Using Two-Dimensional Colloidal Crystals to Understand Crystallography

Instructor Notes

Geometric Constructions

The geometric constructions that can be used to relate the spacings of the lattice planes \((d)\) to the diameter of the latex spheres \((D)\) are reproduced in Figure 1. Note that the value of \(D\) is the same in all figures, but \(d\) decreases from Figure 1a to 1d. In all four parts of Figure 1, the red (horizontal) line has a length of \(\left(\frac{\sqrt{3}}{2}\right) \times D\).

To determine the angle between the green and purple lines we need to consider the right triangle bounded by the green, red, and purple lines. For example, in Figure 1c the side of this triangle represented by the green line has a length of \(\left(\frac{5}{2}\right) \times D\), so the angle \(\phi\) between the purple and green lines is defined by:

\[
\tan \phi = \frac{\left(\frac{\sqrt{3}}{2}\right) \times D}{\left(\frac{5}{2}\right) \times D} \quad \rightarrow \quad \phi = \arctan\left(\frac{\sqrt{3}}{5}\right)
\]

Solving for \(\phi\) results in an angle of 19.1°, as indicated in the figure.

Next, we need to find a way to relate \(\phi\), \(d\), and \(D\). The right triangle bounded by the purple, green, and blue lines shares the same angle \(\phi\) with the triangle that we previously considered. The side of the triangle bounded by the green line has a length of \(3 \times D\), and the side bounded by the blue line has a length of \(3 \times d\). Therefore, the relationship between \(d\) and \(D\) is:

\[
\sin \phi = \frac{3 \times d}{3 \times D} \quad \rightarrow \quad D = \frac{d}{\sin (19.1^\circ)}
\]

Similar reasoning can be used to establish the angles and trigonometric relationships shown in Figure 1a, 1b, and 1d.
Figure 1: Geometric constructions for relating the spacings ($d$) between lattice planes (shown as dotted lines) to the latex sphere diameter ($D$).

\[
\sin 60^\circ = \frac{d}{D} \quad \sin 30^\circ = \frac{2d}{2D} \quad \sin 19.1^\circ = \frac{3d}{3D} \quad \sin 13.9^\circ = \frac{4d}{4D}
\]
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Instructions for Students

Introduction

The wave-like properties of electromagnetic radiation are especially apparent when the radiation interacts with objects that are similar in size to the wavelength of the radiation. One result of this interaction is diffraction, which plays a role in everything from rainbows to x-ray crystallography. If the object that the radiation interacts with is regularly spaced, the resulting pattern of diffraction will also have regularities. By analyzing such a diffraction pattern, it is often possible to work backwards to deduce the structure of the object. The most common example of this is in crystallography, where the patterns that result from the diffraction of electromagnetic radiation by a crystal provides structural information about the objects that make up the crystal.

X-rays are usually used for crystal diffraction experiments because, to observe a high-quality diffraction pattern of a molecular crystal, the wavelength of the radiation needs to be similar in magnitude to the spacing of the atoms...i.e., on the order of 0.1 nm (1 Å). One complication in x-ray crystal diffraction is that the information provided by the diffraction pattern is incomplete. Therefore, to work out the structure of a complicated sample, such as a protein crystal, a certain amount of chemical intuition and molecular modeling is required to deduce which structure is consistent with the diffraction pattern.

Typically, crystallography involves the observation of the diffraction patterns of three-dimensional crystals, but it is also possible to collect diffraction patterns from two-dimensional crystals. As the name implies, two-dimensional crystals are ordered in only two dimensions, and their diffraction patterns are easier to analyze than three-dimensional crystals. Two-dimensional crystals often arise when working with thin-films having only a single monolayer of particles, but can also arise in systems such as liquid crystals or concentrated samples of proteins embedded in a cell membrane.
Usually, when chemists use the word ‘crystal’, they are referring to molecular crystals. As the name implies, molecular crystals are orderly arrays of individual molecules. However, crystals can also be formed from larger building blocks. For example, colloidal solutions of micrometer-sized latex spheres can form two- and three-dimensional crystals, as can lyotropic liquid-crystals and metal nanoparticles. Like molecular crystals, colloidal crystals self-assemble and diffract electromagnetic radiation. Whereas x-ray radiation is usually required to observe diffraction from molecular crystals, the larger particles that make up colloidal crystals allow the use of longer wavelength radiation to observe diffraction. The optimal wavelength for observing diffraction from colloidal crystals can be anywhere from a few nanometers to a few microns depending on the size of the particles that make up the crystal.

