

Aggregation of solutes in bosonic versus fermionic quantum fluids

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Abstract

Quantum fluid droplets made of helium-3 (³He) or helium-4 (⁴He) isotopes have long been considered as ideal cryogenic nanolabs, enabling unique ultracold chemistry and spectroscopy applications. The droplets were believed to provide a homogeneous environment in which dopant atoms and molecules could move and react almost as in free space, but at temperatures close to absolute zero. Here, we report ultrafast X-ray diffraction experiments on xenon-doped ³He and ⁴He nanodroplets, demonstrating that the unavoidable rotational excitation of isolated droplets leads to highly anisotropic and inhomogeneous interactions between the host matrix and enclosed dopants. Superfluid ⁴He droplets are laced with quantum vortices that trap the embedded particles, leading to the formation of filament-shaped clusters. In comparison, dopants in ³He droplets gather in diffuse, ring-shaped structures along the equator. The distorted shapes of droplets carrying both filaments and rings are direct evidence that rotational excitation is the root cause for the inhomogeneous dopant distributions.

36 Teaser

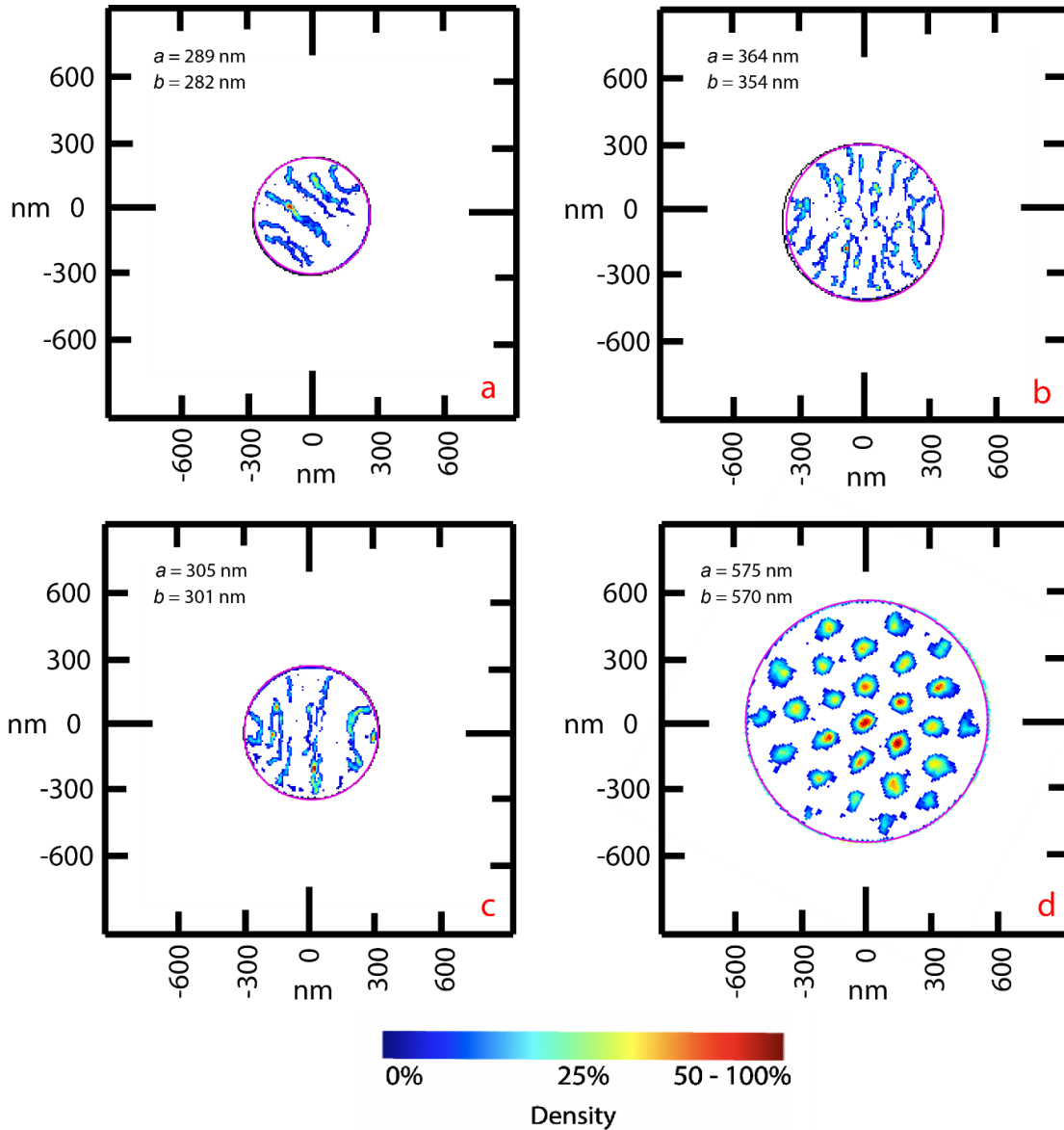
37 Clusters in ^3He and ^4He nanodroplets reveal dramatically different shapes showcasing the
38 effect of superfluidity on aggregation.

