

Category B Proposal to use the LCLS for:
"Nanocrystal Structure Determination"

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My group has an ongoing effort to study the structure of individual nanocrystals by coherent X-ray diffraction (CXD). The beam even from existing sources is sufficiently coherent that the diffraction patterns represent interference from the entire crystal, even if focusing optics is introduced. Because the resulting diffraction patterns are continuous, they can be inverted into images by use of constrained iterative Fourier transformation methods, devised by Fienup and others.

Up to the present we have concentrated on metal nanocrystals in the 150-600nm size range. The first results on gold crystals grown by dewetting from a substrate showed residual strain effects as 50nm stripes within the (otherwise smooth) shape of the crystal [1]. Experiments on Pb allowed us to investigate both the equilibrium crystal shape at high temperature and the supposed "surface melting" that takes place close to the melting point [2]. Chemically synthesized nanocrystals of Ag have turned out to be perfect in that they do not appear to contain internal any structure, and have allowed us to show that our reconstruction methods still work after concentrating the coherent beam with Kirkpatrick-Baez (KB) mirrors in the usual way [3].

In the course of these investigations, we have encountered (at least) two problems that are avoided by use of the LCLS:

- i) We run out of flux below a crystal size of about 100nm (est). This might be avoided by using tighter focusing, but only slowly, since the intensity goes as the sixth power of the linear sample size.
- ii) Sample stability is a bigger problem than we anticipated and this appears to be compounded by radiation effects. The samples move in the beam and we have not yet found a way to adhere them sufficiently to a substrate, at least without damaging them. The snapshot nature of single LCLS pulses would allow us to overcome the sample motion and perhaps allow us to understand the radiation damage effects.

This single-nanocrystal CXD experiment lies directly on the path to one of the main goals of LCLS, which is single-molecule imaging. Since the size of metal nanocrystals can be adjusted all the way from 5nm clusters up to hundreds of nanometers, they would make an excellent choice of experiment to test the early stage performance of the LCLS.

Colloidal nanocrystals are being investigated intensively at

present. In the size range of 20-50nm, they are remarkable for their anomalous optical properties, evidenced by dramatic shifts of their absorption and photoluminescence spectra [4], for example from the ultra-violet down to the visible. These spectral features are found to correlate with the shapes of the crystals [5], currently investigated by Transmission Electron Microscopy (TEM). Smaller nanocrystals, around 5nm, when prepared in monodispersed populations show interesting aggregated states as colloidal crystals, both in 3D and 2D [6]. Sheets of the 2D colloidal crystals have interesting electrical properties showing percolation and tunneling [7]. Smaller still metal nanocrystals, around 2nm, arouse interest as potential catalysts, since the chemical properties of surface atoms become significantly modified and because almost all the metal lies in the surface [8]. This motivates a strong interest in the structure of nanocrystals on all length scales.

An important common theme in the various applications of nanocrystals listed above is that the crystalline identity of individual crystal must be kept distinct. The interesting properties are lost if the nanocrystals are allowed to touch each other. Nanocrystal systems are therefore inherently two component systems with a distinct and well-defined coating layer around the crystals. The coating is also a central feature in all nanocrystal synthesis methods. Synthesis is usually based on self-assembly in the presence of a surfactant. A widely-used method attributed to Murray [9] is chemical reaction of one or two reagents by injection into a high temperature solvent, such as glycol, but always in the presence of a surfactant. Commonly used surfactants are thiols and polyvinyl pyrrolidone (PVP).

The structure of nanocrystals is usually accessed by TEM, which is close to ideal for crystals smaller than the electron extinction length of about 50nm. Sample preparation is also a fundamental issue as the crystals must be attached to a thin supporting membrane. The critical surfactant layer is often lost or disturbed during the sample preparation; it is rarely visible in the published images. X-ray diffraction methods on individual crystals are suitable for larger nanocrystals with current sources and will be suitable for all sizes using the LCLS. The big advantages of using the LCLS are:

- three dimensional structures
- ultra-fast snapshots of moving and evolving nanocrystals
- in situ study of the self-assembly and synthesis of the crystals
- in situ study of interactions between nanocrystals
- time-resolved recording of the introduction of defects or destruction of nanocrystals

A natural extension of this work would be the study of equilibrium fluctuations of supercritical saturated solutions, which are expected to form sub-critical nuclei spontaneously. This would permit testing of the microscopic theory of classical nucleation, that has not been possible before. According to that theory, solute molecules randomly associate into clusters with a

thermodynamic equilibrium distribution, progressively scarcer for the largest cluster sizes. Once a cluster nucleates that exceeds the critical nucleus size, it becomes thermodynamically stable and grows into a macroscopic crystal. The objective would be to test for the existence of precritical nuclei in equilibrium with a solution close to saturation. This long-term goal will be well-served by the systematic study of established crystals on a range of size scales, preferably in solution under a variety of concentrations and chemical environments.

