

# Using Two-Dimensional Colloidal Crystals To Understand Crystallography

Stephanie A. Bosse and Nikolaus M. Loening\*

Department of Chemistry, Lewis & Clark College, Portland, OR 97219

X-ray crystallography is the primary technique used to determine the three-dimensional structures of molecules, especially large biomolecular systems such as proteins, DNA, and RNA. Despite the impact of this technique in chemistry and structural biology, many undergraduate students receive only a cursory introduction to X-ray crystallography in their lecture classes and rarely have a chance to use the technique in the laboratory owing to lack of access to the equipment. In addition, the sophistication of the mathematics involved in converting an X-ray diffraction pattern into a three-dimensional structure often lessens the pedagogical impact of an X-ray crystallography laboratory experience.

We present here an undergraduate laboratory experiment that allows students to discover the principles of powder and single-crystal crystallography by making two-dimensional colloidal crystals of latex spheres and then studying how these crystals diffract light. By using latex spheres with diameters of 1–5  $\mu\text{m}$ , students are able to prepare crystalline samples in a few minutes. In addition, these crystals diffract monochromatic visible light (rather than X-rays), allowing the experiment to be conducted with inexpensive and readily available laboratory equipment. The resulting diffraction patterns are easily interpreted using trigonometry. Depending on the number of samples analyzed, it is possible for students to complete this experiment in one or two laboratory periods. This experiment is suitable for upper-level physical chemistry laboratory students, but can also be adapted for use in a general chemistry laboratory.

## Background

Since the beginning of the 20th century, monodisperse spherical particles have been studied for their ability to form two-dimensional hexagonal colloidal crystals (1). Latex spheres, in particular, are an attractive material for such studies owing to their ready availability in a number of sizes and with a high degree of monodispersity. Two-dimensional crystals can be formed by spreading a drop of latex spheres suspended in water on a glass slide and then allowing the solvent to dry. Although it has been suggested in the past that electrostatic repulsion or van der Waals attractions plays a role in the packing process, more recent work (2) suggests that the evaporation of the solvent and attractive capillary forces drive the crystallization process. Consequently, altering conditions to slow evaporation slows crystal growth and results in samples with larger crystalline domains. In the past, the study of two- and three-dimensional colloidal crystals has been largely an academic pursuit, but more recently these crystals, including ones formed by latex spheres, have also been extensively studied for use as photonic devices (3).

Regular (three-dimensional) crystals act as three-dimensional diffraction gratings and obey Bragg's law

$$n\lambda = 2d\sin(\theta) \quad (1)$$

where  $n$  is the diffraction order (an integer),  $\lambda$  is the wavelength of the radiation,  $d$  is the spacing of the lattice planes, and  $\theta$  is the angle between the incident beam of radiation and the lattice planes. Similarly, a two-dimensional crystal acts as a two-dimensional diffraction grating (as shown in Figure 1) and the resulting pattern is described by

$$n\lambda = d\sin(\theta) \quad (2)$$

where  $n$ ,  $\lambda$ ,  $d$ , and  $\theta$  are the same as in eq 1. Diffraction is best observed when the spacing of the grating ( $d$ ) is similar in size to the wavelength of radiation. This means that for molecular crystals, where the lattice spacings are on the order of a few tenths of nanometers, X-ray radiation is required to observe a diffraction pattern. As the latex spheres used in this experiment are on the micrometer-scale, it is best to use radiation with a wavelength of  $\sim 1 \mu\text{m}$ . Visible light from a red diode laser or a helium-neon laser is ideally suited for generating diffraction patterns from these crystals.

Whereas the diffraction pattern from a regular diffraction grating is a single row of spots corresponding to different orders of diffraction, the diffraction pattern from a two-dimensional crystal is more complicated because there are multiple ways that the crystal acts as a diffraction grating. Each of these ways is due to a set of lattice planes (although, technically, in the two-dimensional case they should be called lattice lines). Some of the lattice planes that give rise to diffraction spots observed in this experiment are illustrated in Figure 2. By analyzing the angle between the incident beam and these spots, it is possible to use eq 2 to determine the spacings between the planes ( $d$ ) and

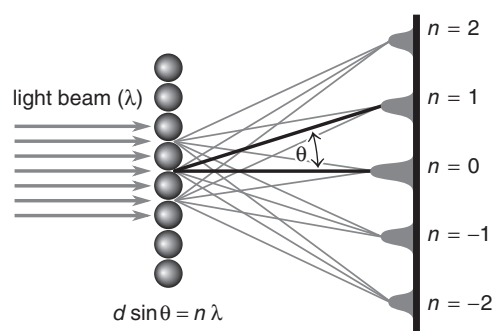


Figure 1. A monolayer of spheres diffracts a beam of coherent monochromatic light in a manner similar to a diffraction grating. Note that each sphere shown in the figure represents a whole row of spheres perpendicular to the plane of the page. The right side of the figure represents the light intensity as a function of  $\theta$ .

