

Understanding missing diffraction reflections

March 5, 2018

Initial configurations are built in two ways: Parallel displaced and Sandwiched (Figure 1). The simulated diffraction patterns for equilibrated systems started in each configuration at 300 K are shown in Figure 2. We observe stronger features in the alkane chain region when the temperature is lowered to 280K (Figure 3). At both temperatures we are missing what appears to be a subharmonic located at ($q_r = 0, q_z = 0.85$) in the experimental pattern. We would like to know why it doesn't appear – whether it has something to do with our system or the math behind the simulated structure factor itself.

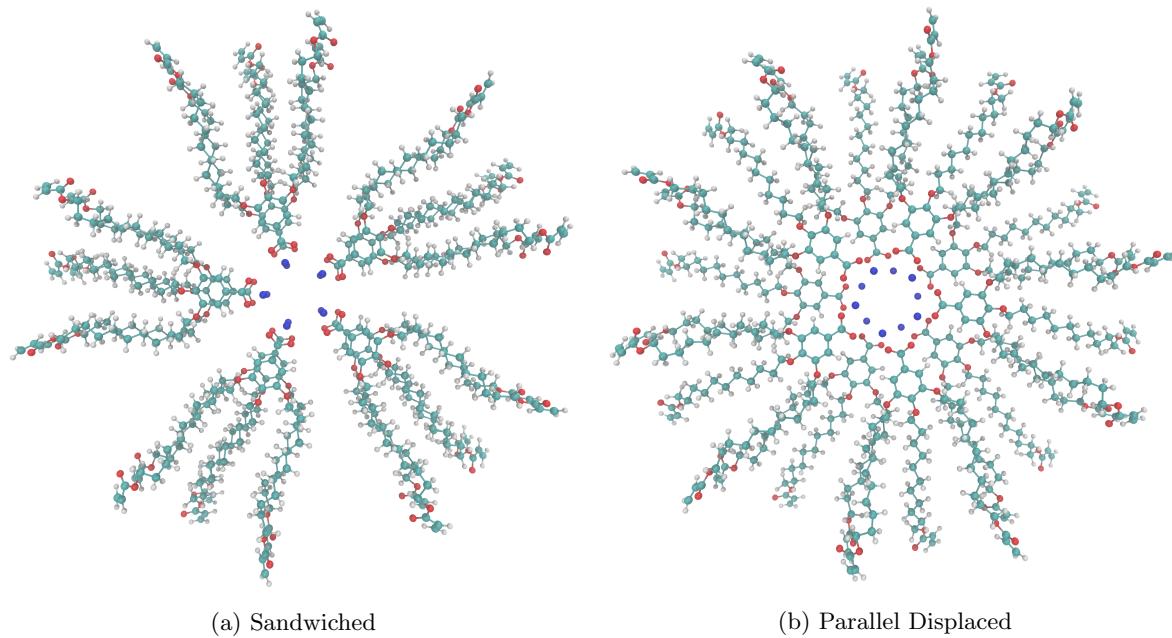


Figure 1

The hypothesis is that the subharmonic appears due to the reflection located at ($q_r = 0, q_z=1.7$) in the experimental pattern. This reflection likely appears because aromatic rings of monomer head groups pi-stack on top of each other 3.7 Å apart. The subharmonic does not appear in our simulated patterns and we need a good explanation for why that is the case. I explored fourier transforms in various dimensions to help increase my understanding.

I first looked at the 1D case. I spaced delta functions 3.7 units (I'll call the units angstroms for simplicity) apart. I adjusted the real space resolution by increasing the number of points between delta functions.

Next, I replaced the delta function with gaussian functions. It turns out, the number of subharmonics is dependent on the real space resolution and the width of the gaussian. A larger sigma value leads to less subharmonics (Figure ??). The same trend seen in Figure ?? is observed as real space resolution is increased for a given sigma. That is, more subharmonics appear as resolution increases. In the context of stacked benzene rings I would expect a more disordered system to have less subharmonics. It is also possible to miss out on subharmonics if the real space resolution is too small (i.e. data is binned into too large of bins).