In this experiment, you will observe the diffraction pattern from a two-dimensional colloidal crystal and then use this information to determine the size of the objects that constitute the crystal. Your sample for this experiment will be a thin film of latex spheres. As the spheres that you will use are on the order of a few microns in diameter, we can use visible light from a helium-neon laser ($\lambda = 0.6328 \, \mu\text{m}$) to acquire a diffraction pattern from your samples.

**Background**

**Bragg’s Law**

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

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

where $n$ is the diffraction order (an integer), $\lambda$ is the wavelength of the radiation, $d$ is the spacing of the scattering planes, and $\theta$ is the angle between the incident beam of radiation and the scattering 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:

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

where $n$, $\lambda$, $d$, and $\theta$ are defined in the same way as in Equation 1. Equation 2 also describes the diffraction pattern produced by one-dimensional diffraction gratings like the ones that you may have encountered in physics experiments (and which produce the same intensity pattern as that shown in Figure 1). The difference between these equations is that the first describes situations where we consider light that reflects from the sample, whereas the second equation describes the situation where the light passes straight through the sample... this is why the equations differ by a factor of two. This is also why the spots in a diffraction pattern are sometimes referred to as reflections. The complication to understanding the diffraction patterns that result from two-dimensional (as well as three-dimensional) crystals is that the
pattern shown in Figure 1 is only one of many ways that a two-dimensional crystal will behave as a diffraction grating.

Consider walking through an apple orchard where the trees have been carefully planted at regular intervals. If we look directly down a row, the apple trees will obviously be in lines, but there are also diagonals for which the apple trees appear to be in lines. A similar effect can be observed when driving by a cornfield. There are multiple angles at which you can see straight down a line of corn stalks and, therefore, as you drive past, you can observe different glimpses down the rows as your angle relative to the field changes. Likewise, for a two-dimensional crystal there are multiple ways that the particles ‘line-up’. In crystallography, each of the ways that particles line-up is referred to as a set of lattice planes or crystallographic planes. Technically, for a two-dimensional system we probably should call these ‘lattice lines’ instead of ‘lattice planes’. However, to keep the nomenclature the same as in the three-dimensional case (where the particles do actually line up along planes), we will continue to use the term planes.

Each set of lattice planes in a crystal contributes a row of spots to the diffraction pattern. As the sets of lattice planes are at different angles and/or have different spacings ($d$ in Equations 1 and 2), there will be multiple rows of spots in the diffraction patterns for a two-dimensional crystal that are at different distances from the center spot and rotated with respect to one another. For example, the top-left of Figure 2 shows a number of circles that are meant to represent the hexagonal packing of the latex sphere samples that you will investigate. The dashed vertical lines represent one set of lattice planes; the spacing between these planes is $d$ in Equation 2. This set of planes will lead to the diffraction pattern shown on the bottom-left of Figure 2. Of course, this is not the only way that the crystal diffracts light. Represented
Figure 2: Each set of lattice planes results in a different set of diffraction spots. In this figure, three sets of lattice planes are illustrated as dashed lines. All three sets happen to have the same value of $d$, but are rotated by 120° with respect to one another. The shading is only to help illustrate the lattice planes and does not indicate anything special about the shaded spheres. As the lattice planes have the same value of $d$, the resulting diffraction patterns look the same but are rotated with respect to one another by 120°. As all of these lattice planes diffract light simultaneously in an experiment, the experimental diffraction pattern will look more like the pattern shown at the bottom-right.

In the middle of Figure 2 are two other sets of lattice planes. These sets happen to have the same value for $d$ but are rotated by 120° with respect to one another and, consequently, lead to diffraction patterns with spots that appear at the same values of $\theta$ but are rotated by 120°. As all of these sets of lattice planes act as diffraction gratings simultaneously in an experiment, the diffraction pattern that you actually will see will be a superposition of the individual diffraction patterns, as shown at the bottom-right of Figure 2.

