Simulated Structure Factors

Benjamin J. Coscia

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1 Calculation of the structure factor

The structure factor, S($\mathbf{q}$), relates the observed intensity per atom to that observed by a single scattering unit. Incident plane waves falling on a material have a wave vector, K_i, whose length is $\dfrac{2\pi}{\lambda}$, where λ is the wavelength. The diffracted wave vector, K_f, has the same length as K_i if the diffraction process is elastic. We will assume elasticity going forward. The scattering vector, $\mathbf{q}$ is defined as $K_f - K_i$. Since K_f and K_i are the same length, the scattering vector must lie on the surface of a sphere of radius $\dfrac{2\pi}{\lambda}$. This sphere is called the Ewald Sphere and diffraction will only occur for reciprocal lattice points that lie on its surface.

The amplitude and phase of the scattered waves is the vector sum of all scattered waves from all atoms:

$$\Psi_s(\mathbf{q}) = \sum_{j=1}^{N} f_j e^{-i\mathbf{q}\cdot\mathbf{R_j}} \tag{1}$$

where f_j is the atomic form factor of atom j and $\mathbf{R_j}$ is the position of the atom in real space. Note that Equation **??** is the definition of the discrete fourier transform.

The scattered intensity is obtained by multiplying Equation **??** by its complex conjugate:

$$I(\mathbf{q}) = \Psi_s(\mathbf{q}) \cdot \overline{\Psi_s}(\mathbf{q}) = \sum_{j=1}^{N} f_j e^{-i\mathbf{q}\cdot\mathbf{R_j}} \times \sum_{k=1}^{N} f_k e^{-i\mathbf{q}\cdot\mathbf{R_k}} = \sum_{j=1}^{N}\sum_{j=k}^{N} f_j f_k e^{-i\mathbf{q}\cdot(\mathbf{R_j}-\mathbf{R_k})} \tag{2}$$

Computationally, one should calculate the fourier transform of the atomic coordinates with a fast fourier transform, calculate its complex conjugate and multiply them together. The structure factor is typically normalized as $1/\sum_{j=1}^{N} f_j^2$ so that it is independent of system size, and the general equation for the structure factor becomes:

$$S(\mathbf{q}) = \frac{1}{\sum_{j=1}^{N} f_j^2} \sum_{j=1}^{N}\sum_{j=k}^{N} f_j f_k e^{-i\mathbf{q}\cdot(\mathbf{R_j}-\mathbf{R_k})} \tag{3}$$

If all atoms are identical, equation **??** simplifies to:

$$S(\mathbf{q}) = \frac{1}{N} \sum_{j=1}^{N}\sum_{j=k}^{N} e^{-i\mathbf{q}\cdot(\mathbf{R_j}-\mathbf{R_k})} \tag{4}$$

The atomic form factor, f_j is more complicated than how it is represented in Equation **??**. The atomic form factor is the scattering contribution from a single isolated atom. They are calculated as the fourier transform of the electron density, $\rho(\mathbf{r})$, which is typically calculated using quantum techniques. Since $\rho(\mathbf{r})$ is a spatially dependent function, f_j is actually a function of $\mathbf{q}$, $f(\mathbf{q})$. Values of $f(\mathbf{q})$ for each element are tabulated in the International Tables for Crystallography. For $\mathbf{q} = \mathbf{0}$, the atomic form factor is equal to the number of electrons possessed by the atom.

The resolution in each dimension of reciprocal space is determined by the size of the unit cell studied. In order to calculate the structure factor, the system's 3D coordinates must be discretized into regularly sampled points using a histogramming method. Applying equation **??** to the histogram will yield a grid with
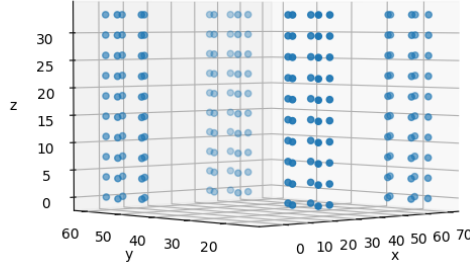
Figure 1

Fourier bin sizes of $\frac{2\pi}{L_i}$ (i = (x,y,z)). The fourier transform of an array of values returns a same length array of frequencies. Increasing the number of bins in the histogram will not change the size of the Fourier space bins, rather it will increase the maximum accessible value of q.

