Experimental report

10/02/2021

Proposal: **6-02-596** **Council:** 4/2019

Title: Stochastic Dynamics in Carbon-based Mesoscopic Liquids for Thermal-energy Storage

Research area: Chemistry

This proposal is a new proposal

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Samples: corannulene, C20H10

Instrument	Requested days	Allocated days	From	To
IN16B	5	3	17/09/2020	20/09/2020

Abstract:

We have recently studied the emergence of liquid phases in fullerene derivatives. These materials are characterised by typical particle sizes in the nanometer domain and much-shorter effective interparticle interactions. As such, they may be regarded as a new class of mesoscopic media exhibiting new properties markedly different from the parent compound C60. So far, our investigations have focused on the microscopic mechanisms of pre-melting and melting using a combination of quasielastic neutron scattering (IRIS \& OSIRIS at ISIS) along with computational modelling. Corannulene represents the most interesting case, exhibiting a well-defined solid-to-liquid transition just above 500 K, as well as a deep-supercooling regime extending over 100 K below melting, a feature that renders it a competitive candidate for thermal-energy storage applications. In this IN16B experiment, we seek to explore longer timescales into the nanosecond regime in corannulene. We anticipate that these experiments will provide new insights into the spatial & temporal character of the stochastic dynamics and underlying diffusion mechanisms in these novel fluids, including direct comparison with simulations.

Stochastic Dynamics in Carbon-based Mesoscopic Liquids for Thermal-energy Storage

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The primary aim of this experiment was to use IN16B for the first time to extend our previous neutron-scattering work to the microelectron-volt regime, in order to access the longer (nanosecond) timescales associated with the emergence of dynamically disordered solid and fluid phases in corannulene, a fullerene adduct of nanometer dimensions with yet-to-be-tapped potential for the storage of thermal and chemical energy.

Experiment on IN16B

We used a powder polycrystalline specimen of corannulene loaded into a high-temperature cylindrical cell housed in a furnace to cover the temperature range T=290-540 K. The experiment used the standard Si(111) configuration of IN16B all throughout, giving us access to an energy-transfer range of ±30 μeV with μeV resolution.

Over the course of the experiment, full QuasiElastic Neutron Scattering (QENS) datasets were collected at selected temperatures, supplemented by Fixed-Window Scans in between these temperatures at energy transfers of 0.0, 0.8, 1.3 and 2.6 μeV. On heating, the sample was subjected to heat-cool cycles across the order-disorder transition within the solid phase at T = 390 K, in order to check its reversibility. Owing to time constraints, we could only enter the liquid phase above 530 K once, and we took this opportunity to collect one dataset in the molten state just above the melting point. Subsequent cooling below the melting point confirmed the supercooling and associated hysteresis already observed in our calorimetric data – see proposal text.

Results

Figure 1 shows representative QENS datasets collected during the experiment, averaged over all momentum transfers accessible on the instrument. At the lower temperatures within the ordered-solid phase, the energy-transfer range of the standard IN16B configuration is suitable to obtain reliable spectral widths – see orange and green data in this figure. In the disordered solid phase, this energy window becomes increasingly too narrow, leading to a substantial clipping of QENS line shapes, particularly at the higher temperatures – see purple trace in the figure. The situation becomes considerably more unfavourable within the melt. These considerations are further corroborated by the integrated intensities shown in Figure 2 at several temperatures, where we note the presence of well-defined Bragg features arising from both inter- and intramolecular spatio-temporal correlations. The gradual drop-off within the ordered solid phase can be ascribed to an increase in the Debye-Waller factor up to ca. 400 K. The more dramatic drop in spectral intensities with momentum transfer above this temperature and, particularly, within the liquid phase indicate that a very significant fraction of the QENS signal is outside the spectral range of these measurements.

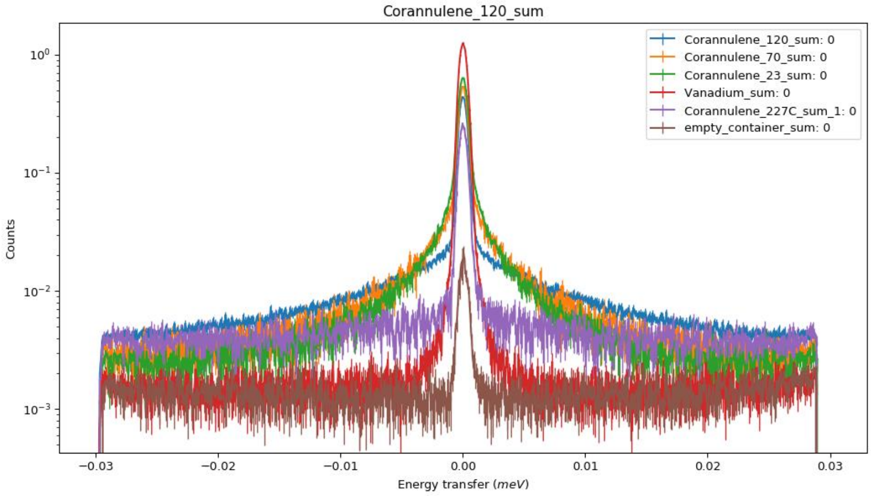

Fig. 1 QENS spectra for corannulene as a function of temperature, along with the response of vanadium and the empty cell. For corannulene: green (T=296 K); orange (T=343 K); blue (green (T=393 K); purple (T=500 K).

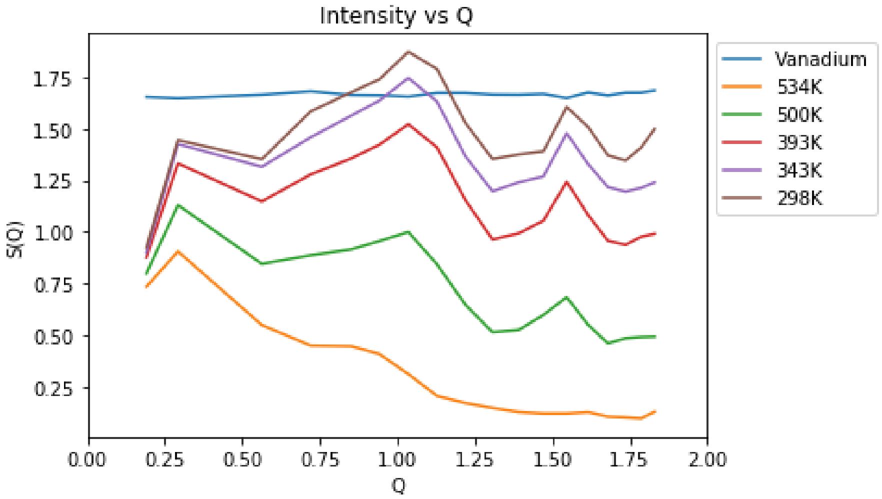

Fig. 2 Total integrated intensities as a function of momentum transfer for corannulene. The dataset at T=534 K corresponds to the molten state.

Outlook

In this experiment, we have established a suitable protocol to study corannulene at intermediate temperatures up to ca 550 K, including the effects of supercooling from the melt. We find that the standard configuration on IN16B is suitable to obtain high-quality QENS data within the ordered solid phase and the onset of dynamical disorder in the solid, but not on the higher temperature end of the disordered-solid phase or the liquid. Time constraints also limited our ability to study supercooling and hysteresis upon crossing the melting point from above. These phenomena would be amenable to further study on IN16B using the BATS option, with a dynamic range of ±150 μeV and a similar spectral resolution.