There are a number of additional sets of lattice planes that contribute to the diffraction pattern; a few of these are illustrated in Figure 3. Note that the lattice spacing ($d$) is different for each of these sets of planes; the lattice planes shown on the left of the figure have the largest value of $d$ and those on the right have the smallest value. These additional lattice planes (as well as many more with even smaller values of $d$) contribute additional spots to the diffraction pattern and, therefore, the resulting pattern will be much more complicated than the pattern shown at the bottom-right of Figure 2. Note that smaller values of $d$ result in spots that are at larger values of $\theta$, so additional spots from lattice planes with smaller of $d$ will appear further away from the center of the diffraction pattern.
Figure 3: The dotted lines in (a–d) indicate lattice planes (i.e., some of the ways that a two-dimensional hexagonal lattice can act as a diffraction grating). The shading is only to help illustrate the lattice planes and does not indicate anything special about the shaded spheres. The spots in the diffraction pattern that results from the planes shown in (b) will reflect a smaller spacing (d) than those shown in (a). Likewise, the spacing for the planes shown in (c) are smaller than in (b), and the spacing for the planes shown in (d) are even smaller. Note that for (a) and (b), there are equivalent sets of planes at 120° and 240° with respect to the set shown due to the three-fold symmetry of the crystal. For both (c) and (d) there are five additional sets of equivalent planes in addition to the set shown.

**Unit Cells and Miller Indices**

At this point, you have all the background that you need to know for completing the experiment. However, for communicating results we need to come up with a system for describing the lattice planes of the sample. Although we can draw the various lattice planes when reporting results, all of this illustration work will rapidly becomes cumbersome. Wouldn’t it be easier if there was a shorthand for labeling the lattice planes? Such a shorthand (of course) already exists for systematically labeling lattice planes. These labels are called *Miller indices* and can be easily understood once we define the *unit cell* for our two-dimensional crystal of latex spheres.

The *unit cell* is the smallest repeating unit that describes the crystal lattice. For our hexagonal crystals of identical latex spheres, the only requirements for drawing a unit cell are that the unit cell contains a single latex sphere inside of it (or parts of spheres that add up to a single latex sphere) and that it is a shape that we can tile. Otherwise, the choice of unit cell is somewhat arbitrary. One consequence of these requirements for the unit cell is that all valid unit cells for a crystal have the exact same area (or volume, in the case of a three-dimensional crystal). Figure 4 illustrates a few of the infinite number of unit cells that we can use to describe our crystals of latex spheres. Although any of these unit cells can be used, some are easier to work with than others. First, parallelograms are easier to work with than hexagons, so we will use one of the unit cells illustrated in the top row of Figure 4.
Second, it is conventional to use the unit cell that minimizes the perimeter, so of the four unit cells shown in the top row of Figure 4, we will use the unit cell shown in Figure 4a.

Although the choice of unit cell is mathematically arbitrary, for reporting results it is important to use the conventional unit cell for a given crystal packing (or, otherwise, to carefully specify your choice of unit cell). This is because the values of the Miller indices depend on the choice of unit cell. The lattice planes for a crystal will be the same regardless of our choice of unit cell, but which Miller indices corresponds to which plane depends on which unit cell we choose to describe our system. For two-dimensional hexagonal lattices, like the ones that you will encounter in this experiment, the unit cell conventionally used is the one shown in Figure 4a, as explained in the preceding paragraph.

Mathematically, any two vectors that are not co-linear can be used as the coordinate system for a two-dimensional system (i.e., the axes). In many situations the most convenient way to define the coordinate system is to use two vectors that are 90° apart from one another, such as the x and y axes that are commonly used for drawing graphs. In crystallography, however, the sides of the unit cell are used to define the coordinate system (i.e., the crystallographic axes) for the sample. Consequently, the axes of the coordinate system are not necessarily 90° apart. Figure 5a illustrates the axes appropriate for our choice of unit cell. We will label these axes x’ and y’. The length of the unit cell along the x’-axis is a and along the y’-axis is b; the
Figure 5: The first figure (a) shows the coordinate system used for our unit cell, the tick marks are spaced in units of $a$ along the $x'$-axis and in units of $b$ along the $y'$-axis. The labels in (b–d) indicate where the lattice lines (indicated by dotted lines) intersect the $x'$- and $y'$-axes; these labels are not the Miller indices. Rather, the inverse of these intersection points define the Miller indices as explained in the text. The set of planes in (b) correspond to the Miller index $(01)$, the set of planes in (c) correspond to $(1\bar{1})$, and the set of planes in (d) correspond to $(2\bar{1})$.

tick marks along the axes are in units of $a$ and $b$. For our unit cell it happens to be the case that $a = b$, but this is not generally true of other unit cells.