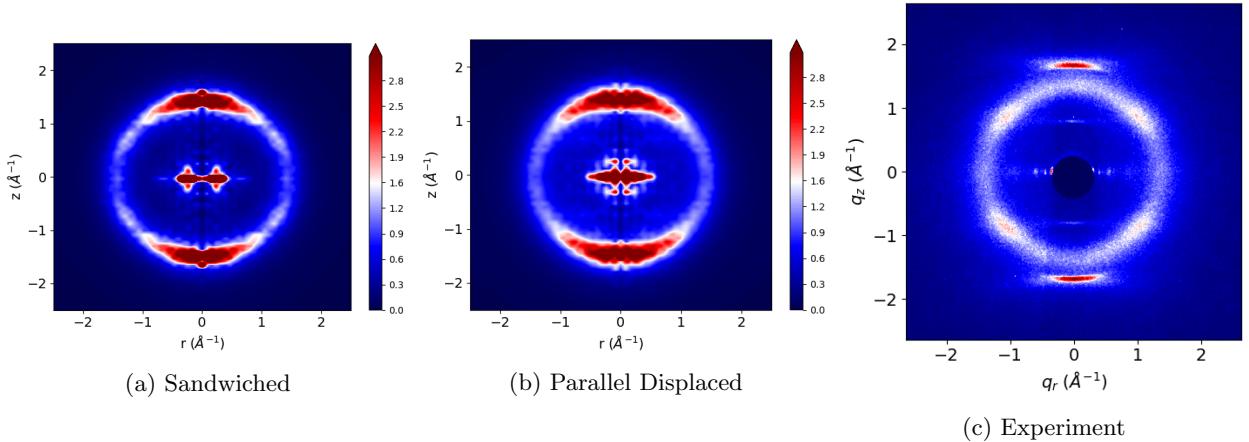


Figure 2

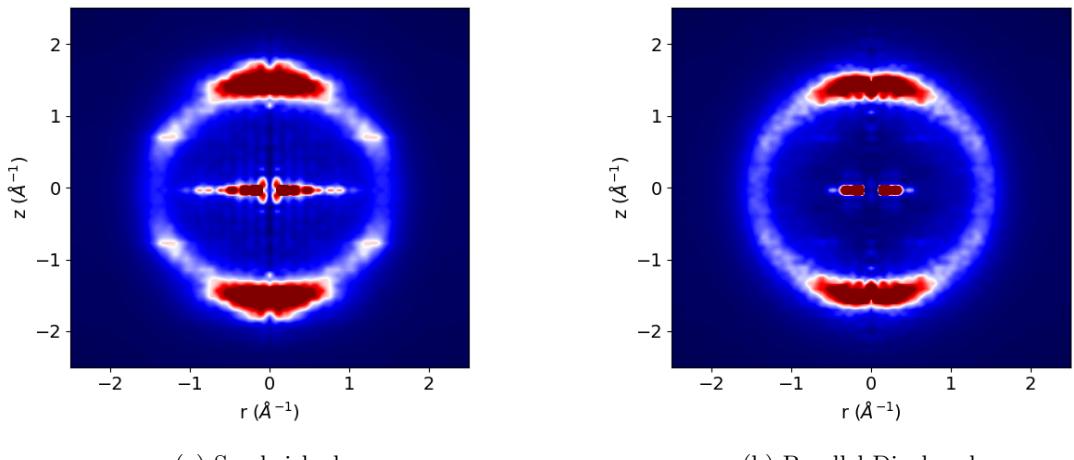


Figure 3

None of these subharmonics would actually show up in the experimental pattern (except maybe the first one) because the wavelength of the X-rays is too large (1.54 Å). And there are no subharmonics corresponding to a real space separation greater than 3.7 Å. In order for the 7.4 Å reflection to show up, rings need to be spaced 7.4 Å vertically. Then there would be a 3.7 Å subharmonic which shows up as the π -stacking reflection. In all plots, subharmonics are always weaker in intensity than the fundamental frequency. So the question remains, why is the π -stacking reflection stronger than the 7.4 Å reflection?