39 Introduction

40 Quantum fluid nanodroplets made of liquid helium are exceptional hosts for isolated
41 cryogenic matrix applications (1-5). The droplets readily pick up atoms and molecules (6),
42 providing unique opportunities to study the formation of molecular complexes close to absolute
43 zero temperatures. Indeed, the large degree of quantum mechanical delocalization in helium
44 enables unique matrix configurations around the dopants, giving rise to a perfectly tailored void
45 around each particular molecule (3).

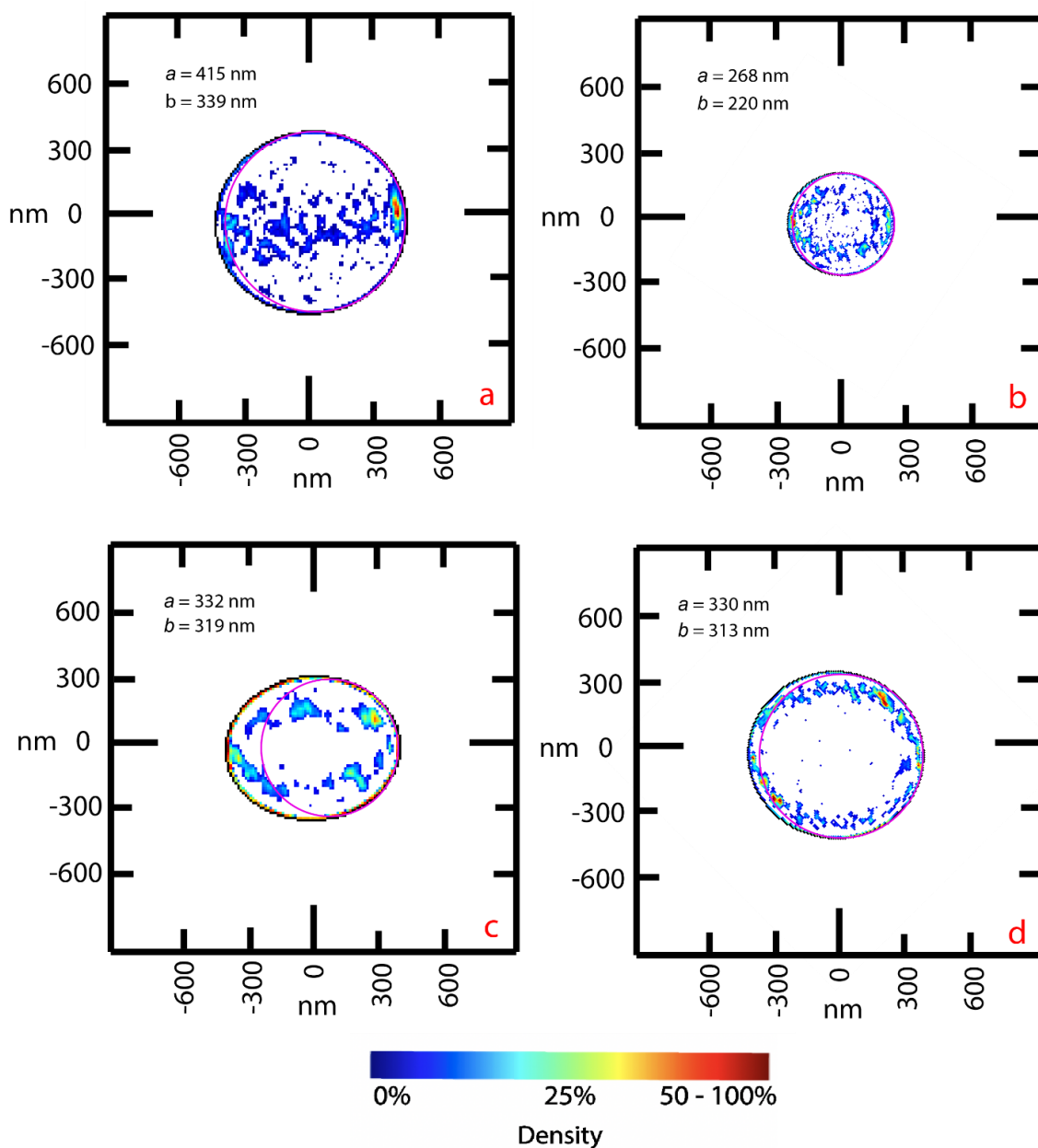
46 Previously, small ^4He droplets containing less than $\sim 10^4$ atoms, roughly 10 nm in
47 diameter, were used for the spectroscopic interrogation of molecules and molecular complexes at
48 a temperature of about 0.4 K (1-5). It was long believed that, unlike immobilized dopant
49 molecules in solid matrices, dopants in helium nanodroplets could move unhindered and
50 stochastically (3, 7). Recent ultrafast X-ray coherent diffractive imaging (CDI) experiments with
51 large xenon-doped superfluid ^4He droplets, a few hundreds of nm in diameter, have revealed a
52 dramatically different scenario (8-10). Instead of forming the once proposed ramified entities (7),
53 dopant atoms were found to aggregate in arrays of elongated filament-shaped clusters (9, 10).
54 This effect was assigned to inhomogeneities within the droplets due to the presence of quantum
55 vortices, which attract dopant particles (11-14). The vortices were found to originate from an
56 unavoidable rotational excitation of free helium droplets in the beam (8, 15-17), implying that
57 the superfluid nature of ^4He enhances the inhomogeneity of matrix-dopant interactions.

