

# ASSIGNMENT 4: SOLUTIONS

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# THE EIKONAL APPROXIMATION

## PREREQUISITES

The chapters *Bulk Scattering* and *Surface Scattering* from the *Theory Handbook*.

## THEORETICAL BACKGROUND

This section is largely a repeat of information in the *Theory Handbook*. In atom scattering experiments, a “probe” beam with wavevector  $\mathbf{k}_i$  is incident on a surface. This wavevector is given by:

$$\mathbf{k}_i = \mathbf{K}_i + k_{iz}\hat{\mathbf{z}},$$

where  $\mathbf{K}_i$  is the in-plane component of the wavevector, and  $k_{iz}$  is the perpendicular component. The probe is then scattered to all azimuthal directions, emerging with a final wavevector  $\mathbf{k}_f$ . This final wavevector is given by:

$$\mathbf{k}_f = \mathbf{K}_f + k_{fz}\hat{\mathbf{z}},$$

where all symbols are similarly defined.

What do we aim to find in this section? We wish to measure the intensity of the diffracted beam along each possible azimuth. Note that, in this section, we only consider “in-plane” scattering (where the source, detector, and the scattering point are all coplanar).

### Laue Condition

The maxima in the intensities of the scattered waves are of interest to us. A scattering maximum is observable if an event satisfies the “Laue condition”. This states that the parallel momentum transfer  $\Delta\mathbf{K}$  for the scattering is the same as any in-plane reciprocal lattice vector  $\mathbf{G}$ . We denote the final wavevector  $\mathbf{k}_f$  as  $\mathbf{k}_G$  for any diffracted wave meeting the Laue condition, for any given reciprocal lattice vector  $\mathbf{G}$ .

If the scattering is elastic, as in this exercise, we additionally know that the final and incident wavevectors  $|\mathbf{k}_G|$  and  $|\mathbf{k}_i|$  are equal for all reciprocal lattice vectors  $\mathbf{G}$ .

## Scattering Intensities

Recall that we intend to find the intensity of the scattered beams. How do we do this? To begin, we consider scattering from a single scattering centre. This is assigned an index  $j$ . It has a position vector  $\mathbf{R}_j$  on the surface. What is a scattering centre? A scattering centre is any pointlike defect (*e.g.* a surface adsorbate or a bubble in a liquid) in a material from which only a single scattering event occurs. A good example is the scattering of an x-ray from an electron. The x-ray interacts only once with the electron (scattering centre) and is deflected, following a probabilistic intensity distribution, due to the quantum nature of the interaction. For a flat surface (as in this exercise), it is reasonable to model the scattering centres as continuously distributed across the surface. What can this be interpreted as? There is little preference for scattering at any one particular point, as opposed to another.

As in the tutorial on hard wall potentials, we assume that the surface potential can be well-modelled by a static hard-wall potential. We do not consider any attractive component of the potential when constructing the hard-wall potential. If we additionally assume that the corrugation function  $\zeta(\mathbf{R})$  varies little with position, then we can apply the “Rayleigh assumption”. This states that the incident and final beams are planar waves. How do we make use of this assumption? Recalling that we can write the two important quantities (the wavevector and the position) as:

$$\begin{aligned}\mathbf{k}_i &= \mathbf{K}_i + k_{iz}\hat{\mathbf{z}}; \\ \mathbf{r}_i &= \mathbf{R}_i + z\hat{\mathbf{z}},\end{aligned}$$

where  $z$  is the  $z$ -coordinate of a point above the plane, and  $\mathbf{R}_j$  is the position vector of a point in the plane, the phase of the plane wave is determined by the dot product of these two quantities. Thus the wavevector can be written as

$$\psi(\mathbf{R}_j, z) = e^{i\mathbf{r}_i \cdot \mathbf{k}_i} + \sum_{\mathbf{G}} A_j(\mathbf{G}) e^{i(\mathbf{k}_i + \mathbf{G}) \cdot \mathbf{r}_i},$$

which can be conveniently expanded into components as

$$\psi(\mathbf{R}_j, z) = e^{i(\mathbf{K}_i \cdot \mathbf{R}_j + k_{iz}z)} + \sum_{\mathbf{G}} A_j(\mathbf{G}) e^{i((\mathbf{K}_i + \mathbf{G}) \cdot \mathbf{R}_j + k_{Gz}z)}.$$

