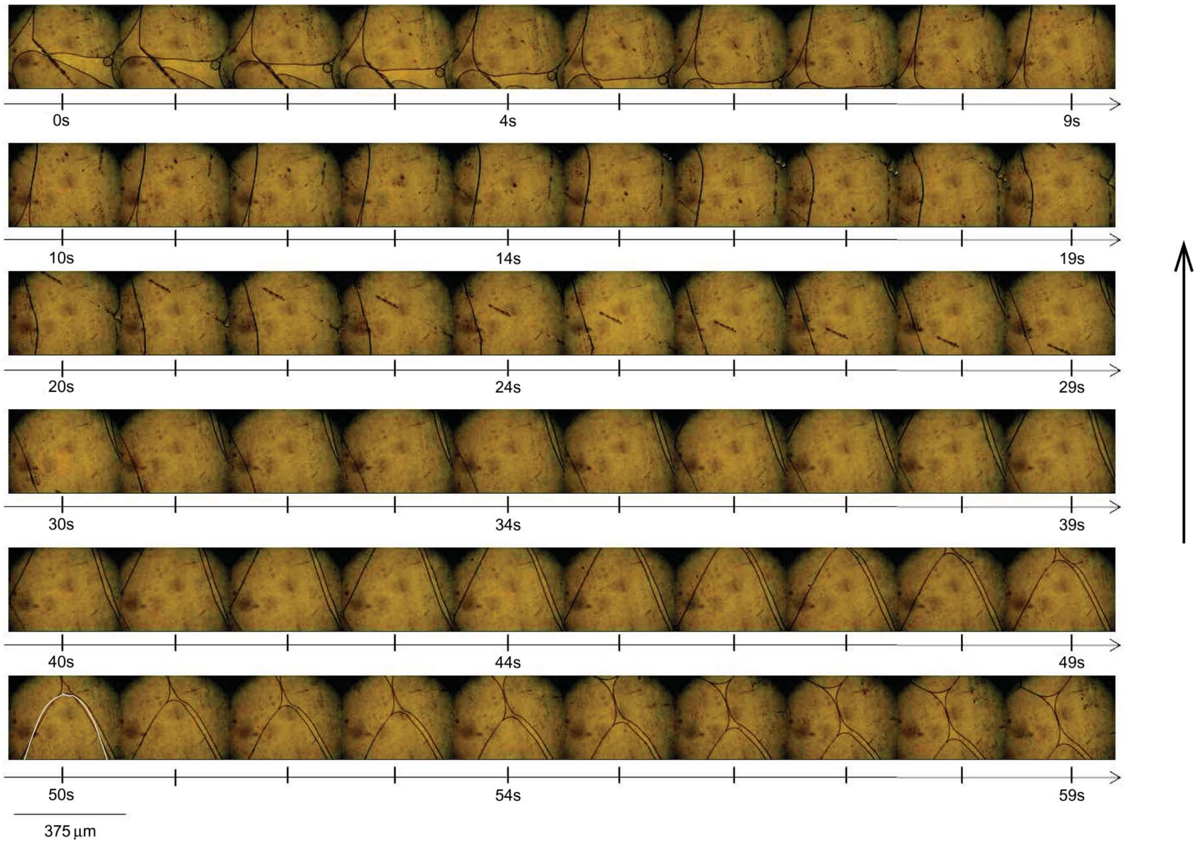

Figure 2. Time evolution of the liquid-crystal foam structure for a shear rate of 20 s^{-1}. Cells are typically elongated and larger than the microscope's field of view; the white curve in the bottom left-hand corner snapshot is an arc of ellipse superimposed on a wall. The arrow shows the direction of applied shear (colour version online).