To provide unequivocal proof for the link between inhomogeneous dopant distributions, the superfluid nature of ^4He droplets, and their rotational excitation, comparative measurements are required on fermionic ^3He and superfluid, bosonic ^4He droplets. It is important to note that ^3He can also enter the superfluid state, but does so at much lower temperatures ($T \sim 1 \text{ mK}$) (18, 19) than are present in our experiment ($T \sim 0.15 \text{ K}$) (20). Thus, ^3He droplets act as a normal fluid under our experimental conditions and serve as a reference droplet devoid of vortices. Here, we present a comparative study of the aggregation of xenon atoms in sub micrometer sized ^3He and ^4He droplets. Our results show that, in fact, dopants are subject to a high degree of spatial confinement within both ^3He and ^4He nanodroplets, with each isotope giving rise to dramatically different dopant morphologies.



70

71 Fig. 1. Outlines (black) and xenon dopant density distributions (blue-red) of superfluid ^4He
 72 droplets. Panels a-d show results for four different representative ^4He droplets. The values a and
 73 b of the long and short half axis, respectively, of the droplet's projection onto the detector plane
 74 are given in each panel. For visualization, circular contours (magenta) have been superimposed
 75 on the droplets with a radius equal to that of the minor half axis. Closer inspection reveals
 76 slightly elliptical distortions, most prominent in droplet b.



77

78 Fig. 2. Outlines (black) and Xe dopant density distributions (blue-red) of normal fluid ^3He

79 droplets. Panels a-d show results for four different representative ^3He droplets. The values of the

80 long and short half axis of the droplet's projection onto the detector plane are given in each

81 panel. For visualization, circular contours (magenta) have been superimposed on the droplets

82 with a radius equal to that of the minor half axis. Note the partly significant elliptical distortions

83 of the droplet outlines.

Results

Figures 1 and 2 show plane projections of ^4He and ^3He droplets, respectively, with their reconstructed Xe dopant density distributions for a variety of representative droplets (10). The details on the reconstruction of density from diffraction images and the description of the results are described in the Materials and Methods (MM) section. The ^3He and ^4He droplets studied in this work have similar diameters in the range of 400-600 nm, containing on the order of 10^9 helium atoms per droplet. Corresponding diffraction images are presented in the Supplementary Materials (SM).

