A versatile chamber for X-ray scattering on liquid jets with sample recycling

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We introduce the setup of a versatile sample chamber for X-ray scattering experiments on liquids delivered by μ-jets. The simple implementation at X-ray light sources, adaptability to different nozzle types and the availability of a microscope for observation of the jet flow allow for its broad application. In combination with an inbuilt recycling circle a continuous flow operation is provided. Functionality of the system was demonstrated in a rheology study at PETRA III.

I. INTRODUCTION

The microfluidic behaviour of liquids and their response to shear forces in injection devices has become of increasing scientific and technological interest in the last decades [1–4]. Non-linear stress responses of non-Newtonian liquids occur when the liquids are sheared, e.g. when compressed into μm-sized jets. Experiments at synchrotron radiation and Free Electron Laser facilities (FEL) apply these jets for sample delivery purposes [5, 6], e.g. for the production of supercooled liquids by evaporative cooling [7–10], the delivery of radiation sensitive materials [11–13] and time-resolved rheology experiments [14–16]. Free flowing jets as sample environment have the advantage of a self-refreshing sample and lack of solid boundaries, however, finite sample quantities can limit the applicability. The requirements change with each application, yet the demand for a stable and light-weight system working with low sample volumes remains. Therefore, we designed a compact-sized system that allows for easy transport between different facilities. It fits different nozzle types and sizes and is equipped with a sample recycling system to allow for a continuous flow with limited sample volumes. An application at beamline P10 at PETRA III demonstrated the functionality of the concept. In a study on structural rheology of colloidal systems a range of different shear rates and Péclet numbers and their influence on shear-induced particle ordering in liquid jets has been investigated [14].

II. SAMPLE CHAMBER LAYOUT AND CAPABILITIES

The custom-made sample chamber that extends previous versions [17] consists of a CF40 cube of 70 mm edge length and flanges containing Kapton windows for the connection to the beamline (see Fig. 1). A nozzle enters the chamber from the top, creating a vertical-flowing liquid jet that is collected approximately 30 mm further down in a funnel-like collection device. Two additional windows on the side of the cube perpendicular to the beam path allow for observation of the jet during measurements via a microscope. The microscope is movable via three motors. Sufficient back-illumination of the sample is provided by a LED flashing with 1 ms exposure time at 10 Hz repetition, therefore not only the jetting regime is observable but also the transition from the jetting regime to break-up into droplets can be tracked [18, 19]. For reduction of background scattering and in consideration of flow stabilities the chamber is flushed with a continuous flow of about 1 L/h helium during X-ray scattering experiments.

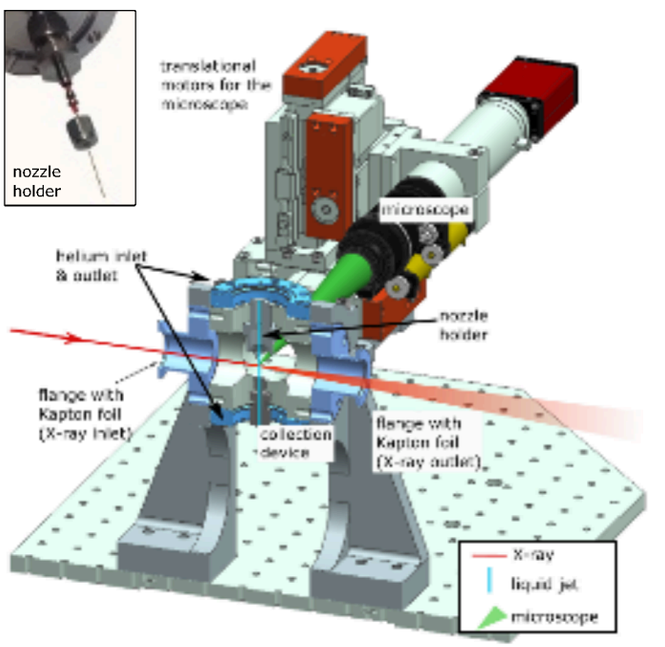

FIG. 1. Cut of the sample chamber and the microscope looking into the CF40 cube (blue) through a window at the backside of the chamber. The X-rays enter from the left through a flange covered with Kapton foil and exit to the outlet on the right. The nozzle holder (shown in the inset) is mounted on the top of the chamber and the collection device for the liquids is attached at the bottom.

