Capturing nanoscale fireworks.

Imaging single nanoparticle explosions with femtosecond temporal and nanometre spatial resolution

Many ultrafast non-equilibrium phenomena such as chemical reactions, phase transitions and light-matter interactions, remain uncharted due to the lack of imaging methods combining high spatial and temporal resolutions. X-ray free-electron lasers (FELs) with intense, femtosecond flashes open up unprecedented opportunities to resolve complex ultrafast dynamics even in isolated nanosized samples. We superheated single xenon nanoclusters using an intense infrared pulse and imaged the following expansion with single X-ray FEL pulses. Thereby, we resolved nanometre-scale surface softening within 100 fs of the heating pulse. Our study is the first time-resolved visualisation of irreversible femtosecond processes in free, individual nanometre-sized samples.

Conventional imaging methods such as electron or optical microscopy provide either high spatial or high temporal resolution, but fail to incorporate both. X-ray FELs open new opportunities to capture phenomena with a single exposure on a femtosecond timescale and with nanometre spatial resolution. Following the demonstration of the diffractive single-particle imaging approach at the FEL FLASH at DESY [1,2], subsequent studies on non-equilibrium dynamics provided unique insights into shock waves in materials [3] and protein quakes [4]. Studies at FLASH indicated that diffraction images provide indirect information about transient nanoplasma states [5]. However, most experiments to date were static or limited to picosecond temporal resolutions, while measurements on particle ensembles often lack the desired precision due to averaging effects. In the present study, we captured structural dynamics on the femtosecond timescale in free, single nanoparticles. Our study paves the way towards high-resolution femtosecond imaging of individual nanoparticles without the interaction with surroundings and under well-defined conditions.

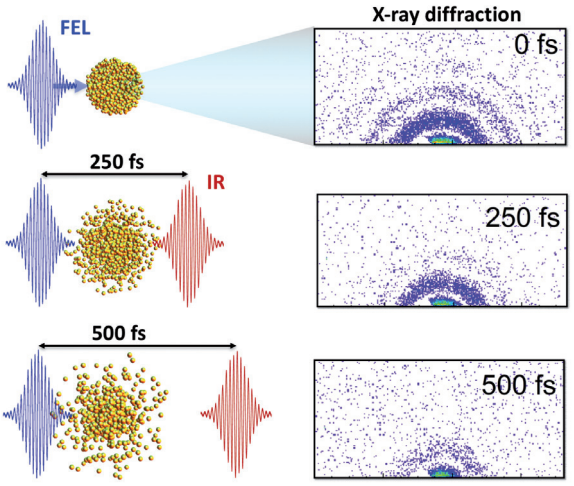

Figure 1

X-ray diffraction patterns of pristine and pre-heated xenon clusters. The top panel shows diffraction from a pristine spherical cluster. Shown below are the diffraction patterns produced 250 fs (middle) and 500 fs (bottom) after the exciting NIR pulse.

In our experiment, individual xenon clusters with radii around 20 nm were exposed to a single near-infrared (NIR) laser pump and a subsequent X-ray laser probe pulse at the Linac Coherent Light Source (LCLS). The heating NIR laser pulse, with a wavelength of 800 nm and pulse duration of 70 fs, ionised and transformed single xenon clusters into a non-equilibrium nanoplasma evolving on the femtosecond timescale. We imaged the following cluster expansion by recording the diffraction from the nanosamples with delayed X-ray FEL pulses with 0.8 nm wavelength.

The X-ray diffraction from pristine and superheated clusters is shown in Fig. 1. The top panel demonstrates patterns recorded from a spherical xenon cluster similar to far-field diffraction from a pinhole. The diffraction image changes dramatically within hundreds of femtoseconds after the heating NIR pulse excited the cluster. The loss of higher order information can be identified already after 250 fs and becomes apparent 500 fs after the heating pulse.

At first glance, one would expect very different diffraction patterns based on the assumption that the NIR pulse causes an explosion of the cluster. This model is reasonable as the NIR pulse ionises and heats the electrons trapped inside the cluster. These confined hot electrons initiate the cluster expansion as they transfer their kinetic energy to the ions. In the first order approximation, the cluster explosion can be compared to a constantly increasing pinhole leading to a finer spacing in the far-field diffraction.