Most outlines are ellipses, consistent with spheroidal, rotating droplets (8, 15, 17, 21, 22). In previous studies, it was found that a cryogenic fluid expansion into vacuum readily produces rotating ^4He and ^3He droplets (15, 17). It was also found that droplets of different isotopes have very similar average aspect ratios of about 1.05 for their projections on the detector plane (17). We hypothesized that during the passage of fluid helium through the nozzle, the fluid interacts with the nozzle channel walls and acquires vorticity, which is eventually transferred to the droplets. Figure 1 illustrates several ^4He droplets and their dopant density distributions. As previously demonstrated (9, 10), the droplets contain several strongly aligned tracks of high density, which are assigned to xenon atoms aggregating inside the cores of quantum vortices. Vortices in Figs. 1a-c are viewed from the side, while vortices in Fig. 1d point toward the viewer, revealing their arrangement in a triangular lattice configuration that closely resembles the arrangements of vortices observed in rotating cylinders filled with ^4He (11, 14) and in trapped Bose-Einstein condensates (23).

Results are dramatically different for xenon-doped ^3He droplets, as illustrated in Fig. 2. Here, xenon clusters either appear as a stripe (Fig. 2a) or as elliptical structures (Fig. 2b-d) that are aligned along the droplets' long axes. In Fig. 2d, xenon atoms form a loose ring of clusters on the droplet's periphery. During the imaging event, the X-ray beam forms an arbitrary angle with the droplet's figure axis; therefore, their real aspect ratios are larger than indicated by their outlines in Figs. 1 and 2, which correspond to projections of the droplets on the detector plane. The images are characterized by the two half axes of the droplet's projection, referred to as a and b ($a > b$), corresponding to a projection aspect ratio, $AR = a/b$. The formation of rings is observed in ^3He droplets having $AR = 1.04$ to $AR = 1.2$ (Fig. 2). A smaller amount of data was obtained for ^4He droplets during the same experimental run. Most of the intense, reconstructable ^4He images have a small aspect ratio ($AR < 1.05$). However, the results obtained during our previous studies show the formation of vortex arrays in droplets having up to $AR = 2.4$ (9). Thus, we observe confinement of dopants across a wide range of aspect ratios.

The lower boundaries for the droplet's angular velocity, estimated from their aspect ratios (17), are $\approx 1.1 \cdot 10^7$ rad/s and $\approx 1.5 \cdot 10^6$ rad/s for the droplets in Figs. 2c and 2d, respectively. In comparison, the angular velocity of the ^4He droplet in Fig. 1d is estimated to be $\approx 1.7 \cdot 10^6$ rad/s based on the areal density of the vortices and using the Feynman relation (24). The pronounced alignment of the xenon cluster contours along the long axes of the ^3He droplets strongly suggests that the xenon dopants form rings in the droplets' equatorial planes, with their apparent ellipticity determined by the viewing angle.

Statistically, there is a large difference between the shapes of the xenon density distributions within ^3He and ^4He droplets. No aligned filaments, which are characteristic for

superfluid ^4He droplets, are observed in ^3He droplets. Instead, these fermionic droplets contain diffuse ring-shaped structures. It is unlikely that the ring structures could be attributed to any impurities. The ^3He gas used was 99.9% pure with the remaining 0.1% being mostly ^4He . Considering that ^4He 's solubility in ^3He is $\sim 0.1\%$ at 0.15 K, any residual ^4He will likely be dissolved in the ^3He droplets. Even if any pockets of a ^4He -rich phase were formed, they would be too small to give rise to any measurable effects in the diffraction patterns (17).

Discussion

It is immediately apparent from the dopant density distributions presented in Figs. 1 and 2 that helium nanodroplets are not homogenous nanolabs. In both isotopes, dopants are subject to unavoidable, high degrees of spatial confinement due to the droplets' rotation. In ^4He , vortex-bound xenon is aligned along the minor axis of the droplets, as discussed in more detail elsewhere (9), whereas in ^3He , xenon is confined along the droplet equator. The direct relation between the direction of the ^3He droplet's long axis and the concentration of xenon along the equator is visually apparent in Fig. 2. The distorted shapes of ^3He and ^4He droplets carrying dopant rings and filaments, respectively, are direct evidence that rotational excitation is indeed the root cause for the inhomogeneous dopant distributions.