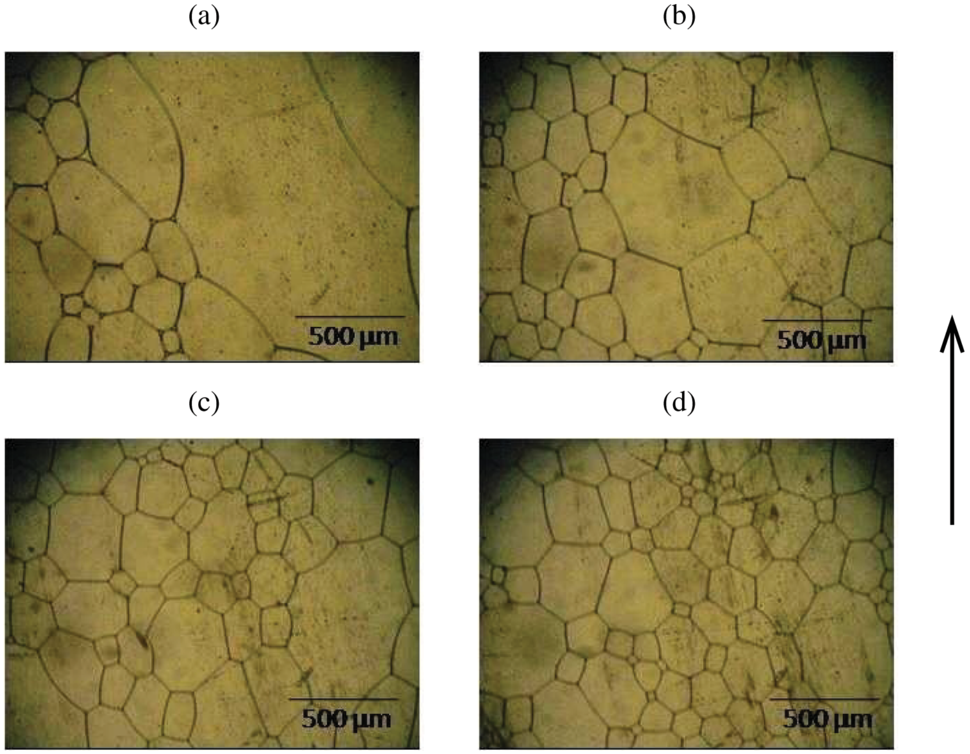

Figure 3. Optical micrographs of a sheared ionic liquid crystal between polarisers, at shear rates: (a) 70 s^{-1}, (b) 100 s^{-1}, (c) 160 s^{-1} and (d) 200 s^{-1}. The arrow shows the direction of applied shear (colour version online).

stabilisation period, to allow a steady state to be reached. After frame extraction (using the Adobe Photoshop software), images were subjected to careful visual inspection to make sure that there was no overlap between any two images of a given set. Note the indistinct observation of bright lines and other features inside walls and junctions, as seen in [7], due to the lower image resolution.

Sixteen out of each set of 20 micrographs corresponding to a particular shear rate have been treated using the image analysis software ImageJ [9]. For each image, all of the cells completely included in the photographed area were individually fitted with generalised polygons (closed polylines), the sides of which are arcs of circle. The area of each cell was computed by counting the number of pixels in the region bounded by the polyline. For all cells for which sides and angles could be unambiguously defined, the angles were measured between the tangents to each pair of arcs of circle at their point of intersection. For each set of images corresponding to a given shear rate, the number of cells with a given number of sides, their average area, and the angles between all the cells walls were determined. This was done in order to compare the morphological properties of our steady-state patterns with those of static foams.

Figure 4 shows the internal cell angles versus the shear rate. These cluster around 120°, as would be expected of an equilibrium liquid foam of uniform film tension. However, cells with fewer than six sides tend to have smaller internal angles, whereas those with more than six sides tend to have larger internal angles. This happens for all shear rates and therefore is likely not an artifact of the poor statistics at lower shear rates, or of the fact that not all films are arcs of