To determine the Miller index for a set of lattice planes, we just need to determine where the planes intersect the axes and then take the reciprocal of these values. For example, Figure 5b shows the same set of lattice planes as in Figure 3a. The planes are labeled according to where they intersect the $x'$- and $y'$-axes (in units of $a$ and $b$). Planes that are parallel to an axis never intersect it, which is denoted by using the symbol for infinity ($\infty$). The Miller
indices are derived by taking the reciprocal of intersection points, so the plane that intersects that \( x' \)-axis at \( \infty \) and the \( y' \)-axis at 1 has the Miller index \( \left( \frac{1}{\infty} \frac{1}{1} \right) = (01) \). By convention, no comma is used between the numbers in the Miller index. Note that for three-dimensional crystals a third value needs to be included in the Miller index to indicate the reciprocal of the intersection of the plane with the \( z' \)-axis.

There are a few caveats to determining the Miller index for a plane. First, we cannot take the reciprocal of 0 as \( \frac{1}{0} \) is mathematically undefined, so there is no way to derive the Miller index for a set of planes by using a plane that passes through the origin (i.e., through (0,0)). Instead, use any of the other planes in the set. Second, the Miller index is always specified in whole numbers. If we end up with fractions when we take the reciprocal, then we need to multiply by the least common multiple of the denominators to make everything whole. In addition, if possible, we try to express the numbers as positive integers. For example, the plane that intersects the axes at \( \infty \) and 2 has the index \( \left( \frac{1}{\infty} \frac{1}{2} \right) = (0\frac{1}{2}) \). The least common multiple in this case is 2, so after multiplying through by 2, we arrive at an index of (01). Likewise, the plane that intersects the axes at \( \infty \) and \(-3 \) has the index \( \left( \frac{1}{\infty} \frac{1}{3} \right) = (0\frac{1}{3}) \). This time, we multiply through by \(-3 \), which leaves us with the index (01). At this point, you may have realized that the Miller index for all of the planes in Figure 5b is (01). This is one reason why Miller indices are convenient; they allow us to specify an entire set of planes using a single index.

A slightly more complicated case is shown in Figure 5c. Taking the plane that intersects the axes at 1 and \(-1 \), we find the Miller index \( \left( \frac{1}{1} \frac{1}{-1} \right) = (1 - 1) \). In this case, we are stuck with one of the values in the index being negative, as multiplying by \(-1 \) will still leave us with an index where one of the values is negative. By convention, negative values are denoted by putting a bar over the number, so \( (1 - 1) \) becomes the Miller index \( (1\overline{1}) \). As in the previous case, deriving the Miller index using other planes shows that all of the planes in Figure 5c share the index (1\overline{1}). Likewise, all of the planes in Figure 5d are described by the Miller index (21).

**Symmetry-Related Miller Indices**

Let us go back and look again at Figure 2. This figure shows how three symmetry-related sets of planes produce symmetrical spots in the diffraction pattern. One of the three sets of planes corresponds to the Miller index (01). A bit of work reveals that the Miller indices for the other two sets of planes are (10) and (11). These three sets of lattice planes have the same value for the spacing \( d \) and are symmetry related by a 120° rotation. As was explained earlier, these planes give rise to identical looking sets of spots that are related by a 120° rotation about the center of the diffraction pattern. Due to their symmetry relationship, we can group the (01), (10), and (11) planes together into a single group called the (01) planes. Note the use of curly braces, which are used to indicate that we are now talking about a group of symmetry-related sets of planes.
Higher-Order Diffraction and Modern Crystallography: Figure 1 Revisited