Clusters formed in fermionic ^3He and bosonic ^4He droplets exhibit distinctly different structures. Thus, nuclear spin, which has no impact on any property of ordinary solvents at higher temperatures, plays a crucial role in determining the aggregation dynamics of dopants at low temperatures. We propose that the mechanism for cluster formation in large helium droplets differs between superfluid ^4He versus normal fluid ^3He . In ^4He , single xenon atoms are picked up

149 by the droplet, rapidly thermalize, and begin to move freely within the confines of the droplet's
150 boundaries (3). Atoms form clusters upon collisions. At the same time, xenon atoms and small
151 clusters are attracted to the cores of the vortices by hydrodynamic forces (11-14) and form large,
152 filament-shaped aggregates. In comparison, in a ^3He droplet devoid of vortices, xenon clusters
153 will likely form throughout the entire droplet volume, followed by coalescence into larger
154 globular cluster-cluster aggregates. However, due to the high viscosity of ^3He droplets, dopants
155 assume the same angular velocity as the host and congregate close to the droplet's surface along
156 the equator, i.e., in a plane perpendicular to the direction of the angular momentum. The
157 positions of the dopants are defined by a balance between centrifugal forces and the dopants'
158 solvation potential (25). In principle, similar ring-shaped clusters are expected to be formed in
159 classical rotating droplets (e.g., water droplets with heavy colloidal clusters), however we are
160 unaware of such studies. The ring-shaped xenon structures appear to consist of separate, small
161 (~ 50 nm) clusters, some of which exhibit branched shapes. The structures are likely defined
162 during their formation and remain frozen at the low droplet temperature. The clusters appear to
163 be separated and do not collapse into larger cluster-cluster aggregates, indicating that some
164 mechanism stabilizes the porous network. Previously, it was proposed that some weakly
165 interacting atoms (e.g., Magnesium) may form a so-called foam (26-28), where the atoms stay at
166 sub-nm distance because of the shell of surrounding helium atoms. Whereas X-ray diffraction
167 could be a useful technique for identifying the foam state, the resolution of the current small-
168 angle soft X-ray scattering experiment of about 20 nm is insufficient to resolve spatial features
169 on this level of detail. It is conceivable that the clusters have some interlinks that are too thin to
170 be detected. The smallest compact cluster that can be detected in this work contains ~ 1000 xenon
171 atoms and will appear in an image as approximately 3×3 pixels in size. This limit is set by the

threshold of the phase retrieval algorithm and the spatial resolution of the measurements (10). Future high-resolution experiments may shed more light on the atomic structure of aggregates obtained at temperatures close to 0 K.

The few 100-nm sized droplets in this study, which are produced from fragmentation of the supercritical fluid in the cryogenic nozzle, are marked by large angular velocities of 10^6 - 10^7 rad/s. This contrasts with the results for small droplets of few nm in diameter produced via aggregation of helium atoms. For example, extensive spectroscopy experiments on molecules in small (a few nm) ^4He droplets did not indicate any presence of quantum vortices (29). On the other hand, centrifugal displacement of molecules from the droplet's center was discussed (30). The locations of molecules in small droplets could not be identified in the previous spectroscopy studies on either ^3He or ^4He , and the dopants are often assumed to reside close to the droplet's center (3, 4). We observe that vortices in ^4He are typically separated by distances of 100-200 nm, thus smaller droplets of 150 - 200 nm in diameter may contain just a single vortex. This shows that smaller ^4He droplets between 50 - 100 nm in diameter may be devoid of vortices. Some other techniques of producing helium droplets at small velocity, other than in a molecular beam, may be considered to produce ^4He droplets devoid of vortices.

Materials and Methods

Production and doping of ^3He and ^4He droplets:

Large nanodroplets are produced by expanding pressurized ^4He (99.9999%) or ^3He (99.9%) fluid through a cryogenic nozzle into vacuum with a stagnation pressure of $P_0 = 20$ bar and a nozzle temperature $T_0 = 5$ K (3, 8, 17, 31). At these expansion conditions, droplets with

average radii of ~ 160 nm and ~ 350 nm were produced for ^3He and ^4He , respectively (17). Once in vacuum, the droplets evaporatively cool to respective temperatures of 0.15 K for ^3He (20) and 0.38 K for ^4He (32). The droplets exit the source chamber with an average velocity of about 160 m/s for ^3He and 190 m/s for ^4He and subsequently enter the pickup chamber, which is filled with xenon (99.9%) gas. The droplets collide with, and pick up, several xenon atoms, evaporating off ~ 750 ^3He or ~ 250 ^4He atoms with the pickup of each xenon atom. The amount of xenon added is measured by monitoring the relative depletion of the mass $M = 8$ signal for ^4He (or $M = 6$ for ^3He), representative of He_2^+ ions, in a quadrupole mass spectrometer installed in the terminal vacuum chamber (8). The droplets in Figs. 1 and 2 contain $\sim 10^9$ helium atoms and between 10^5 - 10^6 xenon atoms. The ^3He gas was collected, purified and recirculated by a gas-recycling system as described elsewhere (17).