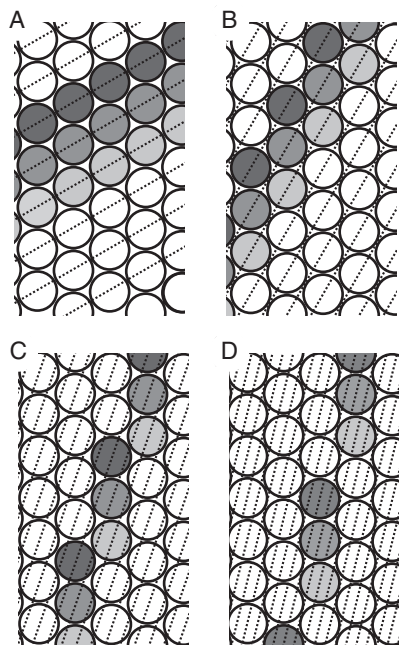


Figure 2. Dotted lines indicate lattice planes (i.e., some of the ways that the hexagonal lattice formed by the spheres can act as a diffraction grating). The spacing of the planes decreases from (A) to (D); shading indicate spheres along three of the planes. For the planes shown in (A) there are two additional sets of planes with the same spacing at  $120^\circ$  and  $240^\circ$  to the planes shown, reflecting the three-fold symmetry of the crystal; the Miller indices for the three sets of planes are (10), (01), and (11). Likewise, there are two additional sets of planes with the same spacing at  $120^\circ$  and  $240^\circ$  to the planes shown in (B); the three sets have Miller indices (12), (21), and (1 $\bar{1}$ ). For (C) there are six sets of lattice planes with identical values for the spacing. Three of these are at  $120^\circ$  increments with respect to one another and have Miller indices (1 $\bar{2}$ ), (31), and (23). The other group of three are rotated by  $\sim 38^\circ$  with respect to the first three sets of planes and have Miller indices (2 $\bar{1}$ ), (13), and (32). Like (C), there are six sets of lattice planes with identical values for the spacing shown in (D). The three with Miller indices (1 $\bar{3}$ ), (41), and (34) are at intervals of  $120^\circ$ . The other three, with Miller indices (3 $\bar{1}$ ), (43), and (14), are also at intervals of  $120^\circ$  but offset by  $\sim 32^\circ$  with respect to the first three sets of planes.

then, as explained in the following, relate this to the diameter of the spheres ( $D$ ). A more extensive theory describing the diffraction patterns generated by two-dimensional crystals of spherical objects is provided by Krieger and O'Neill (4). Although Krieger and O'Neill suggested the use of such crystals for a student laboratory experiment, the only procedure published for undergraduate education (5) lacks instructions for interpreting the results. The diffraction patterns observed in this experiment are similar to ones that can be produced using two-dimensional micrometer-scale patterns, such as the slides available through the Institute for Chemical Education (6).

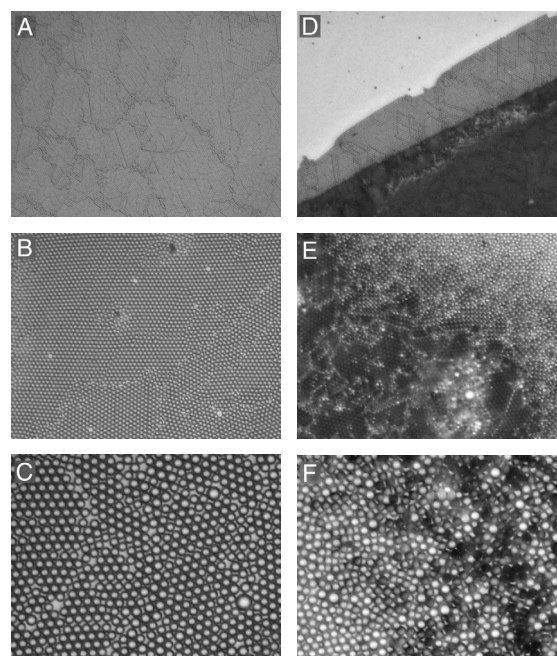


Figure 3. Images of latex sphere crystals acquired using a compound optical microscope. All images were acquired with the same level of magnification. From top to bottom, the images are of samples made using  $0.99\ \mu\text{m}$  (A, D),  $2.13\ \mu\text{m}$  (B, E), and  $5.2\ \mu\text{m}$  (C, F) spheres. The images on the left (A–C) illustrate monolayer regions. The images of the right (D–F) show transitions between monolayer (light gray) and multilayer (dark gray) regions of the samples. The inferior polydispersity of the  $5.2\ \mu\text{m}$  sample relative to the other samples is visually apparent in (C).