Next, I explored 2D fourier transforms of grids of data that somewhat resemble the LLC system. I created parallel columns of points spaced 3.7\AA apart. Each point is represented as a 2-dimensional gaussian function. In Figure ?? I show examples of simple configurations made up of one and two columns.

Next, I explored columns with points spaced 7.4 Å apart. Figure ?? shows the fourier transform of a single column. In Figure ?? we see that the intensity of each parallel line is about the same. Recall that the line corresponding to the fundamental frequency (7.4 Å real space) needs to be weaker in intensity than its first subharmonic in order to be consistent with experiment. Turns out, we can choose values of σ_x and σ_y that make this happen. If we change $\sigma_y=0.4$, we observe a faded effect at high frequency values. In this way we would observe the π -stacking reflection as more intense than the 7.4 Å reflection. It is also important that σ_x stays low, otherwise, the reflection disappears from the middle (Figure ??).

And now I move into 3D. The only difference in its calculation is that I use `numpy.fft.fftn` instead of the 2D version. I come to the same conclusion as in the 2D case. Lines appear that are spaced apart

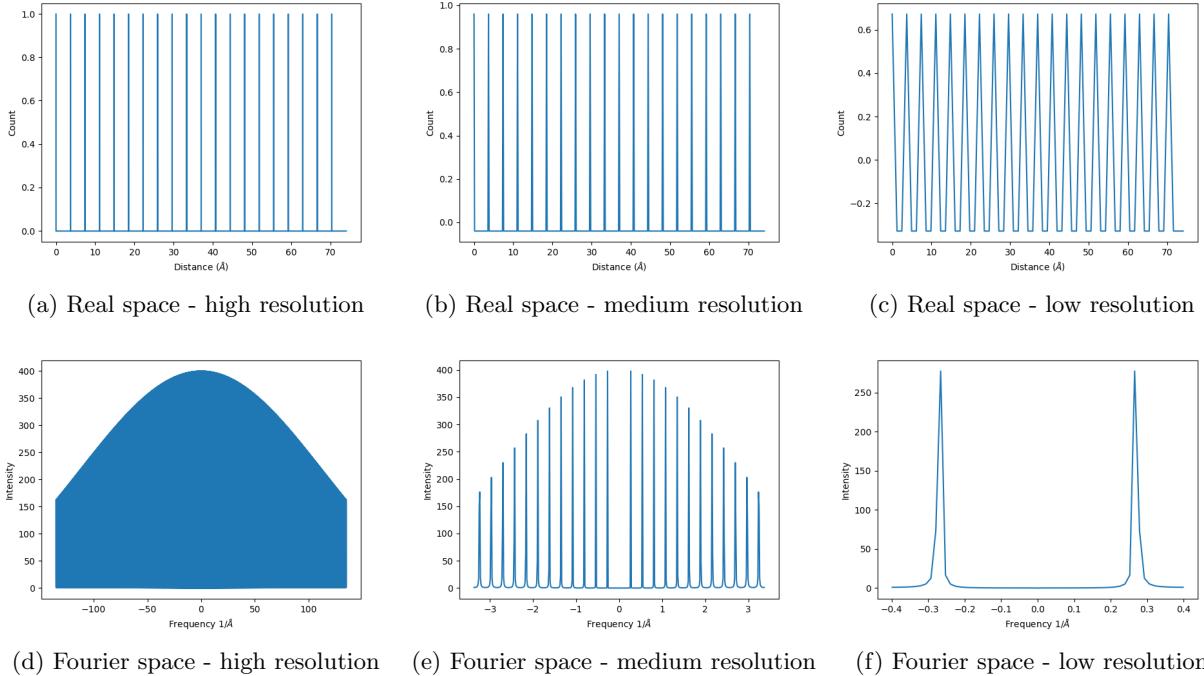


Figure 4: Less subharmonics are present as resolution decreases

by a distance equal to the inverse of the distance between points in the z direction (Figure ??). If there is disorder in the z-direction (high σ) then lines at low z frequency fade (Figure ??). If there is disorder in the x (or y) direction, then intensity at low x frequencies fade (Figure ??).