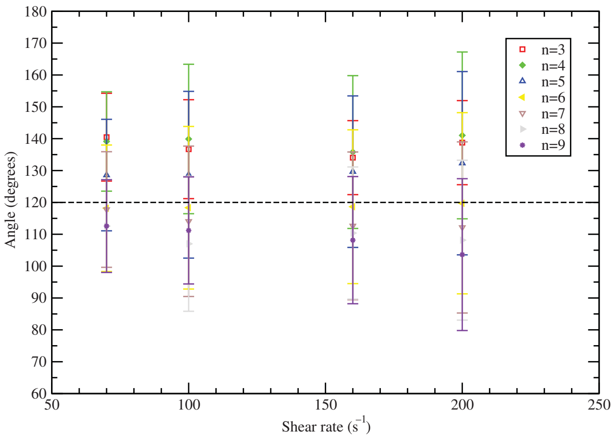

Figure 4. Internal cell angles versus the shear rate (colour version online).

circle (although most are). It may be an indication that smaller and larger cells are, respectively, stretched and compressed in the direction of shear.

In Figure 5 we present the frequency histograms for the cell number of sides at the four different shear rates. The mean numbers of cell sides are collected in Table 1. These approach six from below with increasing shear rate. The standard deviations are quite large (much larger than for the coarsening foams of [7]), consistently with the presence of many four- and five-sided cells in the micrographs of Figure 3, especially at the lowest shear rate. This is in contrast with the morphologies of equilibrium foams, where five- and six-sided cells predominate (see [6] and references therein). It should be noted that Euler's theorem and von Neumann's law only require the mean number of cell sides to be six for any 2d foam, but do not impose a form for the distribution; in fairly ordered foams most cells have five, six or seven sides, but in more disordered foams (such as ours) this is not usually the case (see [7], and references 7–11 cited there).

Finally Figure 6 displays the average cell area versus the shear rate, for all cells and for *n*-sided cells, $n = 3$–9. There is a clear trend towards smaller cells at higher shear rates, but no precise dependence can be extracted without further data. This appears to be slightly non-monotonic for all cells except those with nine or more sides.

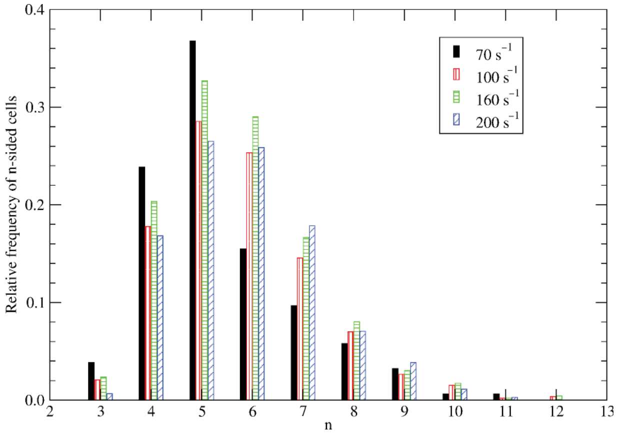

Figure 5. Frequency histograms for the cell number of sides for different shear rates (colour version online).

Table 1. Mean and standard deviation of the cell number of sides, as well as the total numbers of cells used in the statistical analyses, for the different shear rates under study.

Shear rate (s^{-1})	$\langle n \rangle$	Standard deviation	Number of cells
70	5.4	1.5	155
100	5.7	1.5	529
160	5.7	1.5	462
200	5.9	1.4	1064

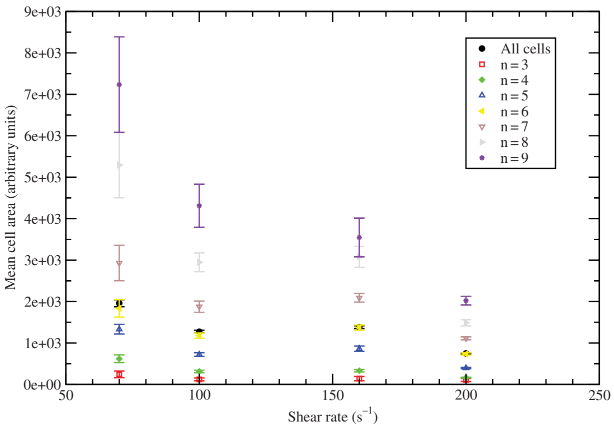

Figure 6. Mean cell area versus the shear rate (colour version online).