The first exponential is the incident beam, and the sum is a linear combination of all possible diffracted beams. The weightings  $A_j$  for each term in the sum do not evolve with time. Therefore they can be treated as a constant for each term in the sum. How do we interpret this equation? As the first term represents the incident beam, it has an intensity normalised to unity. The scattered beams will not have

unitary intensity, as there are many of them that the incident beam can scatter into! This is the origin of our constants  $A_j$ .

How do we proceed in our calculation of the intensity? We must consider what our boundary conditions are. We apply the boundary condition that, for all scattering centres, the wave amplitude must be zero at the boundary. This can be written as:

$$\psi(\mathbf{R}_j, \zeta(\mathbf{R}_j)) = 0,$$

which applies for all scattering centres at positions  $\mathbf{R}_j$ . Why do we use this condition? Using the hard wall potential, the potential energy is infinite outside of some known region. The consequence of this is that the wavevector cannot exist outside of this region! Setting it as 0 at the boundary naturally follows. With some rearrangement, we can utilise the information given by the condition. This yields

$$\sum_{\mathbf{G}} A_j(\mathbf{G}) e^{i((k_{Gz}-k_{iz})\zeta(\mathbf{R}_j)+\mathbf{G}\cdot\mathbf{R}_j)} = -1.$$

To provide an approximate solution for the weightings  $A_j$ , we apply the ‘‘Eikonal Approximation’’. This states that the out-of-plane wavevector for the scattered wave  $k_{Gz}$  varies slowly as the reciprocal lattice vector  $\mathbf{G}$  changes. What is the consequence of this? Since the change is small, a Taylor expansion can be used [1]. With some manipulation, we obtain an integral over a unit cell on the surface, denoted  $S$ . This reduces to:

$$\begin{aligned} A_j(\mathbf{G}) &\approx -\frac{1}{S} \int_S e^{-i((k_{Gz}-k_{iz})\zeta(\mathbf{R}_j)+\mathbf{G}\cdot\mathbf{R}_j)} d^2\mathbf{R}_j; \\ &\approx \kappa_j e^{i((k_{Gz}-k_{iz})\zeta(\mathbf{R}_j)+\mathbf{G}\cdot\mathbf{R}_j)}, \end{aligned}$$

where  $\kappa_j$  is a constant. Note we can freely interchange  $\mathbf{G}$  and  $-\mathbf{G}$  - as the reciprocal lattice vectors are arbitrary, and centrosymmetric. Does this equation have any limitations? It neglects both multiple scattering and selective adsorption resonance. These are not necessarily negligible in experiment.

How do we obtain the amplitude of scattering? We sum the above expression for  $A_j$  across all of the centres on the surface of a unit cell. This obtains:

$$\begin{aligned} A(\mathbf{G}) &= \sum_j A_j(\mathbf{G}); \\ &= \sum_j \kappa_j e^{i((k_{Gz}-k_{iz})\zeta(\mathbf{R}_j)+\mathbf{G}\cdot\mathbf{R}_j)}, \end{aligned}$$

which is the product of a so-called ‘‘form factor’’ and a ‘‘structure factor’’.

In the following exercise, we will assume that the form factor  $A_j$  is the same for all scattering centres, and that it can be normalised to 1. This simplifies the calculation. In addition, we assume that the individual atoms of the surface behave identically, and that the scattering centres are continuously distributed across the cell.

