Physics 513R Crystallography and Diffraction, Spring 2008 Homework 4A

$$\boxed{\frac{1}{\sqrt{2\pi}\sigma}e^{-\frac{x^2}{2\sigma^2}}}$$

[A] Show that a normalized **gaussian** peak shape of width σ (see equation at the right) integrates to 1 as expected over the range from $-\infty$ to $+\infty$. Show that its Fourier transform is also a normalized gaussian, but with a width of $1/\sigma$. You may use a symbolic computing package and print the output as long as you manually complete the task of getting the output into the standard form.

[B] **Structure factors**. Consider a cubic structure with eight atoms of the same type ($f = 1$): *atomlist* = {{0,0,0}, {0,1/2,1/2}, {1/2,0,1/2}, {1/2,1/2,0}, {3/4,3/4,3/4}, {3/4,1/4,1/4}, {1/4,3/4,1/4}, {1/4,1/4,3/4}} and *scatfaclist* = {1,1,1,1,1,1,1,1}.

(1) Create a routine that takes three arguments: a list of atoms, a list of scattering factors and an {*h*, *k*, *l*} vector, and returns a structure factor as output. Its might have the following form:

```
structurefactor[atomlist_, scatfaclist_, hkl_] :=
Sum[scatfaclist[[m]]*Exp[2*Pi*I*hkl.atomlist[[m]]], {m, Length[atomlist]}]
```

(2) Use this routine to determine the magnitudes and phases of the structure factors for all *h*, *k* and *l* indices in the range between 0 and 4.

(3) Search your structure-factor results for systematic-absences and other patterns, and use what you find to determine the correct space-group symmetry. You may consult the International Tables for systematic-absence rules if necessary.

[C] Forward and inverse **Fourier transforms**

(1) Create a structure model by randomly placing two atoms in a 2D box of size 1 (use unitless coordinates). Plot the locations of these two atoms. This could be accomplished in Mathematica using the following commands.

```
atom1 = {RandomReal[],RandomReal[]};
atom2 = {RandomReal[],RandomReal[]};
atomlist = {atom1, atom2};
Graphics[{PointSize[0.05],Red,Point[atom1],Blue,Point[atom2]},
   PlotRange→{{0,1},{0,1}},Frame->True]
```

Let the two atoms have different scattering factors $f_1 = 1$ and $f_2 = 2$.

(2) Using these atomic positions and scattering factors, calculate structure factors for all Bragg peaks with *h* and *k* indices between -4 and +4. Each entry in the resulting list will include both an *hkl* vector and its structure factor, e.g. `sflist = {...,{{1,1,0}, 2 + 4i},...}`.

(3) Finally, create a routine that performs inverse Fourier transform on your structure factors. It should take a real-space vector and a list of structure factors as input, and return the real-space density as output.

```
ift[sflist_, xyz_] :=
Sum[sflist[[n,2]]*Exp[-2*Pi*I*sflist[[n,1]].xyz], {n, Length[sflist]}]
```

Use this routine to recover the electron density associated with your model structure, and create a nice contour plot of this density in the range where *x* and *y* run between 0 and 1. If you do this correctly, the strong density peaks should agree well with the original atomic positions.

```
ContourPlot[Evaluate[ift[sFlist,{x,y}]],{x,0,1},{y,0,1},
   Contours→{Automatic,15},PlotRange→All]
```

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[D] **Patterson functions**

(1) Let there be three atoms of the same type ($f = 1$) in a 2D box of size 1 (unitless coordinates) at {{0.7, 0.9},{0.7, 0.2},{0.4, 0.4}}. Plot their locations.

(2) As in the previous exercise, calculate structure factors for all Bragg peaks with h and k indices in the range between -4 and +4, placing the results in a list called *sFlist*.

(3) Create a list called *sMlist* that is similar to *sFlist*, but where each structure factor is replaced by its own absolute value.

(4) Perform an inverse Fourier transform on your structure factors (i.e. *sFlist*) and provide a contour plot of the resulting density in the range where x and y run between 0 and 1.

(5) Perform an inverse Fourier transform on your structure factors magnitudes (i.e. *sMlist*) and provide a contour plot of the resulting density in the same range. This is called the Patterson function or Patterson density. Determine and record the approximate locations of the strongest peaks (other than {0,0}) in the pattern.

(6) Assuming that you have one atom at the origin. Construct all possible atomic models that are consistent with the peaks in the Patterson function.

[E] **Direct Methods of solving the phase problem**.

(1) Let there be four atoms of the same type ($f = 1$) in a 2D box of size 1 (unitless coordinates) at `{{0.31,0.12},{0.69,0.88}, {0.40,0.45},{0.60,0.55}}`. Plot their locations and calculate the structure factor list *sFlist* as in the previous exercise. Observe that each of the structure factors is real, so that each one has a phase of either 0 or π. This is because the structure is centrosymmetric about the point at the center of the box. Each phase can be represented by ±1, which is more convenient for our purposes.