In Equations 1 and 2, as well as in Figure 1, the symbol \( n \) was used to denote the order of diffraction. However, the convention in modern crystallography is that the value of \( n \) is absorbed into the Miller indices (and there, into \( d \)) so that the diffraction equation is:

\[
\lambda = d \sin \theta
\]

Instead of referring to things as higher order spots, the convention is to instead consider them to arise from ‘higher-order’ lattice planes. For example, Figure 1 shows a series of spots with order 0, 1, 2, 3, \ldots, arising from the (10) planes. The modern convention is to consider these spots as first order \( (n = 1) \) and arising from the (10), (20), (30), \ldots, lattice planes. The (20) planes are parallel to the (10) planes, but are spaced at half the interval, so \( d \) for the (20) planes is exactly half of \( d \) for the (10) planes. Likewise, there are three (30) planes for every (10) plane, four (40) planes for every (10) plane, and so on. As the ‘higher-order’ planes have smaller values of \( d \), they produce spots with larger values of \( \theta \), as we would expect based on Equation 2.

This convention of absorbing the diffraction order into the Miller indices seems counter-intuitive, as the ‘higher-order’ planes do not represent rational lattice planes. That is, if you draw a diagram with the ‘higher-order’ planes you will observe that many of the planes do not intersect any of the objects in the sample. If we go back to the apple orchard analogy, this would be like imagining additional rows of apple trees in between the rows of trees that are actually there! The utility of this convention appears when working through the mathematics of crystal diffraction for systems more complicated than the one that we will investigate in this experiment. In addition, this convention makes it more convenient to label diffraction patterns and to keep track of which spot is which. Instead of labeling things as the “first order spot from the (10) planes”, the “second order spot from the (10) planes”, etc., we can instead label the spots as “10”, “20”, etc. Note that when referring to planes we include parentheses but when referring to spots (reflections) we do not use the parentheses. Figure 6 illustrates how Figure 1 can be relabeled using this convention.

Safety

In this experiment you will be working with helium-neon lasers. The lasers that we will use are powerful enough to damage your eyes in only a few seconds, so you must never look directly into them. You should wear laser safety goggles when you work with the laser beam, particularly when aligning. In order to see the diffraction patterns, you will need to remove the safety goggles; when you do this, be extremely cautious!

With or without goggles on, you must remove all metal objects from your hands (rings, bracelets, watches, etc.) before working with the laser. Otherwise, there is a risk that the laser beam will be reflected into somebody’s eyes. Finally, you must be very careful when you bend over (for example, to pick something up from the floor). This is because we will
Figure 6: Schematic showing some of the diffraction spots arising from the \{10\} planes. Note that this figure is the same as Figure 1 except that the diffraction spots have been relabeled. The center spot \( n = 0 \) is always referred to as the (00) spot and arises from light that passes straight through the crystal.

setup the laser on a table at waist level; anytime you bend over your eyes will pass through the same plane as the laser beam increasing the risk of the beam hitting your eyes.

The latex samples used for the experiment are non-toxic and can be washed down the sink when you are finished with them.

**Procedure**

**Thin-Film Construction**

Put a small drop of one of the latex sphere solutions onto a glass plate. Carefully smear this drop with a glass stirring rod, and then allow the sample to dry. It is important to make the film as thin as possible so that you will end up with a monolayer of latex spheres. It is highly unlikely that this procedure will result in a uniform monolayer for the entire sample. Fortunately, you only need a small region of the sample to form a monolayer of latex spheres in order to get reasonable results. As the sample dries, place it under a microscope and record your observations. You should be able to see the individual latex spheres packing together as the solvent evaporates. Repeat this procedure until you have samples of three sizes of latex spheres. Also, note that one way to identify ‘good’ samples is that they have an iridescent sheen.

If you have trouble obtaining large crystalline regions on your slides (which is often the case for the smaller spheres), try varying the conditions. You might want to consider adding solvent, changing the ionic strength of the solution, or drying the slides more slowly \( \text{i.e.,} \) do not leave them under the microscope light and/or place them in a refrigerator. The latex spheres that we are using are coated with anionic sulfate groups, so they will have a net
negative charge. Try making predictions about how different counterions will affect the way that the spheres interact as they crystallize, and then try them out.