4. Conclusions

In summary, we have studied the effect of a controlled shear on the morphology of our (possibly non-equilibrium) LC foam. Our results suggest that there is a threshold shear rate between which the foam-like patterns do not form. Furthermore, above this threshold there appears to be a correlation between shear rate and mean cell size, with larger shear rates producing smaller cells. The internal cell angles and cell side distributions deviate somewhat from those pertaining to an equilibrium foam, especially at the *lower* shear rates. This may, however, be an artifact of poorer statistics (owing to the smaller number of cells present) combined with the tendency of cell walls to become pinned at contaminants and surface imperfections of the shearing system. In any case we would not expect our fresh-made foam to exhibit the known asymptotic properties or coarsened 2d foams [6].

It is extremely difficult to give a quantitative estimate of the conditions under which our foams may form, and their shear flow may be sustained, on account of the large number of unknown parameters: to the best of the authors' knowledge, the viscosity, the anchoring energy and the surface tension of ionic liquids have not been measured in the smectic phase. It is our hope that the results presented here will stimulate further research, which would enable a more detailed understanding of these puzzling phenomena.

In future work we plan to investigate the effects of (i) temperature (up to the equilibrium phase transition); (ii) film thickness, either under continuous shear as in this paper, or after the application of an initial shear followed by coarsening, as in [7]; and (iii) water content, as ionic liquids are known to be hygroscopic. Water content might be of particular importance, as it is known that many ionic liquids also form lyotropic smectic phases (i.e. they are soaps).

Acknowledgements

We are grateful to Fundação para a Ciência e Tecnologia (POCI 2010) and FEDER for funding under projects numbers SFRH/BPD/14848/2003, PTDC/QUI/70383/2006, POCI/CTM/56382/2004 and PTDC/FIS/65037/2006.

References

[1] Tschierske, C. *Current Opinion Col. Int. Sci.* **2002**, *7*, 355.
[2] Stewart, G.T. *Liq. Cryst.* **2003**, *30*, 541.
[3] Yoshio, M.; Mukai, T.; Ohno, H.; Kato, T. *J. Am. Chem. Soc.* **2004**, *126*, 994. Yoshio, M.; Kagata, T.; Hoshino, K.; Mukai, T.; Ohno, H.; Kato, T. *J. Am. Chem. Soc.* **2006**, *128*, 5570.
[4] Branco, L.C.; Rosa, J.N.; Moura Ramos, J.J.; Afonso, C.A.M. *Chem. Eur. J.* **2002**, *8*, 3671. Mukai, T.; Yoshio, M.; Kato, T.; Yoshizawa, M.; Ohno, H. *Chem. Commun.* **2005**, 1333. Martín-Rapun, R.; Marcos, M.; Omenat, A.; Barberá, J.; Romero, P.; Serrano, J.L. *J. Am. Chem. Soc.* **2005**, *127*, 7397.
[5] Godinho, M.H.; Cruz, C.; Teixeira, P.I.C.; Ferreira, A.J.; Costa, C.; Kulkarni, P.S.; Afonso, C.A.M. *Liq. Cryst.* **2008**, *35*, 103.
[6] Weaire, D.; Hutzler, S. *The Physics of Foams*; Oxford University Press: Oxford, 1999.
[7] Cruz, C.; Godinho, M.H.; Ferreira, A.J.; Kulkarni, P.S.; Afonso, C.A.M.; Teixeira, P.I.C. *Phil. Mag. Lett.* **2008**, *88*, 741.
[8] Kulkarni, P.S.; Branco, L.C.; Crespo, J.G.; Nunes, M.C.; Raymundo, A.; Afonso, C.A.M. *Chem. Eur. J.* **2007**, *13*, 8478.
[9] Rasband, W.S. ImageJ, U.S. National Institutes of Health, Bethesda, MD, USA, http://rsb.info.nih.gov/ij/, 1997–2007.