

Topical White Paper

Fluid gradients for self-assembly: A brief argument for the continued exploration of liquid crystal flows and electrodeposition in microgravity

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Introduction

Phase separation, interfacial tension gradients, and molecular self-assembly are all phenomena frequently observed when manipulating soft condensed matter systems on Earth. Depending on the system these processes can also be quite predictable. For instance, on Earth water droplets placed on hydrophobic surfaces will have contact angles $> 90^\circ$ with limited spread, contrary to their wetting behavior on hydrophilic surfaces. However, in an environment that is in a constant state of free-fall, where the gravitational field is reduced by 10%, such as on the International Space Station (ISS), buoyancy and its effect on fluid convection also become negligible. Fluid flow and phase behavior become less predictable. Thus, continuing the prior example, even if water droplets still remain in contact with a surface in microgravity (μg), the interface between the air and droplets will still remain significantly curved, appearing almost as if they were placed over completely non-wetting surfaces (Fig. 1a). Moreover, the negligible opposing buoyant force would also mean that if immiscible liquid droplets of a less dense character, or air bubbles even (Fig. 1b), were to be suspended within a larger water drop, these immiscible droplets or air bubbles would not migrate toward any one direction unless either artificially propelled by an external force or internal reaction inducing flow. The latter perhaps causing a break in the liquid-air interface, as seen in water coated air bubbles shooting out of a larger water sphere (Fig. 1c-d).

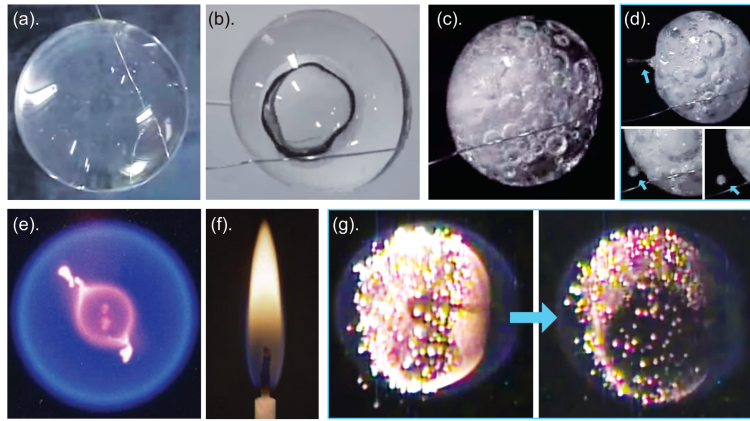


Figure 1: A mostly free-standing water droplet in air (a); the droplet in (a) with an air bubble inserted (temporarily deformed due to the force of its insertion) (b); air bubbles formed rapidly from a seltzer tablet dissolving in (a) (c-d), flame in μ [1] (e), flame in 1g [2] (f), Flamelets breaking up in a flame sphere (g) [3, 4]. Images in (a-d) are from ref. [5, 6].

A still more striking example of the physical distortion that may occur in the absence of buoyancy driven convection in μg are seen in the results of combustion experiments undertaken in Projects *FLEX* and *CFI-G*, (Flame Extinguishment Experiment [7, 8, 1] and Cool Flames Investigation with Gases [4], respectively) that show spherical flames; the yellow-red soot area encapsulated within the bluish fuel burning area (Fig. 1e), as opposed to their teardrop appearance with a classic yellow tip-blue bottom seen in 1g (Fig. 1f). In μg , oxygen diffuses all around the flame at a constant, non-directional rate so the soot area appears "encapsulated", without gravity aided convection to redistribute the air. As burning continues, a Rayleigh-Plateau-like instability emerges within the flame spheres causing several *flamelets* to break off with the ability to re-ignite future flames if not thoroughly quenched (Fig. 1g). Thus, in space, flames can appear quasi-sol-like, with flamelets having movement similar to particles suspended in a viscoelastic medium; their behavior

almost like soft matter emulsions seen on Earth. This progression of instabilities seen in simple experiments performed within the ISS further highlight how unexpected the behaviors of complex fluids in μg are. Ultimately, this unique environment allows for the examination of the impact that fluid mixing, free from buoyancy driven sedimentation or instabilities, has on processes driving the foundation of all complex matter: phase separation and self-assembly.

