Faceted two-dimensional crystals

K. A. Suresh

That a periodic stacking of spheres in three dimensions (3D) results in facets was shown long ago by Kepler[1]. Naturally occurring crystals, in general, exhibit beautiful facets. This was the clue to the idea that the constituent atoms of the crystal must be arranged in a periodic fashion, later confirmed by X-ray studies. What about two-dimensional (2D) solids? Do they exhibit facets? This has been an important question for quite some time. 3D solids have 2D surfaces that are curved for amorphous solids and faceted for crystals. In 2D systems, the atoms or molecules are confined to a plane. Examples are the monomolecular films grown on solid or liquid surfaces. Their boundaries are one-dimensional. If regular crystals were to occur in 2D then facets should appear with the facet boundaries made up of straight lines.

Interestingly, Peierls[2] and Landau[3] showed purely from thermodynamic considerations that at equilibrium and at non-zero temperatures 2D solids cannot have periodicity or long-range positional order. Therefore this theory rules out the possibility of the occurrence of 2D crystals. This leads to the absence of facets. But in a non equilibrium state, i.e. in a dynamical situation, faceted 2D crystals are not forbidden. In fact, computer simulations by Savit and Ziff[4] have shown the possibility of 2D-crystal growth patterns with well-defined facets.

Recently Berge *et al.*[5] reported the important observation of faceted crystals in 2D. Berge *et al.* dissolved sodium dodecyl sulphate (SDS) in water. In such a system, some of the SDS goes into the bulk while some stays on the surface, forming a monolayer. This monolayer exhibits a liquid phase at higher temperatures and a solid phase at lower temperatures. To probe the state of aggregation in the monolayer, Berge *et al.* added minute quantities of the fluorescent dye 12-NBD-stearic acid to the system. These molecules being amphiphilic did not dissolve in the bulk but stayed on the surface. Further, they dissolved in the monolayer in the liquid phase and were expelled from the monolayer in the solid phase. This property was used to detect the liquid–solid phase transition of the monolayer. Under a fluorescence microscope the liquid monolayer containing the dye appeared bright while the solid monolayer without the dye appeared dark. Thus liquid-to-solid phase transition and growth of the solid phase was directly observed. The liquid–solid transition temperatures depended on the concentration of the SDS dissolved in water. These transitions existed only for low SDS concentrations. At high SDS concentrations micelles and 3D crystals were found in the bulk (see Figure 1). Around the SDS concentration of 0.055%, the liquid-to-solid phase transition resulted in the growth of faceted hexagonal crystallites of about 50 microns in size (Figure 2). However, during further growth, these facets became unstable and changed their shapes. One such instability, with zig-zag branches emanating from each corner, is shown in Figure 3. At any given temperature, if the monolayer was allowed to attain equilibrium, the facets smoothened out. At higher SDS concentrations the phase transition from the liquid to the solid phase resulted in domains of smooth boundaries. These observations of faceted crystals in 2D show that during growth the constituent molecules can have long-range positional order although in thermodynamic equilibrium this is not stable.

Berge *et al.* point out important questions that their observations raise. For instance one does not yet know the mechanism of faceted growth in dynamical situations which also allows for a

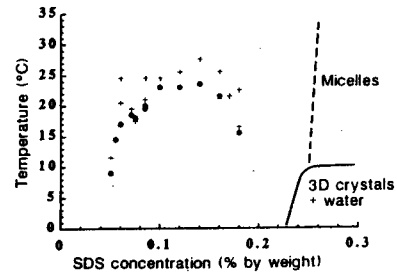

Figure 1. Phase diagram depicting different states of SDS monolayers as a function of concentration and temperature. The circles and the crosses (obtained by two different techniques) represent transition points from the higher-temperature liquid phase to the lower-temperature solid phase. [From Berge *et al.*, *Nature*, 1991, **350**, 322]

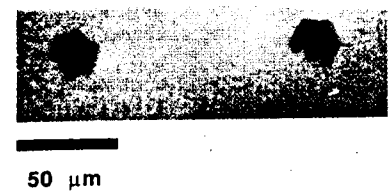

Figure 2. Hexagonally faceted crystal growth observed on cooling the SDS monolayer to solid phase at SDS concentration of 0.055% by weight in water. [From Berge *et al.*, *Nature*, 1991, **350**, 322]

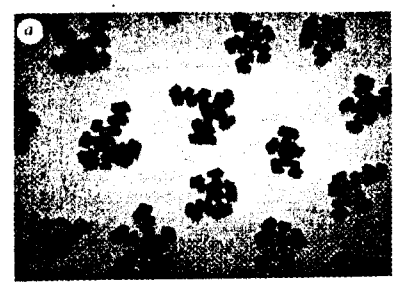

Figure 3. One type of instability observed during growth of faceted morphology in SDS monolayers. [From Berge *et al.*, *Nature*, 1991, **350**, 322]

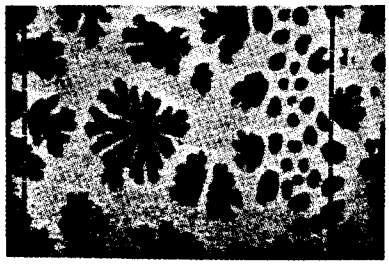

Figure 4. Liquid condensed growth patterns obtained on compressing a myristic-acid monolayer in the liquid expanded phase. The large pattern at the centre is about 200 microns in size. [From Suresh *et al.*, *Europhys. Lett.*, 1988, **6**, 437]

continuous transition from faceted to smooth shapes. It is also not clear whether the earlier computer simulations[4] describe a realistic model of this system. It should be emphasized that these structures are not the only ones found in monolayers. There have been reports of a variety of patterns[6-8] during 2D growth processes in monolayers. One such interesting case is the growth of liquid condensed domains (see Figure 4) obtained on compressing a myristic-acid monolayer in the liquid expanded phase. In the centre of Figure 4 there is a large self-similar pattern. Analysis shows that it has a fractal dimension of 1.8 ± 0.1. These patterns have branches that grow by smooth tip-splitting, and are very different from those shown in Figure 3 where the patterns have branches that grow without tip-splitting and are made up of straight edges. Even in these cases the mechanisms involved are not very clear.

1. Kepler, J., *De Nive Sexangula* (G. Tampach, Frankfurt-on-Main, 1611); see also, Field, J. V., *Kepler's Geometrical Cosmology*, The University of Chicago Press, Chicago, 1988, p. 201.
2. Peieris, R. E., *Helv. Phys. Acta*, 1934, 7, 81.
3. Landau, L. D., *Collected Papers of L. D. Landau*, (ed. Ter Haar, D.), Gordon Breach, New York, 1967, p. 210.
4. Savit, R. and Ziff, R., *Phys. Rev. Lett.*, 1985, **55**, 2515.
5. Berge, B., Faucheux, L., Schwab, K. and Libchaber, A., *Nature*, 1991, **350**, 322.
6. Miller, A., Knoll, W. and Mohwald, H., *Phys. Rev. Lett.*, 1986, **56**, 2633.
7. Suresh, K. A., Nittmann, J. and Rondelez, F., *Europhys. Lett.*, 1988, **6**, 437.
8. Bercegoi, H., Gallet, F., Langevin, D. and Meunier, J., *J. Phys.*, 1989, **50**, 2277.

K. A. Suresh is in the Raman Research Institute, Bangalore 560 080.