These assumptions reduce the sum to an integral. This integral is the two-dimensional Fourier transform of a phase factor, which we can write as

$$A(\mathbf{G}) = -\frac{1}{S} \int_S e^{i((k_{Gz}-k_{iz})\zeta(\mathbf{R})+\mathbf{G}\cdot\mathbf{R})} d^2\mathbf{R}.$$

Following through with the calculation yields

$$A(\mathbf{G}) = -\frac{(2\pi)^2}{S} \mathcal{F}[e^{i(k_{Gz}-k_{iz})\zeta(\mathbf{R})}].$$

Note that the factor of  $2\pi$  is squared, as the Fourier transform used here is two-dimensional.

The intensity  $P(\mathbf{G})$  of a “diffraction channel”  $\mathbf{G}$  is approximately given by:

$$P(\mathbf{G}) = \frac{|k_{Gz}|}{|k_{iz}|} |A(\mathbf{G})|^2,$$

such that the sum of all of the intensities can be written as:

$$\sum_{\mathbf{G}} P(\mathbf{G}) \approx 1,$$

which represents the intensity being normalised. The prefactor  $|k_{Gz}|/|k_{iz}|$  is due to the ratio of incident and final beams. Why is this? If a beam has a larger cross-section, then it is more likely to collide with the detector element in a measuring device. Thus we construct the intensity as the fraction of the total intensity, using the incident wavevector as a reference.

## USING FUNCTIONS

As we have mentioned, there are two methods of using functions: we can either write them in line, or call them from an external library. Dependent on context, it may be clear which of these is appropriate for the task at hand.

### In-line Functions

If a function being defined only needs to be used within the scope of a single piece of code, it is practical to define it within the same file. The definition of a user-defined function is always placed at the *end* of the file.

An example of a user-defined function is given below, where we find the position of a particle moving under constant acceleration.

```

1 % Acceleration due to gravity /ms{-2}
2 g = 9.81;
3
4 % Initial speed /ms{-1}
5 u = 1;
6
7 %time variable
8 t = linspace(0, 10)
9
10 %iterate through the position, using equations of constant
    acceleration – this function is yet to be defined.
11 for j = 0:100:
12     %constacc_distance returns the distance moved under constant
        acceleration
13     x(j) = constacc_distance(g, u, t(j));
14 end
15
16 %plot the position as a function of time
17 plot(t, x)
18
19
20 %define a function that moves a particle under constant
    acceleration
21 function w = constacc_distance(a, u, t)
22 % constacc_distance(a, u, t)
23 % PRECONDITION: – acceleration, a, is the acceleration of the
    particle
24 % – initial speed, u, is the initial velocity of
    the particle
25 % – time, t, is the time coordinate
26 % POSTCONDITION: – w, the distance travelled by the projectile,
    is in metres
27
28     w = u*t + 0.5*a*t^2;
29 end

```

What happens if we encounter a new function, and do not know how to use it? The general method to view the documentation of a function in MATLAB is to run the command "`help <function name>`". Bearing this in mind, it is just, and fair, that the author of any new function must write the documentation (the lines of comments at the start of the definition) to accompany it. It is very important that the documentation of the function is developed well, as the code should be standalone - someone else reading the code should not need to consult the author.

## External Functions

Defining a function in the same file as a program is not often useful; besides for improving readability, the function code can be placed elsewhere, and can still be run in the program. If the function is to be used by multiple files, it is very useful to define a single function, rather than defining it many times. However, it must be *in its own .m file*, and placed in the same working directory as the program being developed.

MATLAB will automatically detect any of the functions defined in the MATLAB path, so it is very easy to put all of the required functions in a single folder. After having done this, the functions can be used in a program by simply calling the function's name, as in the case of when the function is defined in the file. It is possible to have multiple folders in the path, but note that the order of files in the path matters. If there are two conflicting functions of the same name, the first one found in the path will be used.

To change the path, the easiest method is to use the "set path" option in the "file" menu. This allows one to set the directory, as well as its position in the path. For more detail, the internet has many resources on introductory MATLAB that are appropriate.

## TASK

Consider the (001) surface of hexagonal ice (Ih).

