Crystallography Supplement for SoftMatter Submission
Jason M. McMullan and Norman J. Wagner

This document outlines, in greater detail, some of the steps taken for the crystallographic translations detailed in the SoftMatter submission "Directed Self-Assembly of Colloidal Crystals by Dielectrophoretic Ordering Observed with Small Angle Neutron Scattering (SANS)."

A representation of the crystalline plane group *p6mm* is shown in Figure 1. The real space structure is shown on the left and on the right is the simulated scattering pattern created from the inversion of the crystalline basis vectors as detailed in Warren[1]. The interplanar spacings d_a and d_b are equal and translate to scattering vectors q_a and q_b by the relation $q_{hkl} = 2\pi / d_{hkl}$. For the hexagonal lattice of the *p6mm* plane group the inversion is straight forward and results in a scattering pattern offset from the real space structure by 90°.
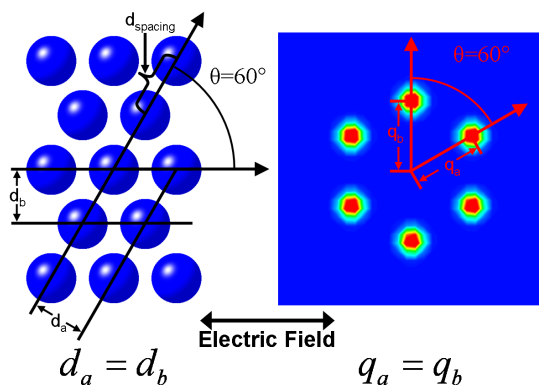

Figure 1. Real space crystalline structure (left) and simulated scattering pattern (right) for the *p6mm* plane group.

The shortest interparticle distance in the crystal, $d_{crystal}$, is the same for all three crystal directions and follows the relation of

$$\frac{d_{hkl}}{d_{crystal}} = \sin(2*60) = \sin(60)$$

which is labeled as $d_{spacing}$ in the figure. This relation is shown below in greater detail.

The inversion of a stretched lattice from the *c2mm* plane group is slightly different. A real space lattice is shown in Figure 2 with an angle $\theta=55°$. The four outer scattering points are shifted to an angle of 55° and all share a constant q value, q_c. The two points in the vertical direction shift to a higher q value, q_d, which indicates a smaller interplanar separation, d_d, that is normal to the scattering vector, q_d.
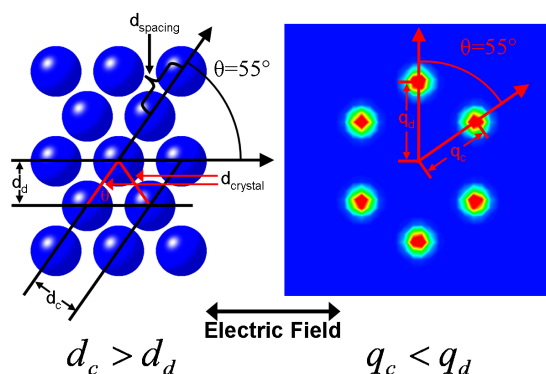
$$d_c > d_d \qquad\qquad q_c < q_d$$

Figure 2. Real space crystalline structure (left) and simulated scattering pattern (right) for the *c2mm* plane group.

When the angle is decreased, in the *c2mm* plane group as shown above in Figure 2, the smallest interparticle separation is now along two crystalline directions, indicated by the red lines labeled $d_{crystal}$ on the real space structure. The relation of the measured interplanar distance, d_{hkl}, to the shortest interparticle distance, $d_{crystal}$, is different for the three sets of planes examined. The three different planar sets are shown in Figure 3 with the two crystalline planes on the left and the compressed planar direction, named the chaining direction, on the right.
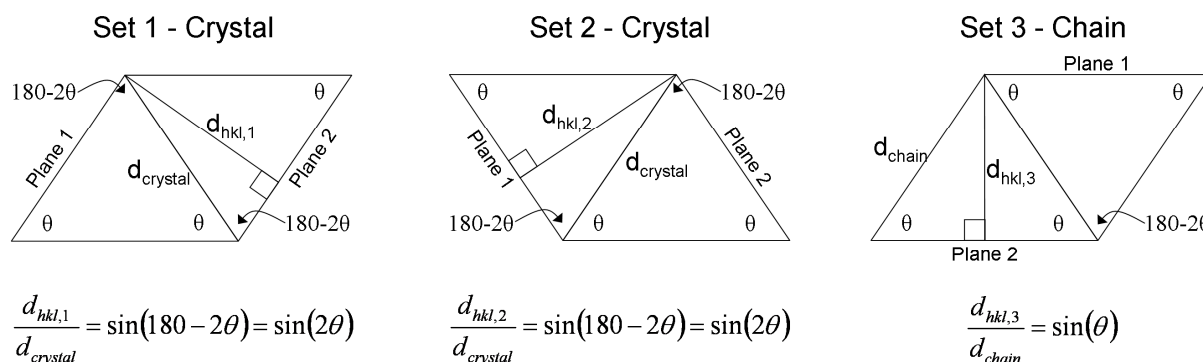

$$\frac{d_{hkl,1}}{d_{crystal}} = \sin(180 - 2\theta) = \sin(2\theta)$$

$$\frac{d_{hkl,2}}{d_{crystal}} = \sin(180 - 2\theta) = \sin(2\theta)$$

$$\frac{d_{hkl,3}}{d_{chain}} = \sin(\theta)$$

Figure 3. Geometric relations of d_{hkl} to $d_{crystal}$ for the three different planar sets (left and center) crystal and (right) chaining.

The geometric relation that shows that the shortest interparticle distance in the crystal, $d_{crystal}$, is defined as

$$\frac{d_{hkl,crystal}}{d_{crystal}} = \sin(2\theta)$$

when examining the two crystalline directions. When instead looking at the chaining planar spacing the relation becomes

$$\frac{d_{hkl,chain}}{d_{crystal}} = \sin(\theta)$$

which shows that $d_{crystal}$ can be measured with any crystal observation direction. The relation of the chaining and the crystal directions is shown in Figure 4.
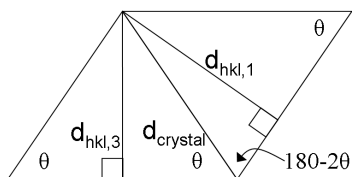
Figure 4. Relation of chaining and crystalline measurement directions.

References
1.   B. E. Warren, *X-Ray Diffraction*, Dover Publications Inc., 1969.