The patterns are interesting, but they still don't fully explain the features. The main problem is that the lines fade starting from the center (0 frequency) of the fourier transform. They are quite strong at high frequency and very low at zero. We see the opposite in the experimental pattern.

To address the problem, we need to make a more complicated system. So I'll start by adding more columns and packing them hexagonally (Figure ??). The dots of the dashed lines in the fourier transform (Figure ??) are spaced apart by the inverse of distance between columns. If we add some uncertainty to the locations of the points in the columns, we see fading of low frequencies as before. Interestingly, the pattern at $x=0$ does not fade despite the x/y uncertainties being as high as in Figure ???. I'd need to do more to verify this, but it appears that the center does not fade in the x direction as long as the uncertainty in the xy directions is larger than the z direction.

The original problem still persists after putting in more columns. That is, the intensity of the horizontal lines at high frequencies is never lower than the value at low frequency. Angle averaging helps resolve this (Figure ??).

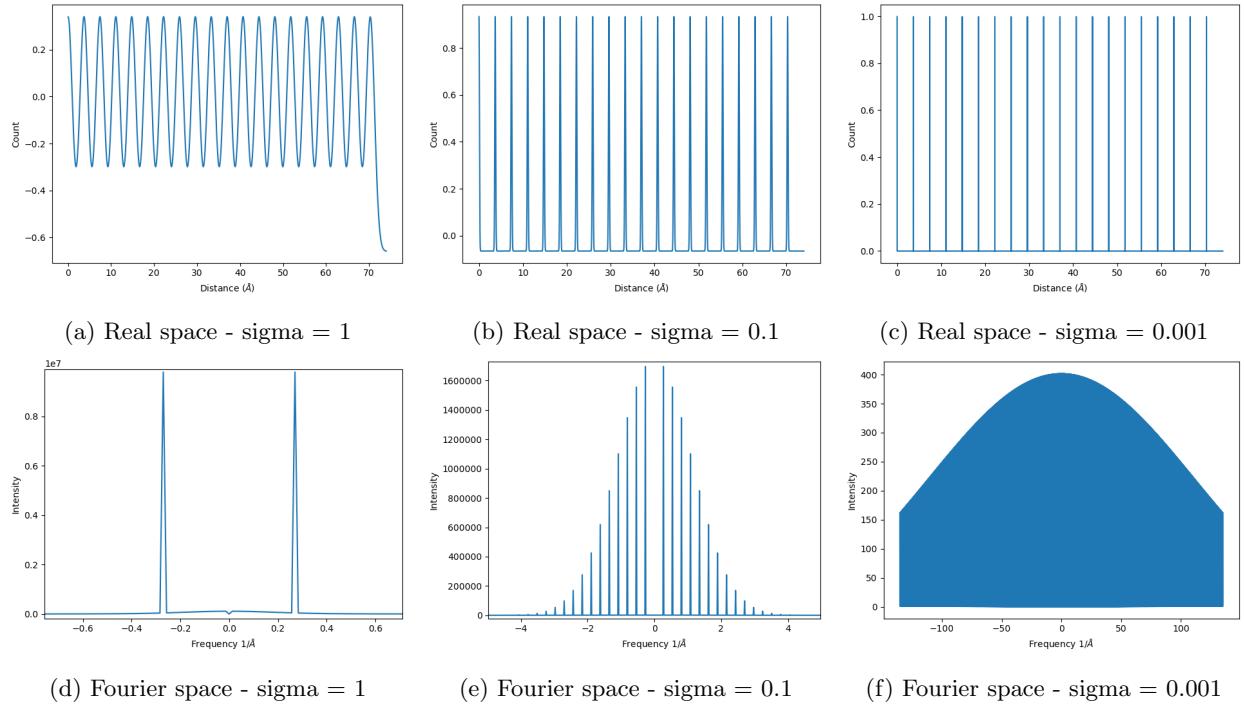


Figure 5: Using high real space resolution (same as Figure ??), it is evident that a smaller sigma leads to more subharmonics. As sigma approaches zero, the behavior is the fourier transform resembles that of delta functions. Otherwise, the fourier transform of a gaussian is a gaussian.