1. Plot the three lowest index diffraction channels along the  $\langle 1\ 0 \rangle$  azimuth on your contour plot of the corrugation function in reciprocal space, from the tutorial on hard wall potentials. These channels correspond to reciprocal lattice vectors, and therefore to a set of planes in real space.
  - (a) Plot the three planes to which these azimuths correspond, in real space.
  - (b) Calculate, and plot, the reciprocal lattice vectors. Verify that these are normal to the planes you have plotted. You may use the function `unitCellVecs` in the class `auxCls`.
2. A beam of  $^4\text{He}$ , with mean beam-energy of  $E_i = 25\text{ meV}$ , and an incident angle of  $\theta_i = 0\text{ rad}$  is incident on the surface. Calculate, and plot, the diffraction intensities for the azimuths above (use a bar chart).
3. The scattering angle  $\delta$  is a variable. Explore the effect of varying the incident angle, the beam energy, and the corrugation. What do you observe? Repeat the above with  $^3\text{He}$ . What do you notice?
4. The scattering angle is fixed at  $\delta = 95.8^\circ$ . The incident angle  $\theta_i$  is now a variable. Compare your code with that in [2] - it should produce similar results.

## Tip 1

It may be useful to define a function to solve this problem: taking the energy, mass and incident angle of a beam as its arguments. The function should return the normal components of the wavevectors,  $k_{iz}$  and  $k_{Gz}$ , assuming the Laue condition is satisfied, and that the scattering is elastic.



### Parameters

Take the lattice parameter to be  $a = 4.52 \text{ \AA}$ , and the corrugation height to be  $(\zeta_{\max} - \zeta_{\min}) = 1 \text{ \AA}$ .

### EXTENSION

1. A more general method, which assumes that the attractive well has its own corrugation function, is detailed in [3]. Implement this in your code, and compare the results with those obtained using the Beeby correction. Try using different corrugation functions for the attractive well. Does it need as many Fourier components as the surface corrugation to provide a reasonable approximation?

### REFERENCES

1. Ellis, J.; Rohlfing, D.; Hinch, B.; Allison, W.; Willis, R. *Vacuum* 1988, 38, 347351.
2. Glebov et al, 2000. *J. Chem. Phys.*, 112(24).
3. Manson, J.R. and Rieder, K.H., 2000. *Phys. Rev. B*, 62(19), p. 13142

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# ADSORBATES

## INTRODUCTION

In this tutorial we consider diffraction from complete layers of adsorbate atoms on a surface, and the effect that this has on the intensity distribution.

## THEORETICAL BACKGROUND

The interaction between the substrate surface and the adatoms will preferentially cause adatoms to adsorb to the surface at specific sites. The adsorbates may remain isolated on the surface, or condense to form “islands”. At low coverages, isolated adsorbates are favoured whereas at high coverages condensation is inevitable.

The presence of adsorbates on a surface can have dramatic effects on the diffracted intensity distribution. When distributed uniformly on the surface, adsorbates lead to a linear reduction in specular ( $\Delta\mathbf{K} = \mathbf{0}$ ) scattering for low coverage. This causes a broadening in the intensity distribution.

If adsorbates condense to form full layers, their electron orbitals overlap and form a quasihard potential (which can be modelled by the hard-wall approximation). In a scattering experiment, the repulsive potential is caused by overlap of the outermost electron orbitals with those of the probe atom, so if there exists a complete adsorbate layer on the substrate then the substrate isn't probed directly. However, in principle the resultant corrugation is a function of both the adsorbate corrugation and the substrate corrugation (since the surface corrugation determines the structure of the adsorbate layer). We are concerned about whether helium scattering is still sensitive to the substrate corrugation when the surface is flat but covered with an adsorbate layer, such as with Cu(111), since this will determine the tolerance of the method to impurities on the surface.