Another extension would be to study the strain field associated with a defect in an otherwise perfect nanocrystal. In a stiff elastic material such as Si, atoms next to a defect are displaced out to a radius of the order of 10nm to 50nm. Diffuse scattering is thereby generated near to the Bragg peaks of the reciprocal lattice, called Huang diffuse scattering (HDS). With the LCLS, the HDS from a single point defect should be measurable with single bunch time resolution. A defect with low symmetry would give rise to a HDS pattern with the corresponding symmetry, that would identify it uniquely; such a characterization is impossible in the ensemble average of many defects with different orientations. The HDS pattern would of course be completely structured by the coherence in a way that would allow its inversion into image frames. The hope is to be able to resolve the evolution in time of a defect cascade originating from implantation of an ion beam directed at a crystalline sample. It would not be necessary to control the time of arrival or the exact location of the impact, if a suitable detector can be built. This is also important for examining spontaneous fluctuations, as described above, and many other ways of introducing defects could be considered.

The experimental setup for nanocrystal diffraction would be quite similar to other single-molecule imaging experiments, except that it would benefit from having a simple diffractometer to hold a (small) array detector at the known Bragg angle of interest. At least for the early-phase experiments, there is no reason to cover all of reciprocal space, just the region surrounding one Bragg peak. This setup might be an extension of existing facilities, for example the 34-ID-C beamline at APS. The beam should be monochromated and focused by KB mirrors to a size small enough to limit the sample volume and so the number of crystals. The sample should be located at the center of the diffractometer that holds a detector at the Bragg angle of the crystalline material being investigated; this is a highly effective way to remove background from solvent and support structures. Monochromatic X-rays will naturally select a small subset of all crystals by chance encounters with the Ewald sphere, which will be spread out over a Debye-Scherrer cone.

Most of the instrument development work needed is associated with the detector and its gating both to the pulse structure of the LCLS and to the experiment. Since this theme is common to almost all science at LCLS, it is better organized by the facility,

according to parameters laid down by the experimental needs. To my limited knowledge, the only detectors capable of reaching the needed time resolution are Avalanche Photodiodes (APDs). However, parallel diffraction data on an array of at least 200x200 pixels is needed to understand the structure of even the simplest nanocrystals, with bigger arrays leading to higher resolution images. So the ideal detector appears to be an array of gated APDs. It is possible that CMOS pixel-array or even CCD technology might be adapted to the necessary gating requirements of the LCLS.

The detector system will have to be sophisticated in being "event"-triggered as would be a particle-physics detector; the event would be either a larger-than-threshold intensity, caused by a fluctuation in the sample, or else an external trigger from the arrival of an external stimulus. Full frames of pixels would only need to be saved around the time of the triggering event for later analysis. Since the experiments envisaged require seeking a small signal on a high background, the background subtraction should be an integral part of the signal processing in each pixel.

This proposal has addressed mainly the scientific areas where I would wish to engage the capabilities of the LCLS. I have been approached by organizers of other proposals, which may include me as a member. I am expecting that category A and category B projects will be grouped as necessary. The specific ways that I might be able to contribute to the advancement of LCLS are:

1. Supply a student, supported by LCLS, for development sample-handling and preparation techniques. These would be tested using current CXD techniques at Argonne, in anticipation of the turn on of LCLS. I don't need to remind you that the UIUC graduate program in condensed matter physics is ranked above Stanford's (by "U.S. News and World Report")!
2. I would be interested to come to LCLS as a consultant at the right time in the project development to participate in planning early-phase experiments. Summer months are the easiest way to do this, but 4-month sabbaticals are also possible.
3. Develop instrumentation, again using my current CXD beamline as a test facility, for the handling and manipulation of samples. One possibility would be to develop a commercial AFM instrument into a 'nanomanipulator' by functionalizing the tip with nanocrystalline material. Adequate methods for co-registration of such a sample and a focused X-ray beam are still lacking at present.

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[2] M. A. Pfeifer, G. J. Williams, I. A. Vartanyants and I. K. Robinson, to be published

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[4] "Size-controlled growth of CdSe nanocrystals in microfluidic reactors", Chan E. M., Mathies R. A. and Alivisatos A. P., *Nano Letters* 3 199 (2003)

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