## Overview of the Experiment

To make two-dimensional latex crystals, students place a drop of latex solution on a glass slide and then smear the drop using a glass rod. For our experiments, we use 8% (in water) solutions of  $0.99$ ,  $2.13$ , or  $5.2\ \mu\text{m}$  sulfate latex spheres from Interfacial Dynamics Corporation (Eugene, OR). As the solvent evaporates, the spheres pack together to form crystalline domains and students can observe this process in real time using an optical microscope. Figure 3 shows images for three different sizes of latex spheres ( $0.99\ \mu\text{m}$  on the top,  $2.13\ \mu\text{m}$  in the center, and  $5.2\ \mu\text{m}$  on the bottom) that we acquired using a compound optical microscope. The images on the left (A–C) illustrate monolayer regions; the inferior polydispersity of the  $5.2\ \mu\text{m}$  sample relative to the other samples is visually apparent. The images on the right (D–F) show transitions between monolayer (light gray) and multilayer (dark gray) regions of the samples.

Microscopes are not necessary to proceed with the experiment; in fact, heating due to the microscope light speeds the evaporation of the solvent and typically results in lower-quality crystals. However, watching a few of the samples crystallize helps demonstrate the process by which a solution becomes an ordered crystal and is the favorite part of the experiment for most students. Typically, samples are dry and ready to analyze

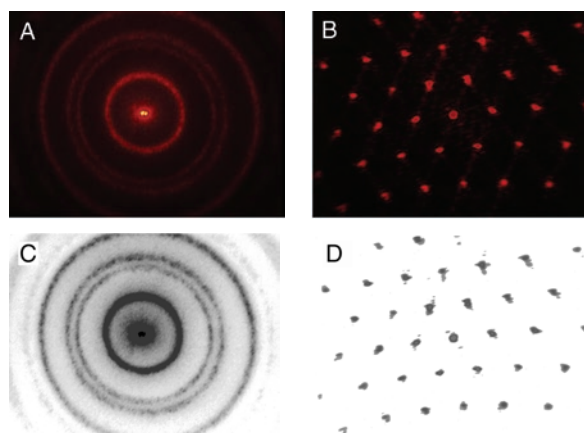


Figure 4. Representative powder (A, C) and single-crystal (B, D) diffraction patterns from a crystalline monolayer region of 2.13  $\mu\text{m}$  latex spheres. The top row shows photographs captured by a student using a digital camera (Olympus C60); the images in the bottom row are the same as the top row except for inversion and contrast-enhancement to better illustrate faint rings and spots in the patterns.

after only a few minutes; good quality samples are identifiable by their iridescent sheen. Placing the samples in a refrigerator as they dry will usually result in larger crystalline domains as this slows the evaporation of the solvent.

After a number of samples have been prepared, the students take their samples to a windowless room where they will collect the diffraction patterns. The students place a sample between a laser and a large expanse of white wall (which serves as the backdrop for the diffraction patterns). Typically, there is about 0.5 m between the laser and the slide, and 1 m between the slide and wall, but smaller or larger distances can easily be used. Our students use helium–neon lasers (4 mW, 632.8 nm light), but diode lasers (i.e., most laser pointers) work equally well as a light source. Care should be taken so that the laser beam is normal to the slide as the diffraction patterns that result from off-angle illumination are more complicated to analyze (see ref 4 for a mathematical treatment).

Once the sample is illuminated with the laser beam, the students move the slide around until the beam strikes a crystalline region of the sample. Typically, the beam is wide enough that it strikes a number of crystalline domains at the same time. The superposition of the resulting diffraction patterns leads to a powder pattern like the one shown in Figure 4A. To obtain a diffraction pattern for a single crystalline domain it is usually necessary to focus the laser beam. To focus the beam, students are asked to place a lens between the laser and the sample. We typically use a concave lens, but any positive (converging) lens will work. Some adjustment is usually necessary so that the sample is at the focal point of the lens and that only a single domain is illuminated; once achieved, a crystal diffraction pattern like the one shown in Figure 4B can be obtained. The three-fold symmetry of this pattern results from the hexagonal lattice formed by the latex spheres. Students are then asked to measure the distance between the center spot and the slide as well as the distances between the center spot and the other spots.