Thus, in this white paper three experiments using liquid crystalline (LC) phases in contact with other fluids are proposed for investigation in μg . LC phases are ideal for observing self-assembly and phase separation because of the clear anisotropy and birefringence traceable by microscopy, among other analytical methods, when significant molecular order is present. Since liquid crystalline phases are states having order between crystalline solids and isotropic liquids, they represent states commonly encountered during materials synthesis and when anisotropic matter becomes concentrated (i.e. lyotropic suspensions of containing the tobacco mosaic virus or DNA). Examined in μg it will be possible to determine if changes in fluid convection inhibit the transport of LC material, thereby leading to altered patterns and rates of self-assembly typically seen in 1g when LCs are in co-flowed with other media. Furthermore, convection in all three experimental cases would be partially or fully aided by evaporation at the interface of the fluids. Studying this process in space could inform how more advanced chemically driven and self-sustaining autonomous machines: catalytic decomposition driven microfluidic devices [9], micromotors propelled by bubble flow and release [10, 11], and other responsive [12] or cell based fluid transport [13] soft materials may be fabricated to aid processes in this environment.

1: Liquid crystalline phase assembly and transport in bubbles containing volatile solvent

Though Project *OASIS* (Observation & Analysis of Smectic Islands in Space [14]) was the first to probe flow gradients in LCs aboard the ISS, it focused primarily on the analysis of *island* (areas containing excess smectic material) growths and flow in free standing smectic LC layers (Fig. 2a). Nevertheless, *OASIS* was vital in showing physical proof that island migration within smectic bubbles having temperature gradients could be reversibly controlled in μg . Flow was from hot to cold and island migration favoring colder regions up to a critical point before breaking up (through Rayleigh instability) to flow back to the warmer pole [15], in contrast to what occurred in 1g experiments [16].

But, how would LC flow gradients and phase separation mechanisms change if volatile solvent evaporation drove them rather than heat? Short alkyl chain alcohols are unique in that they can act as co-solvents and co-surfactants by lowering the interfacial tension between mixture components, enabling flow gradients to emerge through their evaporation [18, 19, 20]. Nematic LC aqueous and non-aqueous ethanol mixtures can have surprisingly complex phase diagrams as well [17], where aqueous ethanol nematic mixtures are seen to form two coexisting stable isotropic phases at room temperature when as little as 3 vol.% water added. Experiments conducted below 0°C also revealed that pure ethanol-nematic mixtures showed the same phenomena emerging on cooling. Prior to this study, this had not been known to occur with the particular nematic used as it was assumed that the phase diagram would be far simpler without a miscibility gap.

Conducting an experiment to examine the convection flows in μg , showing the recirculation of LC and aqueous ethanol rich and poor fractions within an evaporating sample, such that free standing nematic-core ethanol-water-shell droplets can be formed at both the macro- and micro-scale, will allow a unique view of how latent heat driven convection from the ethanol-water-LC interface can impact self-assembly and dis-assembly while mass transfer also occurs inside. Figure

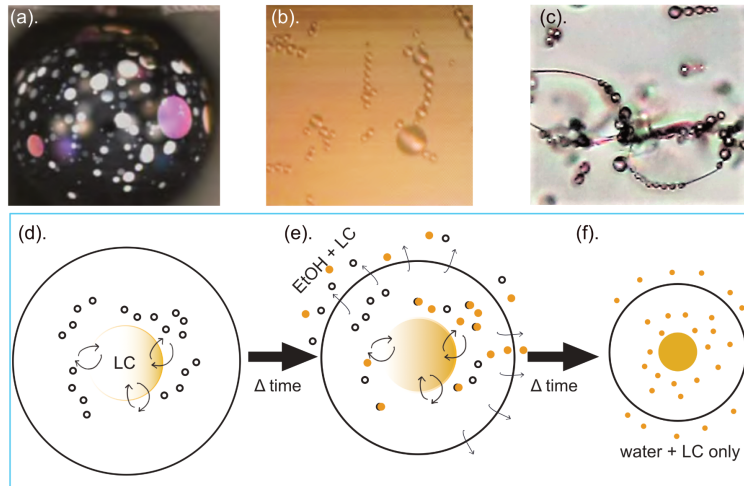


Figure 2: Smectic bubble with islands (a) and droplets aligning in smectic film (b) [14]; (c) Phase separated droplets in ethanol-nematic mixture [17]; (d-f) hypothesized phase separation of nematic LC in a volatile solvent drop in μg