2 Structure factor of hexagonally packed columns

Here, we explore, in depth, a simplified model of an inverted hexagonal phase lyotropic liquid crystal (H_{II} LLC). The simplified model is meant to enhance our understanding of the structure factor of a fully atomistic model of the same material. We are primarily interested in the diffraction patterns produced by the head groups so we model each monomer as a point placed at the center of mass of its head group. The hexagonal phase is made up straight pore columns. Each pore column is composed of columns of stacked monomers which surround the pore's hydrophilic core. Based on simulation, there are likely 5 monomer columns making up each pore, and the pore radius is ca. 1 nm. Experimental WAXS suggests that monomers stack 3.7 Åapart, and SAXS measurements have shown that pores are spaced ca. 4.1 nm apart. Here we took the pore spacing to be 4.25 nm for no good reason. For consistency with simulation, we will look at 4 pores in a monoclinic unit cell with 5 monomer columns per pore.

We are interested in the intensity and dimensions of the R-π reflection, which is a consequence of monomers stacked on top of each other in the z-direction.

2.1 Crystalline liquid crystals

For a perfect, infinite crystal, the intensity of R-π is infinitely sharp. We created a model with perfectly aligned columns. Each columns originates at z=0 and all other points in the column are equally spaced 3.7 Åapart in the z-direction (Figure 1). This essentially creates layers of atoms. The intensity of R-π for systems of various size are shown in Table 1. The intensity of R-π is equal to the number of atoms in the unit cell. The intensity will approach infinity as the system size increases.

We measured the peak width of R-π in the q_r direction using the appropriate slice of the structure factor. Ideally, one should use the angle averaged structure factor for this calculation, but since the angle averaging procedure interpolates between bins, the averaged intensities are lower than expected which slightly changes the shape of the peak. This reflection is radially symmetric about the z-axis, so we fit peak widths to cross-sections at $(0, y, 1.7)^{-1}$ Å.

The distance, d, between peaks in the q_y cross-sections of the structure factor is equal to $2\pi/d$ (Figure 2). We looked at systems with pores spaced 42.5 nm and 212.5 nm apart respectively. The fundamental frequency

L_z (Å)	Points per column	Number of Pores	Number of Atoms	R-π Intensity	FWHM ($\overset{\circ}{A}^{-1}$)
14.8	4	4	80	80	0.34
18.5	5	4	100	100	0.34
37	10	4	200	200	0.34
14.8	4	9	180	180	0.36
18.5	5	9	225	225	0.36
37	10	9	450	450	0.36
14.8	4	16	320	320	0.43
18.5	5	16	400	400	0.43
37	10	16	800	800	0.43

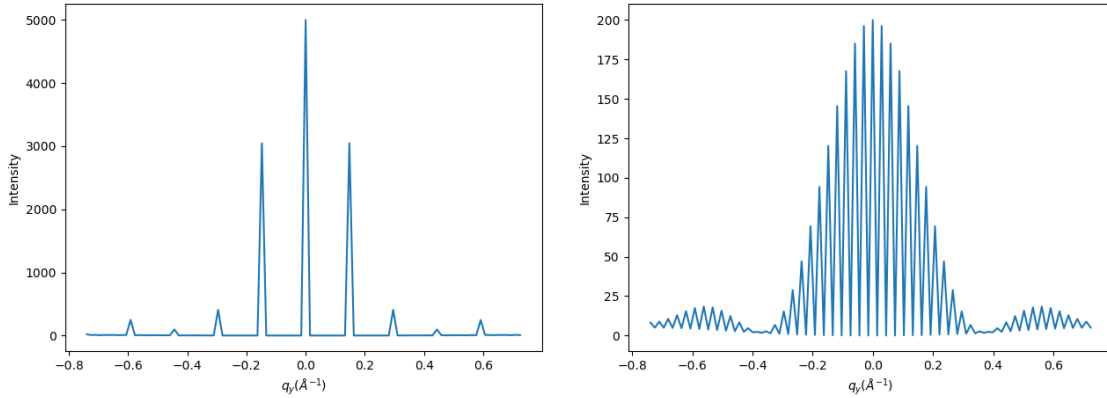Table 1: The intensity of R-π in a perfect crystal is equal to the number of scatterers in the unit cell.