In the following exercise, we wish to evaluate the diffraction from an adsorbate that forms a periodic structure on top of the substrate

surface. We assume that we can write a total corrugation function

$$\zeta(\mathbf{R}) = \zeta_a(\mathbf{R}) + \zeta_s(\mathbf{R}),$$

where the first term is the corrugation of the adsorbate (with its zero defined at the surface), and the second the corrugation of the substrate. The Laue condition for such a surface can now be written as:

$$\begin{aligned}\Delta\mathbf{K} &= \mathbf{G}; \\ &= \mathbf{G}_a \pm \mathbf{G}_s.\end{aligned}$$

We assume that on the timescales of our measurement the adatoms are entirely stationary

## TASK

1. Assuming the surface is as described in the theoretical background, write the Eikonal formula for the diffraction amplitude as the Fourier transform of two phase factors, one for each of the corrugation functions. Note we are still assuming that the scattering centres are continuously distributed across the surface so we use the integral, rather than the sum, formulation. If you wish to consider the discrete case, the exercise simply reduces to using a discrete Fourier transform.
2. Using the convolution theorem, show that the total scattering amplitude can be written as

$$A(\mathbf{G}) \propto (A_a * A_s),$$

and find the proportion required for equality.

3. Calculate the intensity distribution of diffraction from a complete adsorbate layer with hexagonal symmetry of  $(3 \times 3)R\frac{\pi}{6}$  on a hexagonal Cu(111) surface using the corrugation functions (and much of the code) from previous. You should make use of the information in [1]. Assume the incident conditions of the beam are the same as in the task above.

## EXTENSION

1. You may also wish to reproduce the adsorbate/substrate system described by [2].

## REFERENCES

1. Lau et al *J. Phys. Chem. C*, 2018, 122 (16), 8941-8945
2. K.D. Gibson and S.J. Sibener *J. Phys. Chem. C*, 2014, 118 (50), 29077-29083

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# SOLUTIONS

## EIKONAL APPROXIMATION: MAIN TASKS

### Task 1: Question

Plot the three lowest index diffraction channels along the  $\langle 10 \rangle$  azimuth on your contour plot of the corrugation function in reciprocal space, from the tutorial on hard wall potentials. These channels correspond to reciprocal lattice vectors, and therefore to a set of planes in real space.

- Plot the three planes to which these azimuths correspond, in real space.
- Calculate, and plot, the reciprocal lattice vectors. Verify that these are normal to the planes you have plotted. You may use the function `unitCellVecs` in the class `auxCls`.

### Task 1: Solution

If we consider our contour plot of the corrugation function before, which effectively sums up the positions of the atoms, it is trivial to see that there are an infinite set of such planes corresponding to reciprocal lattice vectors of the form  $\mathbf{G} = n\langle 1\ 0 \rangle$  for some integer  $n$ . They are separated by a perpendicular distance of  $a/2$  with normal in the  $x$  direction, so will appear as vertical lines on our plot. Note that we reuse the definition of `sample_zeta_2()` from the hard-wall corrugation tutorial (see appendix).

```
1 %-----
2 % define lattice parameters and compute lattice vectors
3 %-----
4
5 % Lattice parameter /A (Angstroms)
6 a = 4.52;
7
8 % Corrugation depth /A (Angstroms)
9 h = 1;
10
11 % define (hexagonal) unit cell vectors for surface
12 [a1, a2, b1, b2] = auxCls.unitCellVecs(1,a,0);
13 b3 = b2 - b1;
14
```

```

15 %-----
16 %-----
17
18
19
20
21 %-----
22 % grid 2x2 unit cells and evaluate the potential across it
23 %-----
24
25 % a scaling factor for the number of cells included in the
    supercell
26 nCells = 2;
27
28 % Range along x and y axes -- note, norm(a1+2*a2) is the
    perpendicular height of unit cell
29 Lx = nCells*[-a/2 a/2]; Ly = nCells*[-norm(a1+2*a2)/2 norm(a1+2*
    a2)/2];
30
31 % Linspace across x and y axes
32 lx = linspace(Lx(1),Lx(2),30*nCells); lx(end) = [];
33 ly = linspace(Ly(1),Ly(2),50*nCells); ly(end) = [];
34
35 [x,y] = meshgrid(lx,ly);
36 R = [x(:) y(:)];
37
38 % evaluate corrugation at at each point on the real space grid
39 zeta = sample_zeta_2(R, h, b1', b2', b3');
40
41 %-----
42 %-----
43
44
45
46 %-----
47 % plot the scattering planes on top of the contour plot of the
    corrugation
48 %-----
49
50 % x-coords of first 3 planes from origin.
51 planePos = [-a/2 0 a/2]';
52
53 % PLOT:
54 fig2 = figure; hold on;
55
56 % Plot corrugation from tutorial 2.1.
57 pcolor(x,y,zeta); shading flat; axis equal
58
59 % Plot first 3 planes as projections on x-y plane (of any length
    ).
60 p = plot([planePos planePos]', repmat([-5 5]', 1, length(
    planePos)), 'm', 'LineWidth', 1.5);
61
62 legend([p(1) g], 'scattering planes', '<1 0> azimuth');
63
64 %-----
65 %-----