2b shows a hypothetical view of how nematic LC phases can become re-distributed within and out of a large, surface free, bubble originally containing a mixture of ethanol-water. The droplet of LC added to the interior will initially become isotropic as the clearing temperature is met by the surrounding solvent (Fig. 2d), but visualizing the mixing that occurs at the nematic-aqueous ethanol interface will reveal how the nematic phase is dispersed, giving rise to isotropic satellite droplets containing higher fractions of ethanol and water, at first (Fig. 2e). Once the ethanol evaporates over time from these small dispersed satellite droplets, the re-assembly of the nematic phase within can be analyzed (Fig. 2f). Simultaneously, the ethanol evaporating from the large aqueous ethanol bubble encapsulating the initial nematic drop reduce in size, as mass transfer of the ethanol to the surroundings will occur. In the end, a self-emulsified mixture, driven by just evaporative convection, containing a large volume of nematic droplets dispersed within a largely water filled bubble should result, similar to the findings by Durey et al.[19] but with the feature that each droplet will have its own nematic phase subject to the constraints of its size. An even further step would be taking advantage of acoustic levitation methods [21] to help to characterize and elucidate the transport of the LC in and out of the mixed bubble as well.

2: Examining immiscible droplets stabilized in defects within LC rich domains

Another aspect in ref.[17] that remained unexplored and would add to the understanding of transport in μg , was that on cooling the formation of chained droplets (Fig. 2c), similar to those observed in *OASIS* (Fig. 2b), but emerging from a very different origin were also seen. In this case they were isotropic droplets of either pure or aqueous-ethanol rich regions which became entrapped within pockets of LC rich regions as the nematic phase re-assembled. Although these chained droplets were thought to arise from a purely from a kinetic origin, and while they were not the subject of further study in [17], the fact that they do not coalesce while dispersed in the nematic regions until reaching large pockets of ethanol rich areas, and appear to be guided by disclination lines forming in the nematic phase, seem to suggest that with sufficient thermal and concentration gradient control, phase separation occurring within the nematic phase can be exploited to direct the move-

ment of droplets within that could contain fractions of solvent or other material. Though elastic distortions in LC nematic phases can enable the ordered assembly of silica spheres [22] and water drops containing surfactant [23], in these cases the assembly was not through the controlled internal separation of material previously homogeneously dispersed within the phase, as it would be here.

3: Coaxial electrospray of partially miscible fluids (LC-polymer solution)

Taking LC phase transport further and knowing that nematic LCs exhibit various electroconvection instabilities in both AC and DC fields [24], an interesting question to explore would be: How would LCs behave in μg when encapsulated in charged, flowing viscoelastic liquids? Taylor cone formation in sessile and hanging drops containing volatile solvents and polymer solutions can occur when exposed to 1kV – 30kV. The surface tension at the air-fluid interface is countered so that electrostatic forces will geometrically distort the interface to resemble a cone tip and if the potential is increased charged droplets will jet outward from this tip. Since its discovery this electrostatic spraying process has been modified countless times such that the jetting and spraying that develops can result in the formation of nano and microfibers or particles [25].

Although fluid circulation is thought to be largely meridional, and while true in non-viscous liquids [26], the fluid motion in viscoelastic systems and in coaxial systems is still not well characterized. Additional gradients may be present that would not impact the spray of one component non-viscous fluids but conversely impact the mixing of multi-component fluids that are partially miscible with the evaporating component. As seen when nematic phases were coaxially spun to create bi-component fiber mats, mixing that occurs at the interface with aqueous ethanol containing polymer solutions can impact whether the LC phase is successfully encapsulated within or merely coats the sprayed polymer fibers [27].

If performed in μg , a scenario that could happen is that upon reaching the Rayleigh charge limit, once the droplets pinch off from the Taylor cone tip they could very well stay in the vicinity of the cone and perhaps even may become re-absorbed back into its surface, re-diffusing into the bulk and altering mixing patterns there. Moreover, if there is an accumulation of evaporated solvent that remains near the spraying cone, this could also disrupt the stability of the jet causing it to flicker as this vapor would also diffuse back into the cone. Additionally, if this latter case occurs, then the nematic LC phase flowing within should also become restricted in self-assembling as the constant influx of returning solvent would cause a concentration gradient favoring an isotropic state in the core. Of course, though these are only speculations the results gathered from adapting LC coaxial electrospray in this environment would enable a deeper understanding of transfer in between charged fluid-fluid and fluid-air interfaces.

Outlook

Continuing liquid crystalline phase flow experiments in microgravity, particularly with a focus on examining self-assembly and phase separation in mixtures (polymer solutions and volatile liquids) subject to external forces, will inevitably be vital to further work in controlling diverse soft matter in extreme environments, whether on Earth or in space. Such data can offer exciting opportunities to discover improved pathways toward autonomous, chemically driven machines — a concept first introduced by Belousov and Zhabotinsky decades prior [28, 29] — and unified models explaining tissue growth from an active matter and liquid crystalline perspective — a concept in early stages of study today [30].

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