Figure 2: The distance between peaks of the structure factor cross-section at (0, y, 1.7) is equal to the distance between pores in q-space. The first off-center peak of each distribution shows the fundamental frequency. The peaks that follow at higher —**q**— values are subharmonics. Both systems shown are in unit cells with dimensions of 42.5 x 42.5 x 3.7 nm. (a) The pore-to-pore spacing was held at 42.5 nm. The unit cell consists of 100 total pores. The first peak is located at $q_y = .148 \overset{\circ}{A}^{-1}$ which corresponds to $2\pi/.148 = 42.5\overset{\circ}{A}$ in real space. (b) We placed four pores in a unit cell spaced 21.25 nm apart. The first peak appears where expected at $q_y = 0.0296 \overset{\circ}{A}^{-1}$ and all other peaks are separated by the same distance.

appears where expected, based on d. Subharmonics follow the fundamental frequency at equally spaced intervals of width $2\pi/d$.

We quantified the peak width by fitting gaussian curves to the R-π peak cross-sections and measuring ther full width at half maximum. Gaussian profiles appear to give the closest fit to the data (see Figure **??**). We calculated all of FWHMs in 1 using gaussian fits.

The distance between pores does not affect the FWHM of the R-π peak in the q_y direction. We held the size of the unit cell constant at 42.5 x 42.5 x 3.7 nm and varied the number of pores (and consequently, the distance between pores). We generated error bars for the fits based on the covariance of the optimized fit parameters. There is no statistical difference between the calculated values of each FWHM. The uncertainty is lower for systems with less pores since there are more subharmonics available for curve fitting. The values of FWHM in Table **??** are calculated using model systems with 4 pores and the same box dimensions used here.

The finite FWHM of perfectly crystalline systems is due to non-uniform ordering of the columns within the pores. Although all scatterers are aligned and equally spaced in the z-direction, the individual columns of scatterers are offset from the pore center. Therefore, there is a range of similar but different distances between scatter scatterers. There are many opportunities for constructive and destructive interference with wavelengths slightly different than those which contribute to the fundamental frequency. If we place only
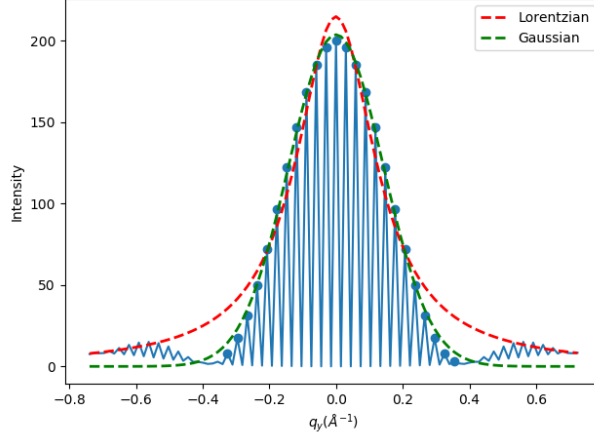
Figure 3: The gaussian functional form more closely matches the data than the Lorentzian functional form. Shown is data for a perfect crystal system with 4 pores and 4 points per column.

L_z (Å)	Number of Pores	Distance between Pores	R-π intensity	FWHM ($\mathring{A}^{-1}$)
37	4	212.5	200	0.331 ± 0.001
37	25	85.0	1250	0.330 ± 0.001
37	100	42.50	5000	0.329 ± 0.014

Table 2: We held the size of the unit cell constant at 42.5 x 42.5 x 3.7 nm and varied the number of pores and distance between pores. The value of FWHM is indistinguishable between the systems.

one column at each pore center, the FWHM becomes infinite (See Figure **??**)

The real system is far from a perfect crystal. Here we explore the influence of 3 sources of disorder on the intensity of R-π:

1. Random z-displacement of columns with respect to all other columns

2. Random rotation of layers about the z-axis

3. Thermal noise

2.2 Imperfectly aligned columns

We randomly aligned columns along the z-axis by adding a random displacement to each column of points. This simulates a system in which columns are uncorrelated. We shifted coordinates where necessary so that all atoms stayed within the unit cell. We held the spacing between each point within each column remained at exactly 3.7 Å. We created trajectories of 1000 independent configurations in order to calculate the average intensity of R-π. 1000 independent configurations gives a reasonably converged average, enough to observe trends.