(2) Create a list called *sMPlist0* that is similar to *sFlist*, but where each entry contains an *hkl* vector, a structure factor magnitude, and a structure factor phase represented as ±1.

```
   sMPlist = {#[[1]],#[[2]]//Abs,#[[2]]//Arg//Cos//Sign}& /@ sFlist;
```

Sort *sMPlist* in order of decreasing structure factor magnitude.

```
                 sMPlist = Sort[sMPlist, #1[[2]]>#2[[2]]&];
```

(3) Strip the phase information from *sMPlist* by setting each phase to zero, and call the result *sMPlist0*. We will use a zero to indicate an "undetermined" phase.

```
                 sMPlist0 = {#[[1]],#[[2]],0}& /@ sMPlist;
```

(4) Set the phase of the hk = {0,0} peak to +1. This is always possible for x-ray diffraction patterns because it F_{00} is always positive. If you find that {0,0}is the 1st reflection in the list, then its phase can be set with the command: `sMPlist0[[1,3]] = 1`. Also fix the origin by setting the phases of two strong reflections to their true values. Use the strongest {odd h, odd k} reflection and the strongest {even h, odd k} or {even h, odd k} reflection.

(5) Download *phaseproblem.nb* from the course website and copy the **evolve** function into the definitions section of your existing notebook. This function takes a list of unphased (or partially phased) structure factors as input and returns the same list again, but with improved phases. It uses only phase-triplet relationships to accomplish this. Recursively apply evolve to *sMPlist0* until the phase list stops changing.

`sMPlist1 = Nest[evolve,sMPlist0,n];` (adjust the integer *n* as needed).

You should find that many phases are still undetermined.

(6) This is the point where guesswork comes in handy. Identify the strongest unphased reflection and set its phase arbitrarily to either –1 or +1. Then start over with **evolve** recursions and run until the phases stop changing.

```
sMPlist1 = Nest[evolve,sMPlist0,n];
```

Repeat this step until all of the reflections have been phased. For some structures, no guessed phases are required. For others, one needs to guess several phases.

(7) Convert *sMPlist1* into an ordinary structure factor list called *sFlist1*, perform an inverse Fourier transform, and produce a contour plot of the resulting density.

```
sFlist1 = {#[[1]],#[[2]]*#[[3]]}& /@ sMPlist1;
```

If you can't find four clearly-recognizable atoms in the density plot, then the phases that you guessed in the previous step are probably wrong. So change your guesses and try again. You should eventually a set of guessed phases that gives you a reasonable density plot. With a little luck, they will give you the <u>correct</u> density plot. Once you feel that you have succeeded, compare the true phases in the original *sMPlist* against your new phases in *sMPlist1*.

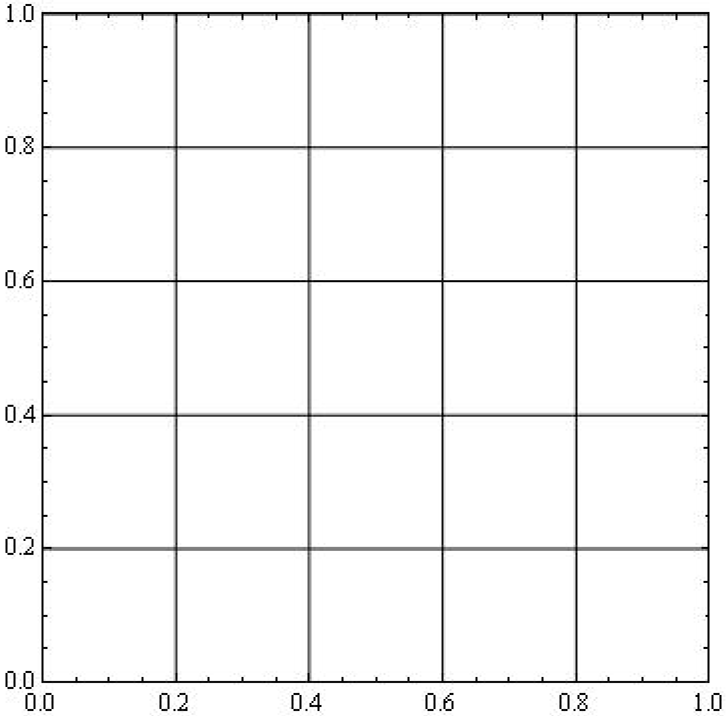
```
(#[[3]]& /@ sMPlist1) - (#[[3]]& /@ sMPlist)
```

How many of the 81 reflections were not correctly phased? Were they strong or weak reflections? Explain this result in terms of the validity of the assumptions underlying the triplet relations.

[F] A pair of identical atoms has been placed in a square unit cell with planar space group *p2*. In two dimensions, the two-fold axis is much like a center of symmetry, so that all structure factors are real and have phases that can be represented by ±1. The strongest 6 Bragg reflections in the range where *h* and *k* vary between ±2 are listed below, along with their structure factors.

```
{{{2,-1},-2.0},{{1,2},-2.0},{{2,0},-1.62},
 {{2,-2},-1.62},{{1,1},-1.62},{{1,-2},+1.62}}
```

Use this information to determine the locations of the atoms to within a block of the grid below.



You can accomplish this by drawing the phase-adjusted Miller planes that correspond to each Bragg reflection, and looking for a spot or region where many of the planes intersect. You might start by printing a square lattice (with *hk* in the range between ±2) on a separate piece of paper and drawing all relevant planes with no phase adjustments. Then, consider that a negative structure factor (i.e. a π phase) means that the planes should actually be drawn in the middle of the gap between the expected zero-phase planes. Once you have this drawing completed, transfer the relevant phase-adjusted planes onto the grid above. This should give you a more intuitive feel for how each structure factor contributes to the electron density.