Monitoring of continuous crystallisation processes by a range of synchrotron radiation techniques have been developed in a series of in situ experiments, using bespoke crystallisers optimised for operation on the beamlines at the Diamond Light Source (DLS). The first of these devices is the KRAIC-D (Kinetically Regulated Automated Input Crystalliser - Diffraction) is a segmented flow crystalliser, adapted for in-beam operation, and developed as a collaboration between Bath, Leeds and Diamond. The design of the KRAIC-D encompasses viewing windows, which facilitate X-ray penetration at set points along the length of the crystalliser. In the segmented flow employed in the KRAIC-D the solution passing a particular set point will always be at the same stage of the crystallisation process. Continuous crystallisation of the model system Carbamazepine (CBZ) in ethanol in the KRAIC-D platform on beamline I11 (high resolution powder diffraction) is presented. The effect of introducing a controlled solid interface into the crystallisation process is investigated, where CBZ form III seeds are introduced in polymorphic purity at different seeding positions (pre- and post-nucleation) throughout the length of the KRAIC-D. The video associated with Chapter 4 corresponds with a post-nucleation CBZ form III experiment where a separation of crystal habit is observed as a result of the different interaction with the flow paths in the solution slugs with the segmented flow.

The second device is the KRAIC-S (Kinetically Regulated Automated Input Crystalliser - Single Crystal) platform installed at I19 (small molecule single crystal beamline) employed to investigate the continuous crystallisation of paracetamol (PCM) in 60:40 water:isopropanol via a range of experiments including unseeded and seeded cooling crystallisations. The unseeded experiments also looked at the crystallisation at different set points along the KRAIC-S (6.7 m and 8.7 m) to investigate crystal growth and crystal rotation at different length scales. The videos associated with Chapter 5 include single crystals produced from the range of experiments investigated. Each video tracks a different single crystal in a solution slug, where through use of the slug triggering mechanism, whereby an optical trigger prompts translation of the motorised stage to artificially suspend the single crystal in the X-ray beam during data collection. These videos complement the diffraction data and can provide explanation for data collections, which do not achieve cell indexation as the single crystal is shown to move in and out of the beam in these videos.

### Details of Electronic Supplementary Information (ESI) – Videos of single crystals tracked in solution slugs

N.B videos are rotated by 180° and thus is observed as residing in the top of solution slug, when in fact the single crystals position themselves in the rear end of a solution slug at the bottom.

**Unseeded PCM Form I**

**6.7 m**

* 20190728\_1517\_0003\_Unseeded PCM\_6\_7m\_Set 1 Video
* 20190728\_1521\_0003\_Unseeded PCM\_6\_7m\_Set 2 Video
* 20190728\_1521\_0009\_Unseeded PCM\_6\_7m\_Set 3 Video
* 20190728\_1559\_0003\_Unseeded PCM\_6\_7m\_Set 4 Video
* 20190728\_1614\_0001\_Unseeded PCM\_6\_7m\_Set 5 Video

**8.7 m**

* Set 1 - No video to accompany diffraction data
* Set 2 - No video to accompany diffraction data
* 20190726\_1839\_0014\_Unseeded PCM\_8\_7m\_Set 3 Video
* 20190726\_1928\_0010\_Unseeded PCM\_8\_7m\_Set 4\_Video
* 20190726\_2023\_0043\_Unseeded PCM\_8\_7m\_Set 5\_Video
* 20190726\_1405\_0014\_Unseeded PCM\_8\_7m\_Video with no accompanying diffraction data

**Seeded PCM Form II**

* 20190727\_2340\_0004\_Seeded PCM form II\_Set 1\_Get Form I\_Video
* 20190727\_2355\_0010\_Seeded PCM form II\_Set 2\_Get Form II\_Video
* 20190728\_0038\_0007\_Seeded PCM form II\_Set 3\_Get Form II\_Video
* 20190728\_0038\_0008\_Seeded PCM form II\_Set 4\_Get Form II\_Video
* 20190727\_1347\_0050\_Seeded PCM form II\_Video with no accompanying diffraction data