The system for producing continuous flow through the

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nozzle is shown as a schematic sketch in Fig. 2. In total four syringe pumps press the liquid sample through the tube system. In the pumping cycle two mid pressure pump modules neMESYS (cetoni) with 5 ml steel syringes provide the flow with up to 100 bar pressure. Both syringes are filled with the sample liquid through a mechanical valve (beige lines) and inject the liquid (green lines) through a pressure sensor and a second valve. The injection lines from both syringes are connected by a T-piece adapter before entering the sample chamber. The switch between both pumps is pressure controlled via the QmixElements software [20]. In the pressure-controlled mode one syringe injects liquid into the system while the other refills. The refilling is faster than the injecting, which enables applying and stabilizing pressure in the freshly refilled syringe. Therefore, uninterrupted flow is ensured.

The collecting vessel at the bottom enables the installation of two further syringes for sample recycling, using two low pressure pump modules from neMESYS with 25 ml glass syringes. In a similar system as in the pumping cycle, the recycling system fills the syringes from the collecting device one after the other. Regulated by electronically switching valves, the first pump presses the collected liquid back to the sample reservoir while the second starts collecting liquid from the jet.

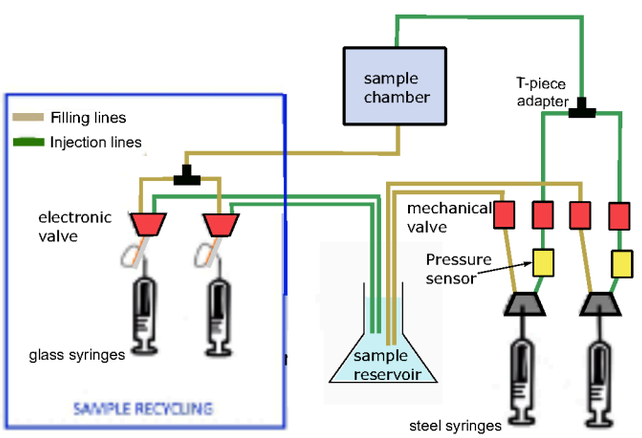

FIG. 2. Schematic sketch of the four syringe pumps driving the jet system. Two mid pressure modules cycle the sample into the liquid jet chamber in continuous flow mode, while two low pressure modules drive the recycling system.

A. A Model Application with Rayleigh Nozzles

The sample chamber setup described above can be used with multiple different injections systems. Test runs performed for this report applied jets generated by polyimide coated micro tubes (Polymicro Technologies) with inner diameters varying from 50-150 μm. The microtubes were cut to a length of less than 15 cm, which, in accordance with the Hagen-Poiseuille equation, resulted in an operating pressure of 10 to 100 bar for different tube sizes. The operation of a continuous flow mode was successfully performed at flow rates between 0.8-3 $\frac{\text{ml}}{\text{min}}$ for spherical colloids in water between 8 and 20 vol% (viscosity determined to 1.3-2.4 mPa·s [21]). Considering the overall tube volume and evaporation losses the system was filled with 50 ml sample volume in continuous flow mode. After starting the pumps, a waiting time of at least two iterations of filling and depleting the syringes reduced the amount of air in the syringe system, which encouraged stable jetting. The recycling system was driven with a flow rate up to 5 $\frac{\text{ml}}{\text{min}}$, removing at least about 1.5 times more volume than what was delivered to cover the whole content of the collecting device, including bubbles and air. For the smallest microtube with a maximum flow rate Q_{max}=1.4 $\frac{\text{ml}}{\text{min}}$ the sample volume required for a continuous flow could be reduced to 25 ml.

B. Implementation example with colloidal liquids

We report the successful use of the chamber in a scattering experiment in small-angle X-ray scattering (SAXS) geometry at beamline P10, PETRA III, Hamburg, Germany. The study investigated structural rearrangement of colloidal silica systems due to shear forces in liquid jets [14].

During this experiment four systems of different viscosities were investigated. Before changing between different colloidal sample systems, all tubes were flushed with pure water for 15 min. In addition, the glass syringes from the recycling system were dismounted and cleaned from residual nanoparticle dispersion. Residual water from the cleaning procedure was ejected from the system by at least two pumping iterations done with air.