X-ray diffraction from Xe-doped ^3He and ^4He droplets:

Xenon-doped droplets are irradiated by a focused X-ray Free-Electron Laser (XFEL) beam operated at 1.5 keV ($\lambda = 0.826$ nm) (8). The FEL beam consists of ultrashort X-ray pulses, containing up to $\sim 10^{12}$ photons/pulse, with a repetition rate of 120 Hz, a pulse energy of 1.5 mJ, and a pulse duration of ~ 100 fs (FWHM). The small pulse length and large number of photons per pulse enables the instantaneous capture of the shapes of individual droplets. Diffraction images are recorded with a *pn*-charge-coupled device (*pn*CCD) detector containing 1024×1024 pixels, each $75 \times 75 \mu\text{m}^2$ in size, which is centered along the FEL beam axis ~ 735 mm downstream from the interaction point. The detector consists of two separate panels (1024×512 pixels each) located closely above and below the X-ray beam. Both panels have a central, rectangular cutout to accommodate the primary X-ray beam.

216 Density retrieval, size, and shape determination:

217 The diffraction patterns are recorded at small scattering angles and, thus, predominantly
218 contain information on the column density of the droplets in the direction perpendicular to the
219 detector plane. During the measurements, roughly 550 diffraction patterns from Xe doped ^3He
220 nanodroplets were obtained, whereas 200 patterns were obtained as a reference for Xe doped ^4He
221 droplets. Among them, only the brightest images containing more than $\sim 10^5$ detected photons
222 were selected for reconstruction (10). Ten brightest hits were selected from the ^4He data, whereas
223 15 hits were selected from the ^3He data. Using an iterative phase retrieval algorithm, termed
224 Droplet Coherent Diffractive Imaging (DCDI), the density profiles of the Xe clusters inside the
225 droplets are reconstructed and the sizes and shapes are determined (10). Similar ^3He and ^4He
226 droplet reconstructions are compared based on size, aspect ratio, and overall number of photons
227 detected.

228 Helium droplet shapes are described by the distances between the center and the surface
229 in three mutually perpendicular directions: $A > B > C$. The observed diffraction patterns do not
230 provide direct access to the actual values of A , B , and C , due to the droplets' unknown
231 orientations with respect to the X-ray beam. Instead, the images are characterized by the two half
232 axes of the projection of a droplet onto the detector plane, which are referred to as a and b ($a >$
233 b), corresponding to a projection aspect ratio, $AR = a/b$. The majority (99%) of helium droplets
234 are close to spherical with $AR < 1.4$ corresponding to oblate, axially symmetric shapes. For those
235 shapes with $AR < 1.4$, the average aspect ratios for each isotope are similar, with $AR = 1.049 \pm$
236 0.003 for ^3He and 1.059 ± 0.005 for ^4He (17).

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Acknowledgements

This material is based upon work supported by the National Science Foundation under Grant No. DMR-1701077 and CHE-1664990 (A.F.V.). C.S., B.W.T., M.B. and O.G. are supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division, through Contract No. DE-AC02-05CH11231. M.B. acknowledges support by the Alexander von Humboldt foundation. Portions of this research were carried out at the Linac Coherent Light Source (LCLS) at the SLAC National Accelerator Laboratory. SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under

Contract No. DE-AC02-76SF00515. Additionally, we acknowledge the Natural Sciences and Engineering Research Council of Canada.

Author Contributions

A.F.V., O.G. and C.B. conceived the experiment, A.J.F., D.V., S.M.O.O'C., S.E., C.A.S., B.W.T., M.B., N.S., M.-F.L., P.W., O.G. and A.F.V. prepared and carried out the experiment. A.J.F., D.V. and A.F.V. performed the data analysis. R.M.T. and W.P. contributed to the development of the phase retrieval algorithm and took part in the preliminary experiments. A.A.H. and C.B. provided support for online data analysis. S.M.O.O'C., W.J. and A.F.V. constructed the recycling apparatus for ^3He gas. A.J.F., O.G. and A.F.V. wrote the manuscript.

Competing Interests Statement

The authors declare no competing financial interests.

Data Availability Statement

Raw data were generated at the Linac Coherent Light Source (LCLS) large-scale facility. Derived data supporting the findings of this study are available from the corresponding author upon request.