**Powder Diffraction**

Once your samples have dried, take them to a windowless room. Use a clamp to hold one of your slides vertically and place it in front of a helium-neon laser. Arrange your experimental setup so that the pattern formed by passing the beam through your sample will be projected onto a flat wall. Be sure that the laser beam is perpendicular to the slide; otherwise, your data will have to be analyzed using a more complicated theory than what is presented in this procedure. Make sure everything is aligned properly, switch on the laser, and then shut off the room lights. If the laser beam passes through a thin domain of the sample where only a monolayer of spheres is present, you should observe a set of concentric rings (or, if you are very lucky, a hexagonal pattern of spots). If you have trouble finding such a domain, try moving the sample so that the beam passes through an edge of the sample (the edges are more likely to have orderly monolayers from which you can get reasonable diffraction patterns). Once you have found a pattern, sketch it in your laboratory notebook.

The pattern of rings that you observe is called a powder diffraction pattern, and results from the relatively wide laser beam passing through a number of neighboring crystalline regions of the sample. Other names for these regions include domains or crystallites. Each domain diffracts the beam into a pattern of spots but, since each domain is oriented differently than the others, the orientation of the spots from each domain is different. The resulting powder diffraction pattern is due to the overlap of all of these differently oriented diffraction patterns. The name ‘powder pattern’ arises from x-ray crystallography where this sort of a pattern is observed from samples consisting of powders of tiny crystals.

**Single-Crystal Diffraction**

Next, place a lens between the laser and the sample. Adjust the position of the lens until the laser beam is focused on the sample. Next, move the sample around perpendicularly to the beam until the beam passes through a single crystalline domain of the sample. When this occurs, you will see a symmetrical pattern of spots on the wall. If you move the sample around, you should be able to find other domains that produce the same pattern of spots, but rotated. If the laser beam is right on the boundary of different domains, you may see two or three superimposed diffraction pattern with different relative angles. Adding together a large number of diffraction patterns from the individual domains results in a powder pattern like the one you probably observed in the previous part of this experiment.

Once you have found a region of the sample that produces a nice diffraction pattern, fix the position of the laser, lens, and sample. Measure the distance from the sample to the central spot on the wall. Next, measure the distances from the central spot to each of the other spots in the diffraction pattern. Then, use trigonometry to relate the distances to the angle of
diffraction ($\theta$) for each spot. Along with the distances, you should also note the symmetry of the diffraction pattern as this has a direct relationship with how the latex spheres are packed together. Finally, make sure that you make a sketch of the diffraction pattern in your lab notebook. Repeat this procedure with samples made from different sizes of latex spheres.

**Report**

In your results, you should have a figure illustrating one of your diffraction patterns. In addition, you should have a table indicating the angles for the spots that you measured for each of your samples as well as the spacings ($d$) between the lattice planes to which these spots correspond. Then, with the help of a bit of trigonometry, use these spacings to determine the distance ($D$) between nearest-neighbor spheres (which will be the same as the diameter of the spheres). Use Miller indices to label your diffraction pattern figure as well as the data in your table.

The triangular graph paper (provided on the last page of this experiment description) is to help you determine the trigonometric identities that relate the various values of $d$ from different sets of planes to the single value of $D$ for each sample. First, imagine that a latex sphere is centered at each of the major intersections on the graph paper and then draw crystallographic planes like in Figure 3. Next, think about how the nearest-neighbor distances correspond to the spacing of the crystal planes. Note that all values of $d$ for a single sample should result in the same nearest-neighbor distance ($D$)! If they are not close to one another, check your method of calculation. The trigonometric relationships between the particle diameter and the spacings between crystallographic planes for some of the spots with smaller values of $d$ can be a bit tricky to derive. If you find yourself stuck, consult with your instructor.

Some questions to think about when putting together your results are:

1. What conditions resulted in the best crystals? Was the rate of evaporation, the ionic strength, or pH of the solution important?
2. Which latex sphere samples (larger or smaller) more readily formed crystals? Why do you think this was the case?
3. Are the particle diameters that you determined using different spots from the same diffraction pattern consistent with one another? Why or why not? If not, is there a systematic trend?
4. Think about the information that can be derived from a powder-diffraction pattern in comparison to a single-crystal diffraction pattern. What additional information can be deduced from a single-crystal diffraction pattern?