Jet velocities v_{jet}=1.7 $\frac{\text{m}}{\text{s}}$-5.3 $\frac{\text{m}}{\text{s}}$ are achieved in nozzles with diameter $2r$=50-150 μm for flow rates Q=0.8-3 $\frac{\text{ml}}{\text{min}}$. Such velocities covered shear rates $\dot{\gamma}=\frac{4Q}{\pi R^3}=(0.9\text{-}5.6)\cdot 10^5\,\text{s}^{-1}$ for our four sample systems with particle radii R=15-77 nm.

Fig. 3 displays a selection of SAXS patterns measured from a colloidal system with R=15 nm in a liquid jet with the setup and procedure described above. The sample was ejected from a 100 μm diameter tube into the helium atmosphere in the chamber. The X-rays scattered from the liquid jet 150 μm downstream from the nozzle tip at different positions d across the jet. The patterns show the summed intensity of 10 diffraction patterns taken with 1 s exposure time each. If the beam impinged on the center of the jet (d=0) the diffraction pattern appeared symmetric and showed an annulus of isointensity scattering at q=0.17 nm^{-1}. This represents the isotropic structure factor of the sample similar to a colloidal liquid in equilibrium [22]. At $d \neq 0$ the intensity in the annulus developed a 2-fold modulation along the azimuthal direction [14, 15, 23]. While the asymmetry of the scattering pattern relates a direction-dependent intensity to a degree of particle ordering, the ovality of the diffraction pattern relates to a change in next-neighbor distance. Both asymmetry and ovality have been discussed for a colloidal dispersion in a previous study [15]. A detailed analysis of the presented data will be shown

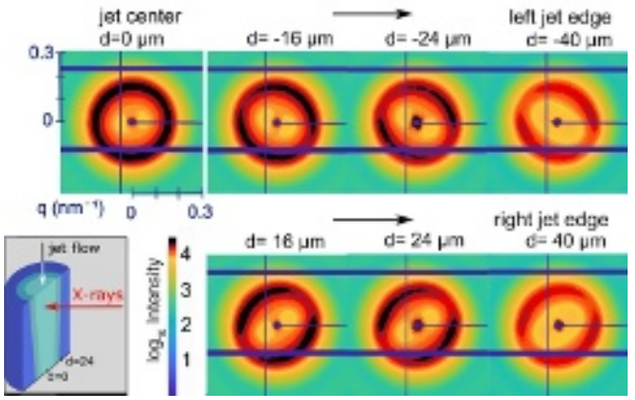

FIG. 3. Scattering patterns at different positions in the horizontal jet profile for a colloidal silica sample. A schematic depiction of the jet is shown in the inset. The patterns were taken 150 μm downstream from the nozzle from a jet of 100 μm diameter. The patterns show an asymmetric intensity distribution for $d \neq 0$ in the q-range up to $\pm 0.3\,\mathrm{nm}^{-1}$ (adapted from [23]).

in a subsequent publication.

III. CONCLUSION

We report the construction of a versatile sample chamber for a liquid jet sample delivery system and document capabilities from first experimental runs. The size of the chamber and the simple installation process of the components allow for flexible applications, which was demonstrated by a structural rheology experiment on colloidal silica particles performed at beamline P10. Especially noteworthy is the recycling system. The reuse of the liquid is reasonable for many samples, even if they show radiation sensitive behaviour. The pulsed structure of XFEL light illuminates only a fraction of the liquid in the jet and even at synchroton radiation sources the particles in the jet are exposed to the X-rays for less than 1 μs at jet velocities of $2\,\frac{\mathrm{m}}{\mathrm{s}}$ or above (assuming a beam size of 1 μm). Taking advantage of the recycling circle enabled the setup of a continuous flow mode in which the jet was maintained over days even with a limited sample volume between 25 ml and 50 ml. With the addition of a microscope illuminated by a flashing LED, we could verify the stability in the jet during the experiment as well as measure in-situ the break-up length of the liquid jet. Especially in cases where the chamber is used in an evacuated state, a measure of jet stability and monitoring of sample freezing in the chamber gain importance. In future experiments the chamber can be adapted for the use of different nozzle types, e.g. High Viscosity Extruders (HVE) or Gas Dynamic Virtual Nozzles (GDNV) [24, 25]. Furthermore, thanks to its versatility, it allows the installation of an additional cube for an extension with an inline microscope.