The intensity of R-π is equal to the number of scatterers per column when we randomly displace columns with respect to each other (See Table **??**). It is independent of the number of pores (and hence number of columns) in the system. The error in the calculated intensities are comparable to the magnitude of the intensity because the intensity of each configuration in the trajectory fluctuates so much.

The q_y width of R-π is infinite when columns are randomly displaced in the z-direction.

2.3 Randomly rotated layers

We observed the influence of correlation between layers by randomly rotating layers of scatterers about the z-axis. We held constant the angle, with respect to the pore center, between scatterers for any given layer.
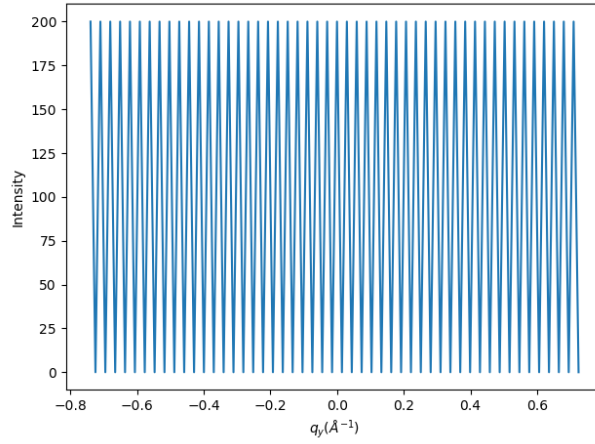
Figure 4: We placed one column of scatterers at each of 4 pore centers, spaced apart by 212.5 nm. Since the y-component of the distance between all scatteres is the same in all cases, subharmonics appear just as strongly as the fundamental frequency. Since the intensity doesn't decay, the FWHM is infinite.

L_z (Å)	Points per column	Number of Pores	R-π Intensity
14.8	4	4	3.98
18.5	5	4	5.05
37	10	4	10.40
14.8	4	9	4.06
18.5	5	9	4.78
37	10	9	10.19
14.8	4	16	4.01
18.5	5	16	4.95
37	10	16	9.61

Table 3: The intensity of R-π is equal to the number of scatters in each column when columns are uncorrelated.
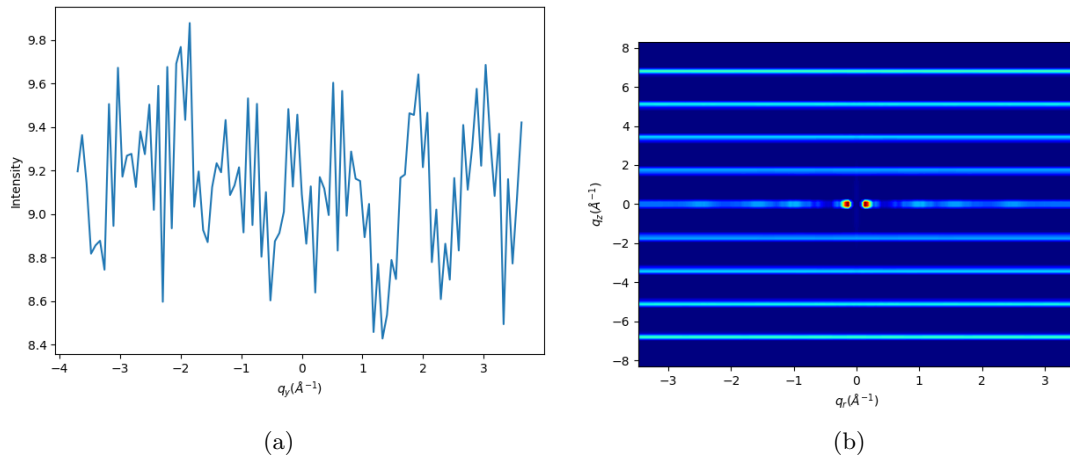

(a)

(b)

Figure 5

5

L_z (Å)	Points per column	Number of Pores	Number of Atoms	R-π Intensity	I(R-π) / natoms
14.8	4	4	80	61.2	.765
18.5	5	4	100	76.7	.767
37	10	4	200	153.2	.766
14.8	4	9	180	125.0	.695
18.5	5	9	225	156.3	.694
37	10	9	450	312.5	.694
14.8	4	16	320	211.1	.659
18.5	5	16	400	264.0	.660
37	10	16	800	528.0	.660

Table 4: The intensity of R-π is equal to the number of scatters in each column when columns are uncorrelated.