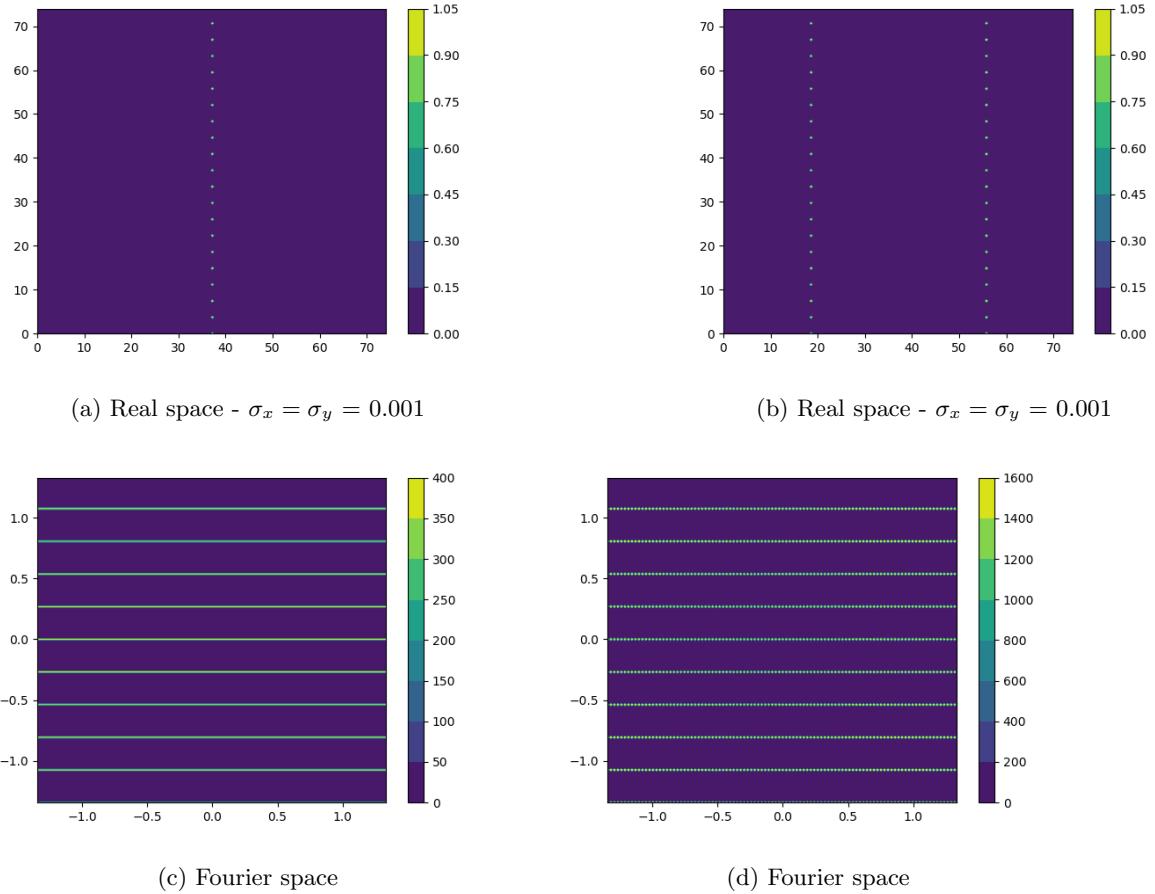
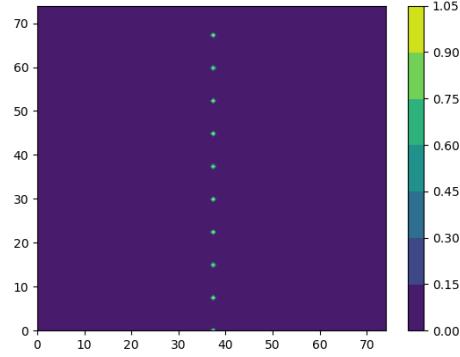
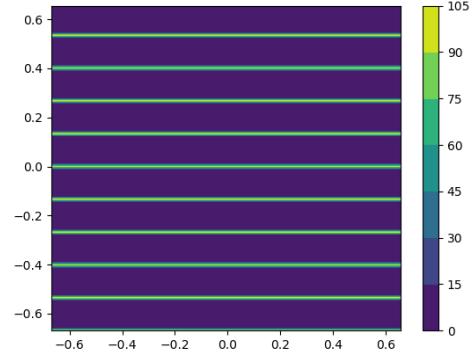


