TAKING SNAPSHOTS OF NANO-STRUCTURES IN SUPERFLUID HELIUM DROPLETS

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Helium droplets are fascinating creations. With a temperature of less than half a degree above absolute zero, they remain liquid, even superfluid—a state in which friction completely vanishes. In this cold environment, embedded dopant particles of atoms or molecules quickly reach their ground state and move freely inside the droplets. When multiple dopants are added, they can coagulate and form very unusual nanostructures. Using the ultrashort, high-intensity X-ray pulses of the European XFEL, we took snapshots of nanostructures formed under these extreme conditions at the new nano-size quantum systems (NQS) experiment station of the SQS instrument.

Equilibrium processes require time to equipartition energy and find the thermodynamically most favourable configuration independent of initial conditions. In an equilibrium state, we can describe why water boils or turns into ice. Our world, however, is made richer by processes occurring far from equilibrium, where structure and pattern formation is controlled by kinetics rather than thermodynamics [1]. The cracking of glass, the formation of snow, and even the assembly of cells in living systems are some of the familiar processes occurring far from equilibrium. However, physical theories describing non-equilibrium systems often only consider factors occurring at the macroscopic level, such as hydrodynamic flows and large-scale turbulence. At the atomic and molecular level, far-from-equilibrium processes are described using macroscopic symmetry scaling laws, which usually neglect the underlying physics on the microscopic scale [1]. This neglect is partly due to the experimental difficulty of studying out-of-equilibrium nanostructures, where particle-by-particle growth is important.

Superfluid helium droplets are unique, self-contained media conducive to growing out-of-equilibrium nanostructures. This viability is due to the droplets' superfluidity, their very cold ambient temperatures of 0.4 K, and the possibility to control the size and composition of embedded dopants, one particle at a time [2]. Superfluid droplets are produced by expanding pressurized helium into vacuum through a cryogenically cooled nozzle. Dopants are captured by the droplets within the pickup cells along the droplets' flight path. Once a dopant is captured, it quickly thermalizes to the droplet temperature and is decelerated until it moves inside without friction. When several dopants are captured, they coalesce and form far-from-equilibrium nanostructures [2]. While some dopant materials form compact clusters at one or several sites in the droplets, some polar molecules form long linear chains. Other studies have shown a core–shell structure of a multicomponent doped droplet or indicated the formation of foam structures. Up to now, these very special structures could only be inferred from spectroscopic measurements on ensembles restricted to small droplet sizes. Imaging these nano-structures can give us unprecedented insights into the processes underlying their formation.

The technological development of X-ray free-electron lasers (FELs) enables X-ray coherent diffractive imaging (XCDI) of single, non-periodic particles. XCDI has so far been applied to single viruses [3], soot particles [4], large solid xenon clusters [5], and silver clusters [6], among others, with a resolution of a few tens of nanometres. For helium droplets, XCDI was first used by the team of Christoph Bostedt, Oliver Gessner, and Andrey Vilesov to investigate the shapes of rotating helium droplets and the structures of quantum vortices inside the droplets [7]. In vortex-containing droplets, nanostructure formation is dominated by the instant attraction of the dopants to the vortex core. In effect, the dopant structure resembles the shape of the vortex core or vortex lattice. These droplets with quantum vortices were produced from the fragmentation of liquid helium. In order to create and image nanostructures not induced by the vortices, we need to produce large superfluid helium droplets that do not interact with the walls of the nozzle channel, where the initial droplet vorticity is possibly acquired. This may be possible by producing droplets from the condensation of cold helium gas.

The schematic of the experiment setup is shown in Figure 1. The average size of the droplets, which is on the order of hundreds of nanometres, can be controlled by varying the nozzle stagnation pressure and temperature. A skimmer separates the nozzle chamber from the doping region, where different types of doping cells for gaseous, liquid, and solid dopants are installed. In this experiment, xenon, silver, acetonitrile, and iodomethane (the last two of which are polar molecules) are used as dopants. The pure or doped droplets reach the interaction point, where they are intercepted by the European XFEL pulses at a photon energy of 1 keV. Figure 2 shows examples of collected diffraction images of pure and differently doped droplets.