Supplementary Information (SI)

Diffraction Images

Figures S1a-d and S2a-d show the diffraction images for Xe-doped ^4He and ^3He droplets, respectively, from which the densities in Fig. 1a-d and 2a-d of the main text were obtained. The images are plotted in the indicated logarithmic color scale and the patterns are cropped to the central 600×600 pixels of the 1024×1024 pixels detector. The diffraction images from ^4He droplets in Fig. S1 exhibit circular ring structures close to the center and speckled patterns in the outer region due to scattering off the embedded Xe clusters. Figure S1d shows Bragg spots in a hexagonal arrangement, indicating that a highly ordered structure is contained inside the droplet. As with diffraction from ^4He , the patterns from ^3He droplets in Fig. S2 exhibit circular ring structures close to the center and speckled patterns in the outer region. However, in comparison to patterns from ^4He droplets, the speckles are extended and seem to be arranged more closely along the rings. The different appearances of the diffraction patterns indicate different density distributions of Xe atoms inside ^4He compared to ^3He droplets, which are presented in Figs. 1 and 2, respectively, in the main text.

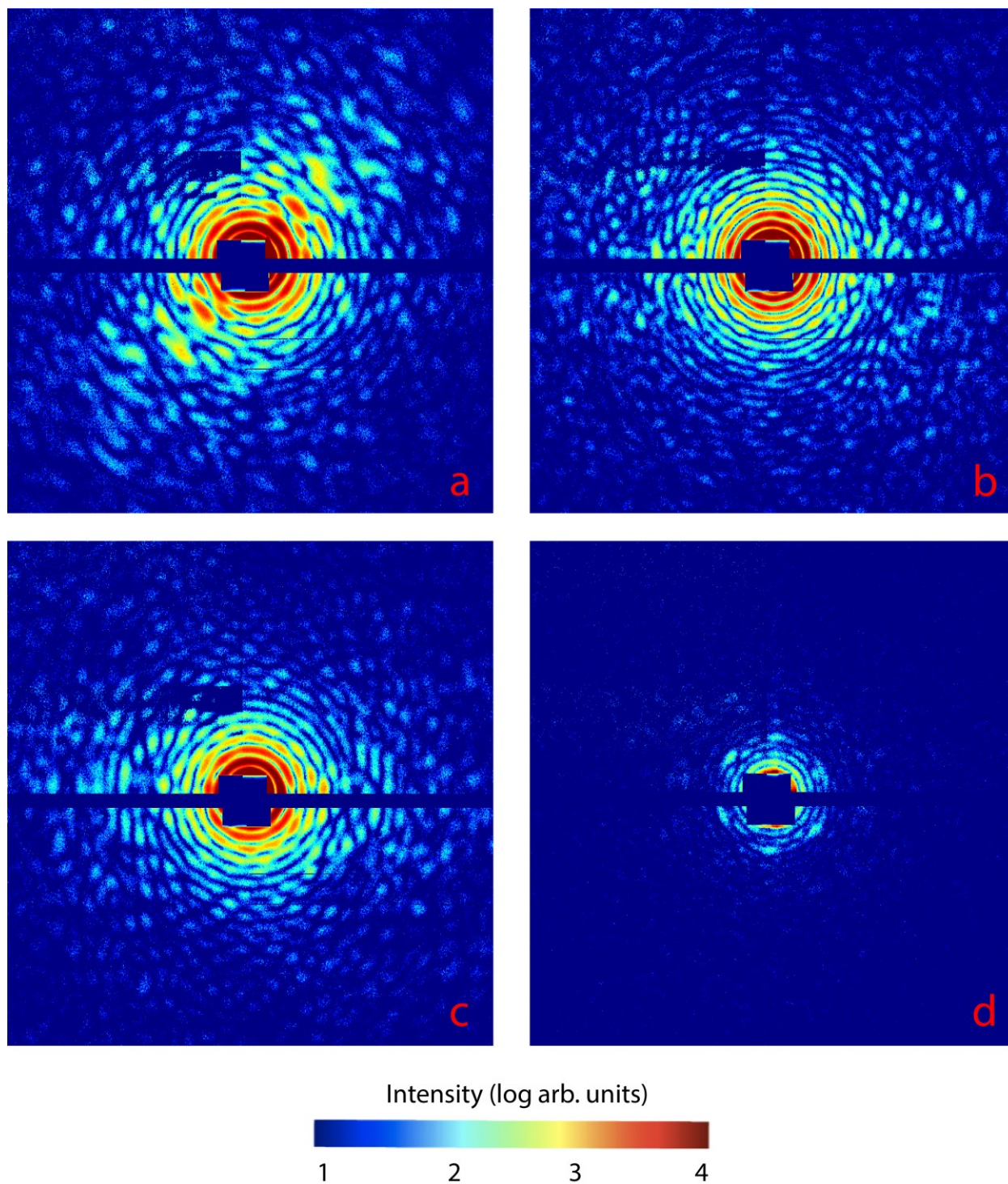
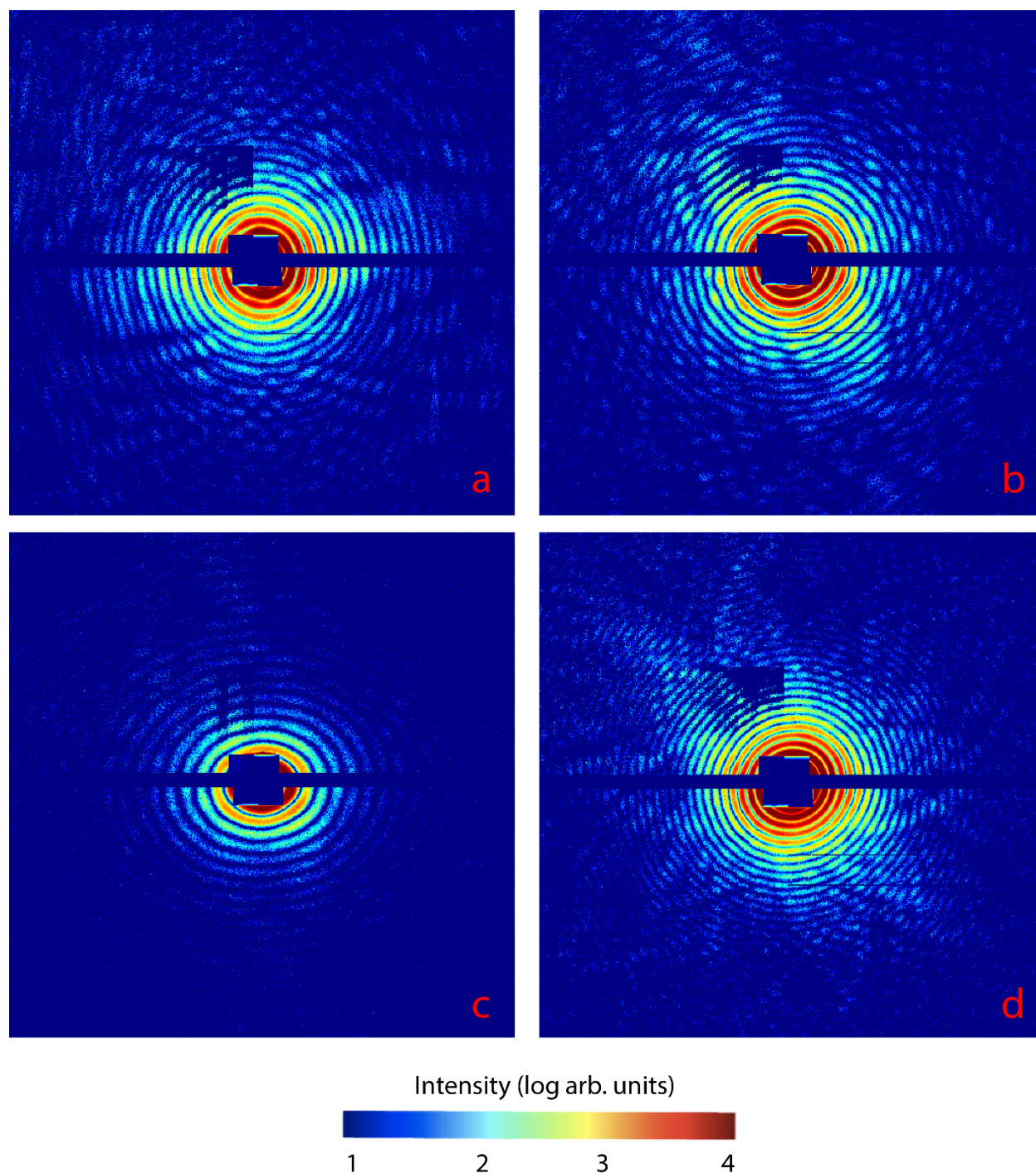


Figure S1. Diffraction images from ^4He nanodroplets in a logarithmic color scale.



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361 Figure S2. Diffraction images from ^3He nanodroplets in a logarithmic color scale.

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