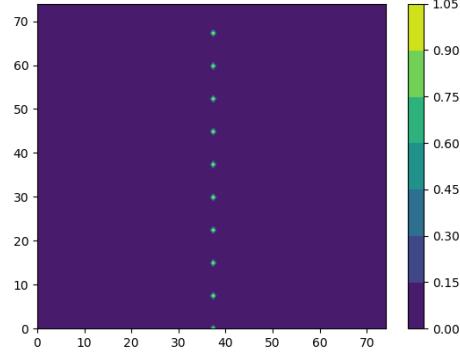
Figure 6: A single column of equispaced scatterers shows up as horizontal lines with spacing equal to the inverse of the distance between scatters. Adding a second column (b) causes the horizontal lines to become dots spaced apart by the inverse of the distance between columns. Adding more columns would follow the same trend.



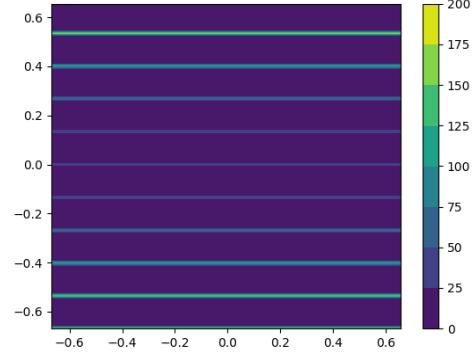
(a) Real space - $\sigma_x = \sigma_y = 0.1$



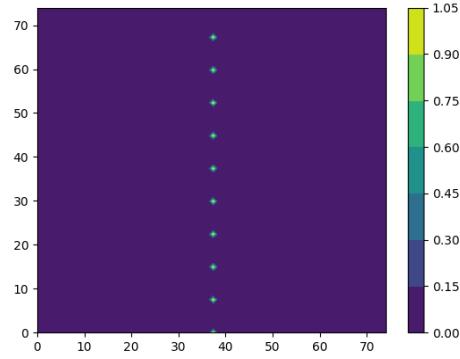
(b) Fourier space



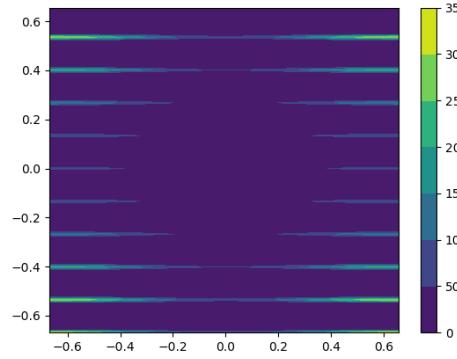
(c) Real space - $\sigma_x = 0.1, \sigma_y = 0.4$



(d) Fourier space



(e) Real space - $\sigma_x = 0.4, \sigma_y = 0.4$



(f) Fourier space

Figure 7: A single column of scatterers spaced 7.4 Å apart shows up as horizontal lines with spacing equal to the inverse of the distance between scatters. One of the subharmonics corresponds to a real spacing distance of 3.7 Å. If we adjust the sigmas of the scattering, we can change the relative intensity of each horizontal line in Fourier space.