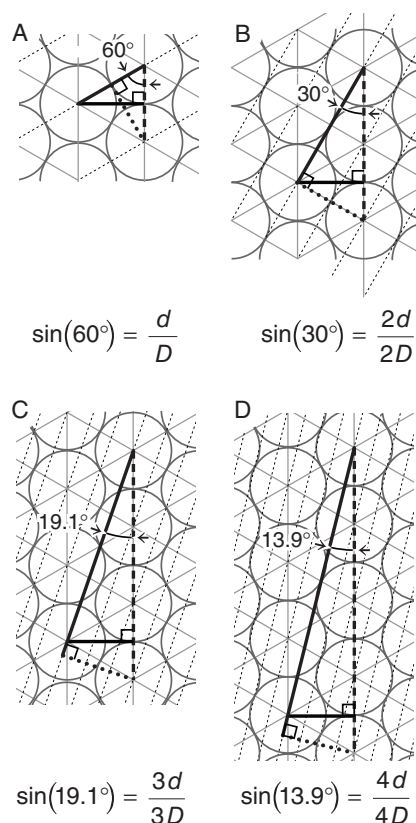


Figure 5. Geometric constructions for relating the spacings,  $d$ , between lattice planes (shown as dotted lines) to the latex sphere diameter,  $D$ . The constructions (A–D) correspond to the lattice planes illustrated in Figure 2. The side of the triangle that corresponds to a multiple of  $d$  is shown as a thick dotted line; the side of the triangle corresponding to an integer multiple of  $D$  is shown as a thick dashed line.

## Hazards

The degree of danger from the light source in this experiment will depend on the class of laser used. In any case, students should be instructed on laser safety to avoid the possibility of eye damage.

## Results and Discussion

Using trigonometry, students are asked to relate the distances that they measured to the angle of diffraction ( $\theta$ ) for each spot. Then, by noting the wavelength of the laser ( $\lambda$ ) and the diffraction order ( $n$ ), students can use eq 2 to determine the spacing ( $d$ ) corresponding to each diffraction spot. Owing to the inverse relationship between  $d$  and  $\theta$ , smaller latex spheres have smaller values of  $d$  and, consequently, larger values of  $\theta$  are observed in the diffraction pattern.

The final step for the students is to relate their several values of  $d$  for a single sample to the average diameter of the latex spheres ( $D$ ). We provide our students with triangular graph paper to

help them work out the trigonometric relationships involved in this conversion (a sheet of this graph paper is included with the online supplement). Usually, our students are able to determine the relationships for the lattice planes shown in Figures 2A and 2B, but run into difficulty for planes with smaller values of  $d$ . Figure 5 illustrates a series of trigonometric constructions that can be used to analyze the data; the use of these constructions is more thoroughly explained in the online supplement.

Our students' data usually agree with the sphere diameters specified by the manufacturer to within one or two percent; larger errors are often due to mistakes in the analysis or because the laser beam was not perpendicular to the plane of the sample.

## Conclusion

By using a simplified crystallographic system, this experiment allows undergraduate students to form crystals of latex spheres, generate diffraction patterns, and then analyze the patterns to determine the size of the spheres within the time-constraints of one or two laboratory periods. This allows us to instruct our students in the fundamentals of crystallography while avoiding the difficulties associated with X-ray diffraction-based experiments.

## Acknowledgment

The authors would like to thank Michael Broide (Lewis & Clark College Physics Department) for his advice and encouragement.

## Literature Cited

1. Perrin, Jean B. *Ann. Chim. Phys.* **1909**, *18*, 5–113.
2. Denkov, Nikolai D.; Velev, Orlin D.; Kralchevsky, Peter A.; Ivanov, Ivan B.; Yoshimura, Hideyuki; Nagayama, Kuniaki. *Langmuir* **1992**, *8*, 3183–3190.
3. Parker, Greg J.; Charlton, Martin D. B. *Physics World*, **2000**, *August*, 29–34.
4. Krieger, Irvin M.; O'Neill, Francis M. J. *Am. Chem. Soc.* **1968**, *90*, 3114–3120.
5. Zare, Richard N.; Spencer, Bertrand H.; Springer, Dwight S. *Laser Experiments for Beginners*; University Science Books: Sausalito, CA, 1995; pp 97–99.
6. Institute for Chemical Education Science Kits. <http://ice.chem.wisc.edu/catalogitems/ScienceKits.htm#OpticalTransforms> (accessed Sep 2007).

## Supporting JCE Online Material

<http://www.jce.divched.org/Journal/Issues/2008/Jan/abs93.html>

Abstract and keywords

Full text (PDF)

Links to cited URLs

Color figure

Supplement

Detailed instructions for students

Detailed explanation of the geometric constructions shown in Figure 5

This experiment is featured on the cover of this issue.

See page 3 of the table of contents for a detailed description of the cover.