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AUTHOR DECLARATIONS

The authors have no conflicts to disclose.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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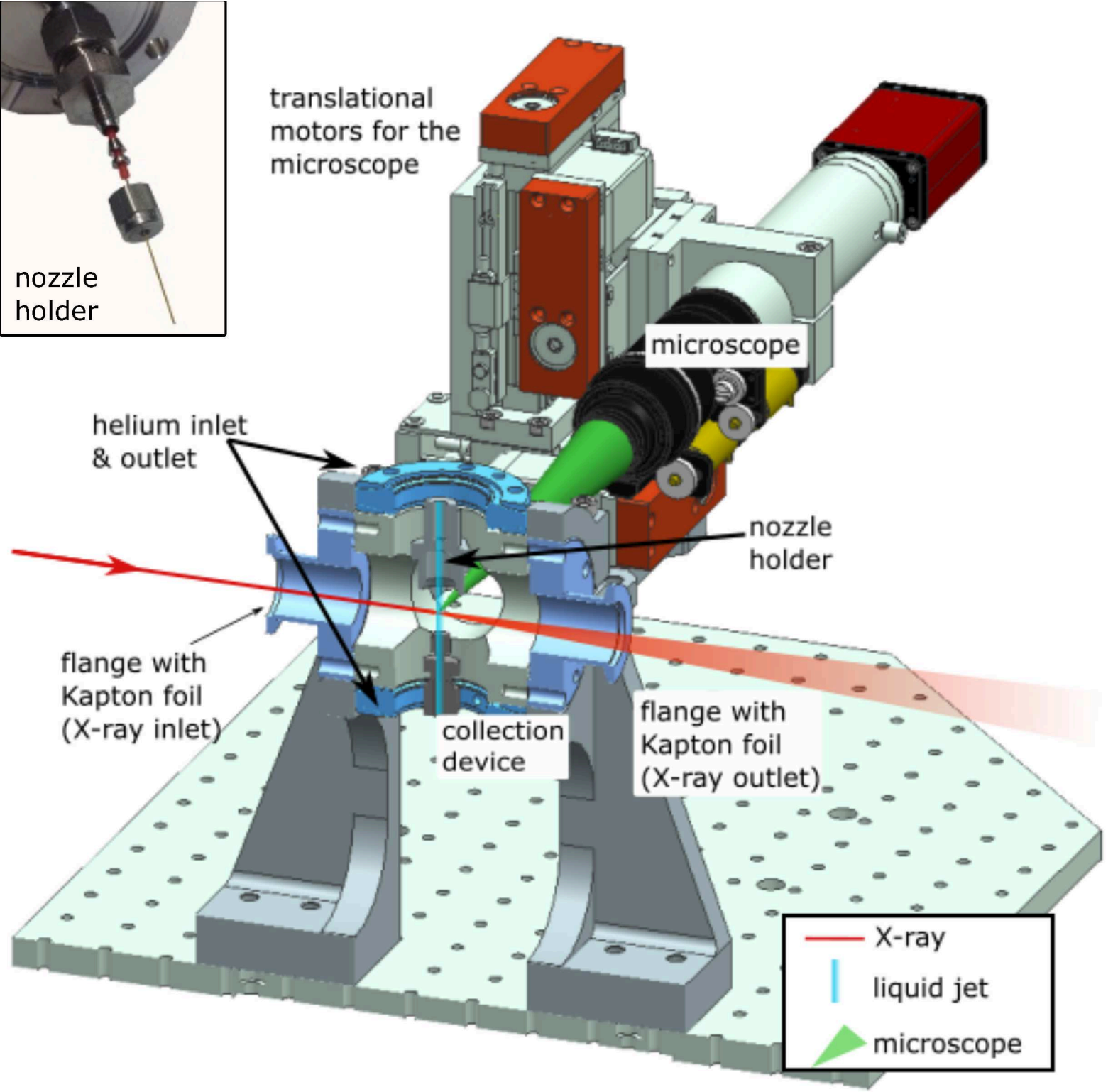
nozzle
holder
translational
motors for the