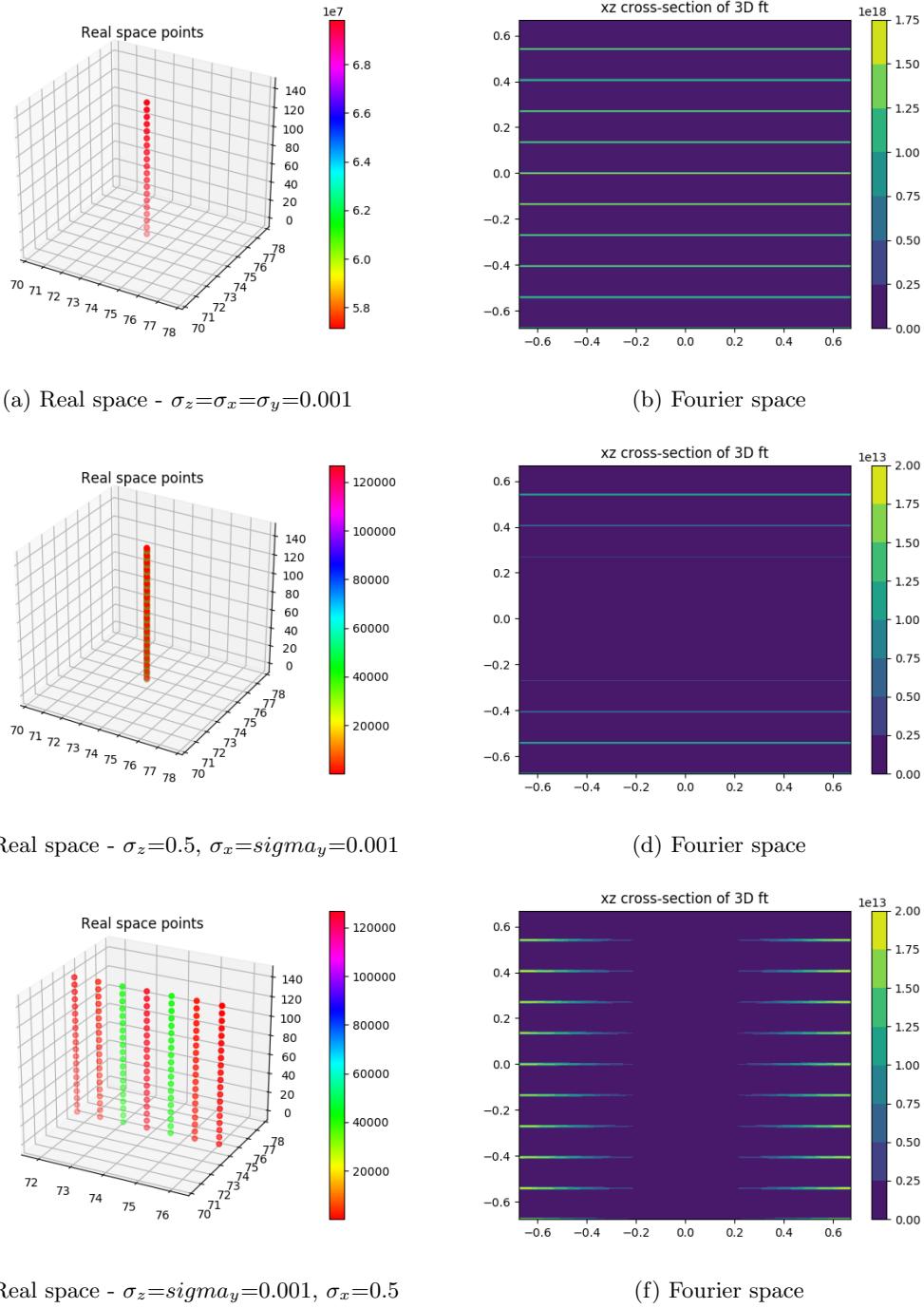


Figure 8: A single column of scatterers spaced 7.4 Å apart in 3D space shows up as horizontal lines with spacing equal to the inverse of the distance between scatters. One of the subharmonics corresponds to a real spacing distance of 3.7 Å. If we adjust the sigmas of the scattering, we can change the relative intensity of each horizontal line in fourier space.