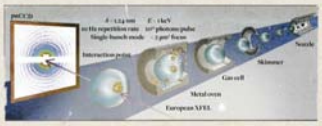

Figure 1: Schematic setup of the helium droplet experiment performed at SQS

Almost all diffraction patterns from pure droplets exhibit the same concentric ring pattern as the example shown in Figure 2. This observation indicates that the droplets are mostly spherical in shape. In contrast, some of the droplets produced at the liquid fragmentation regime from previous experiments at LCLS in the USA, at FERMI in Italy, and using lab-based high-harmonic generation (HHG) showed extreme shape distortions, e.g. pill shapes or dumbbell shapes [7]. Theoretical work supports the idea that the shape of these distorted droplets is controlled by the presence of quantum vortices: the more deformed a droplet, the larger the possible number of vortices [8]. As the shapes of the droplets produced in our experiment are almost spherical, we can assume that these droplets contain either a small number of vortices or none at all.

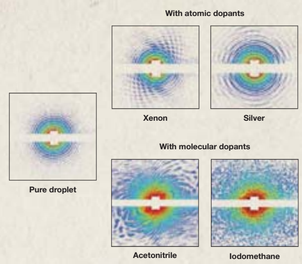

Figure 2: Examples of diffraction images of pure and differently doped helium droplets collected in the experiment

A second aspect of our experiment was to investigate structure formation using different types of dopants. The intermolecular interactions (van der Waals, dipole–dipole, or metallic) of these dopants may alter the overall structure growth in the droplet. Our analyses and reconstructions are still ongoing. However, the observed diffraction patterns from different dopant materials in Figure 2 show distinct features. For example, the diffraction patterns collected from droplets with atomic dopants suggest the presence of one to two cluster cores in the droplet. On the other hand, the diffraction patterns from droplets doped with polar molecules suggest a complicated network of dopant clusters.

These imaging experiments at the SQS instrument open novel avenues for further studying different far-from-equilibrium nanostructures in superfluid droplets almost devoid of vortices. Our preliminary analysis also indicates that structure formation can be controlled by the size of the droplets and the properties of the dopants.

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References

[1] P. Meakin: *Fractals, scaling and growth far from equilibrium* (Cambridge University Press, Cambridge, 1997)
[2] J.P. Toennies, A.F. Vilesov: "Superfluid helium droplets: A uniquely cold nanomatrix for molecules and molecular complexes", Angew. Chem. Int. Ed. 43, 2622–2648 (2004), doi: 10.1002/anie.200300611
[3] M.M. Seibert et al.: "Single mimivirus particles intercepted and imaged with an X-ray laser", Nature 470, 78–U86 (2011), doi: 10.1038/nature09748.
[4] N.D. Loh et al.: "Fractal morphology, imaging and mass spectrometry of single aerosol particles in flight", Nature 486, 513–517 (2012), doi: 10.1038/nature11222
[5] D. Rupp et al.: "Generation and structure of extremely large clusters in pulsed jets", J. Chem. Phys. 141, 044306 (2014), doi: 10.1063/1.4890323
[6] I. Barke et al.: "The 3D-architecture of individual free silver nanoparticles captured by X-ray scattering", Nat. Commun. 6, 6187 (2015), doi: 10.1038/ncomms7187
[7] O. Gessner, A.F. Vilesov: "Imaging quantum vortices in superfluid helium droplets", Annu. Rev. Phys. Chem. 70, 173–198 (2019), doi:10.1146/annurev-physchem-042018-052744
[8] F. Ancilotto et al.: "Spinning superfluid He-4 nanodroplets", Phys. Rev. B 97 (2018), doi: 10.1103/PhysRevB.97.184515