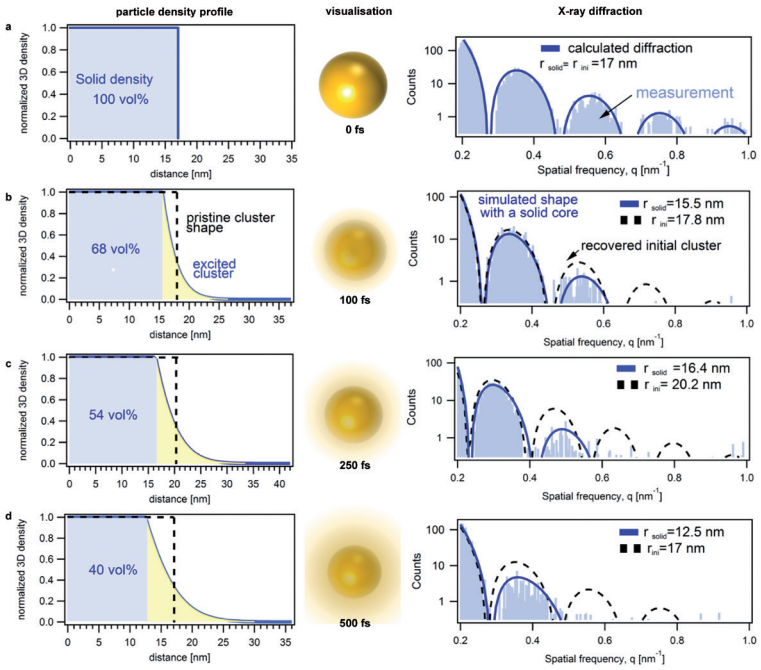

Figure 2

Evolution of the superheated nanoclusters at simultaneous NIR–FEL excitation (a), and 100 fs (b), 250 fs (c) and 500 fs (d) after the NIR pulse. Right panels: Measured diffraction integrated radially (histogram bars), fitted diffraction patterns (solid blue lines) and recovered diffraction from the pristine cluster (dashed lines). The experimental data indicate an inhomogeneous density distribution of the sample in b–d. The decrease in higher-order diffraction signal intensity suggests that the outer parts of the sample dilute due to expansion of the sample. Using the Guinier approximation, we fitted the observed diffraction patterns (solid line) with density profiles (shown on the left). Left panels: Comparison of fitted electron density profiles of the excited clusters (solid blue lines) and the recovered pristine shapes (dashed lines).

However, this aspect is not observed in the present experiment. The changes in the diffraction patterns can be correlated to the structural dynamics analytically in the limit of small scattering angles using the Guinier approximation [6]. The overall shape of the patterns suggests that the expansion first dilutes the outer shells close to the cluster surface, while leaving a core with a uniform electron density. Using the dilute shell – solid core model, the electron density profiles of the clusters can be reconstructed, as exhibited in Fig. 2.

In the right column of Fig. 2, the calculated scattering profiles of the undamaged and the reconstructed core–shell structure are compared to the recorded data. Panel A demonstrates that the pristine cluster can be perfectly fitted assuming a hard sphere with a uniform electron density profile. In panel B, the higher orders disappear rapidly already 100 fs after NIR excitation, but the peaks also broaden towards higher scattering angles, as best observed for the 500 fs data. Moreover, the minima of the heated particles are located at larger scattering angles than the minima of the simulated undamaged particles, as the small-angle information is dominated by the solid density core. This leads to the counter-intuitive situation that the larger expanding particles appear smaller than the unheated particles. This fingerprint can be used to identify potential sample damage in single-particle imaging with X-ray laser pulses.

Our study shows that imaging with X-ray lasers can gain unique insights into dynamics in matter under extreme conditions. The temporal resolution of our method can be significantly improved towards sub-10 fs using improved synchronisation techniques. In the hard X-ray regime, the spatial resolution could be pushed towards atomic resolution. The combination of both could allow one to follow structural changes with atomic resolution on the timescale of electron motion, for example, conformational changes in aerosols, shock fronts in dense plasmas and plasmon oscillations. These goals could be achieved at upcoming high repetition-rate facilities such as the European XFEL.

Contact: Tais Gorkhover, taisgork@slac.stanford.edu
Christoph Bostedt, cbostedt@anl.gov
Jochen Küpper, jochen.kuepper@cfel.de

Authors

Tais Gorkhover, Sebastian Schorb, Ryan Coffee, Marcus Adolph, Lutz Foucar, Daniela Rupp, Andrew Aquila, John D. Bozek, Sascha W. Epp, Benjamin Erk, Lars Gumprecht, Lotte Holmegaard, Andreas Hartmann, Robert Hartmann, Günter Hauser, Peter Holl, Andre Hömke, Per Johnsson, Nils Kimmel, Kai-Uwe Kühnel, Marc Messerschmidt, Christian Reich, Arnaud Rouzée, Benedikt Rudek, Carlo Schmidt, Joachim Schulz, Heike Soltau, Stephan Stern, Georg Weidenspointner, Bill White, Jochen Küpper, Lothar Strüder, Ilme Schlichting, Joachim Ullrich, Daniel Rolles, Artem Rudenko, Thomas Möller and Christoph Bostedt

Affiliation details at:
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