microscope
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X-ray
liquid jet
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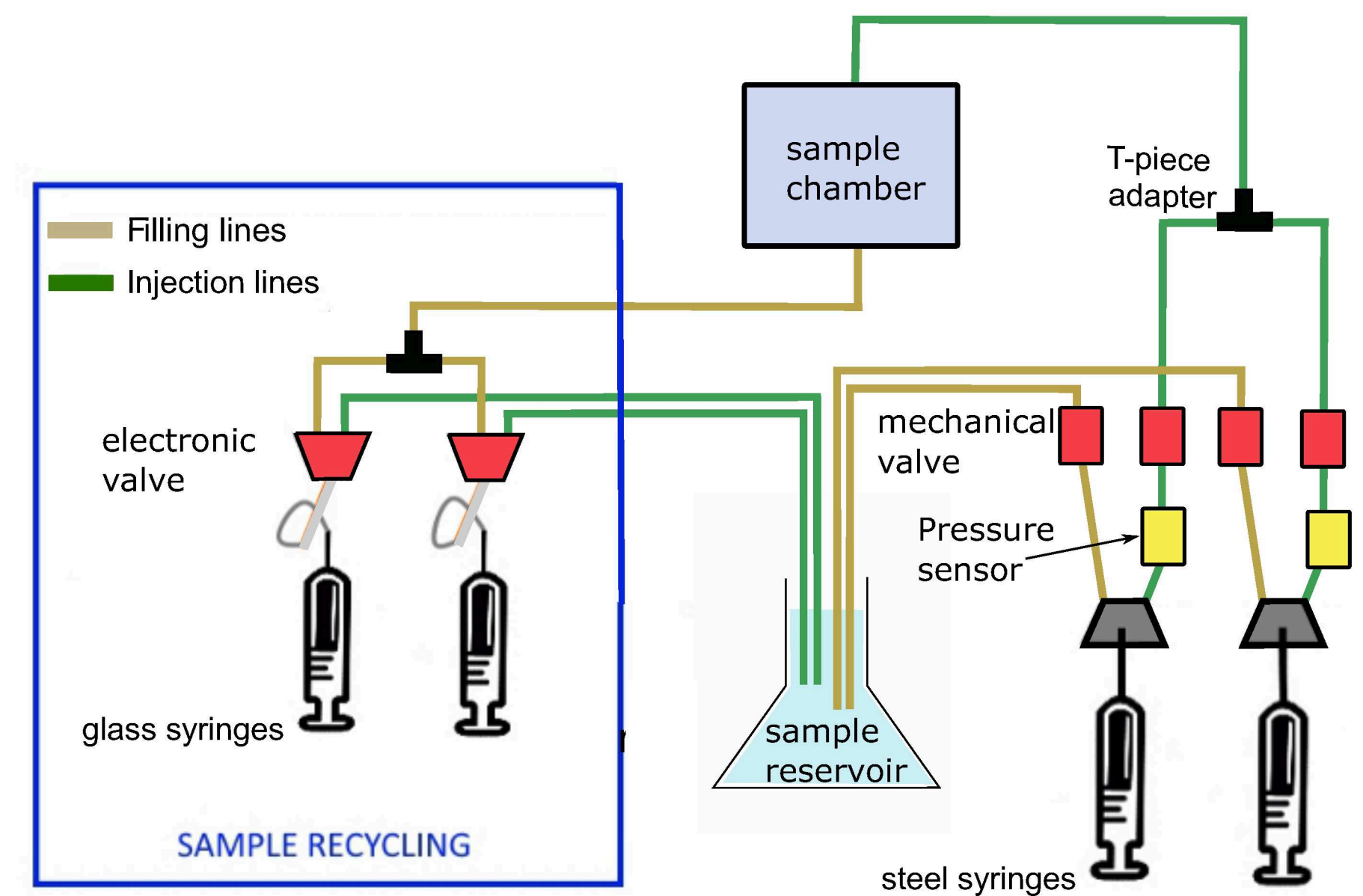
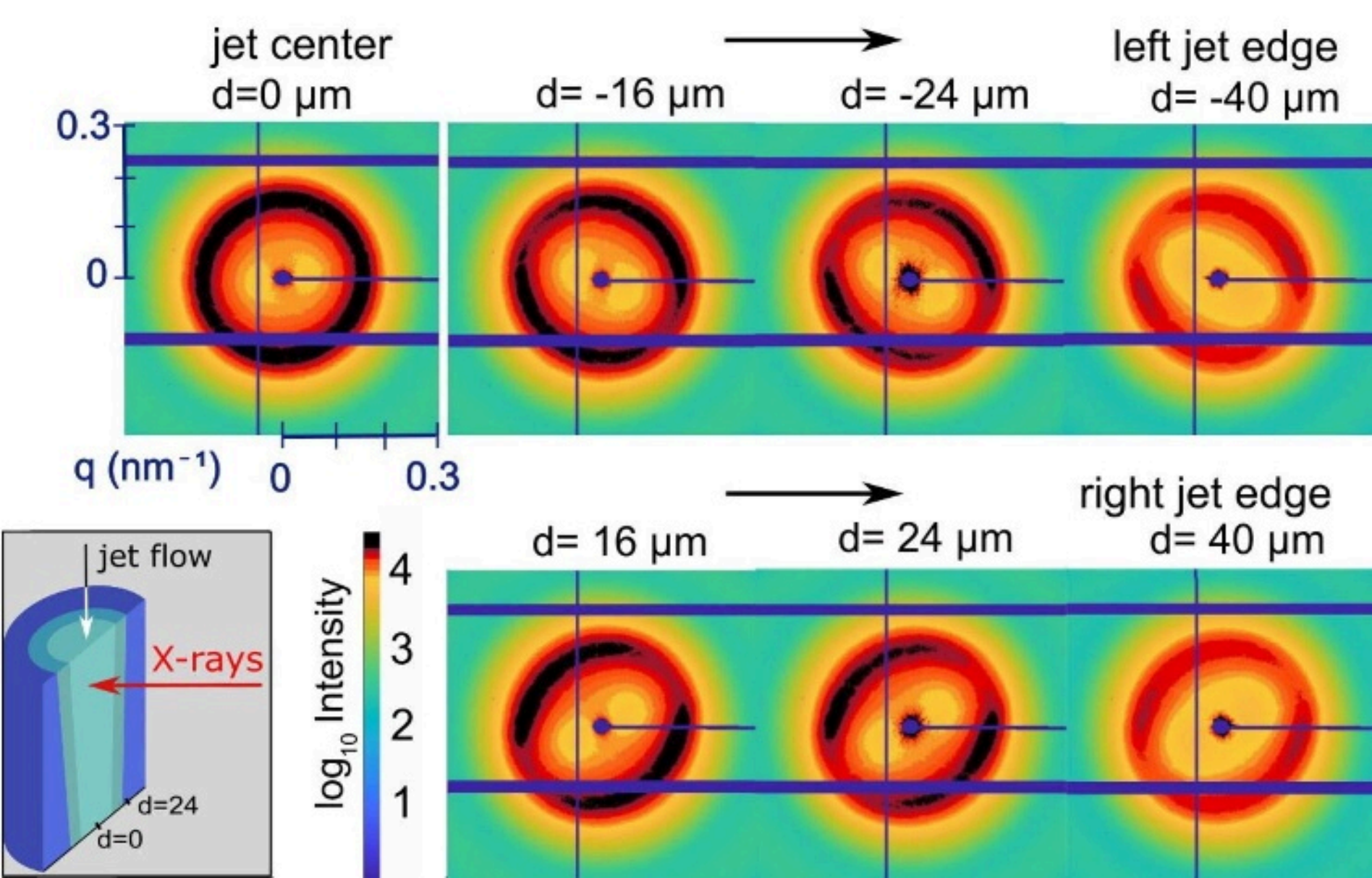

sample chamber
T-piece adapter
Filling lines
Injection lines
electronic valve
mechanical valve
Pressure sensor
glass syringes
sample reservoir
SAMPLE RECYCLING
steel syringes


jet center
d=0 μm
d= -16 μm
d= -24 μm
left jet edge
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0.3
0
q (nm⁻¹)
0
0.3
jet flow
X-rays
d=24
d=0
log10 Intensity
4
3
2
1
d= 16 μm
d= 24 μm
right jet edge
d= 40 μm