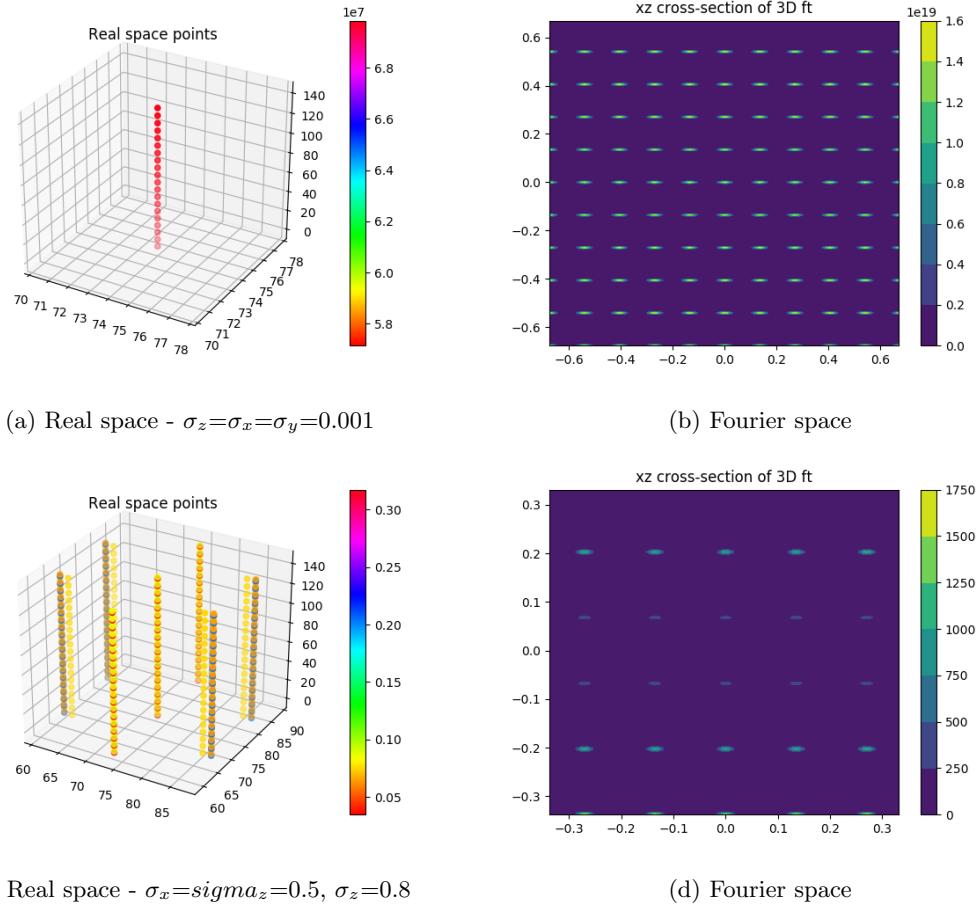
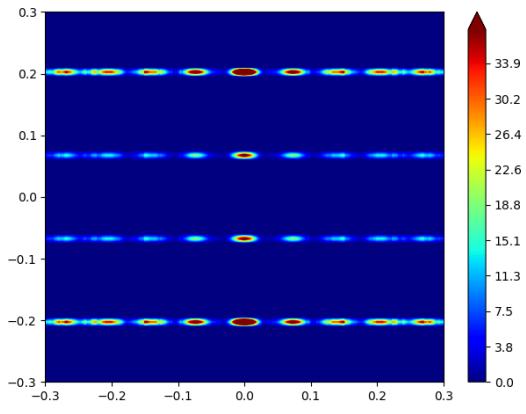


Figure 9



(a) Fourier space - $\sigma_x=sigma_z=0.5$, $\sigma_z=0.8$

Figure 10: Angle averaging the same pattern shown in Figure ?? yields a pattern with the highest intensity concentrated at the center.