```

We would expect that these three planes would be normal to the reciprocal lattice vector  $\mathbf{G} = \langle 1 \ 0 \rangle$ . Thus, we can verify our solution by plotting this vector in real-space:

```

66 %-----
67 % define the reciprocal lattice vectors of interest (along the
    [1 0] direction)
68 %-----
69
70 % separation of first 3 reciprocal vectors in k-space.
71 dGx = 2*pi/(a/2);
72
73 % x- and y-components of first three [1 0] reciprocal lattice
    vectors in both direcs
74 Gx = [-3*dGx:dGx:3*dGx];
75 Gy = zeros(size(Gx));
76
77 % plot the [1 0] azimuth over the above range
78 g = plot(Gx, Gy, '--k', 'LineWidth', 1.5);
79 legend([p(1) g], 'scattering planes', '<1 0> azimuth');
80
81 %-----
82 %-----

```

Remember that `size()` returns a vector of all the dimensions of a matrix whereas `length()` only gives the dimension along the longest axis. When considering a matrix whose dimensions may change, one should always use `size`. Of note is the vector `Gx`, since it will be used in following questions. This vector contains the moduli of the first three non-spectral  $[1\ 0]$  diffraction channels (in both directions), plus the spectral  $G = 0$  channel.

## Task 2: Question

A beam of  $^4\text{He}$ , with mean beam-energy of  $E_i = 25\text{ meV}$ , and an incident angle of  $\Theta_i = 0\text{ rad}$  incident on the surface. Calculate, and plot, the diffraction intensities for the azimuths above (use a bar chart).

## Task 2: Solution

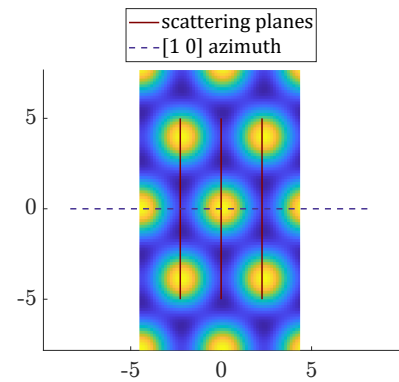
We first define a function `beamprops_1()`. This function returns the normal component of the incoming and outgoing wavevectors. Note the extensive precondition and postcondition statements. It is up to you as a programmer to make sure that your code is used correctly by others (or your future self).

On line 19 we apply the definition of the quantum-mechanical kinetic energy operator. We then use The Laue condition on line 19, subject to the elastic condition that  $k_i = k_f$ ; this determines the set of outgoing angles, for the given set of reciprocal vectors  $\mathbf{G}$ . Only the moduli of these vectors are important here since we are only considering the  $[1\ 0]$  azimuth. To maximise the set of considered outgoing beams, this set should contain as many moduli as possible.

```

1 %-----
2 % define a function beamprops_1
3 %-----

```



**Figure 1** | Plot of the corrugation function of the surface, overlayed with both the scattering planes and the corresponding reciprocal vectors/scattering azimuths.

```

4 function [k_iz, k_Gz] = beamprops_1(energy, mass, inAngle, G)
5     % PRECONDITION: - energy in meV
6     %                 - mass in atomic mass units
7     %                 - inAngle is known and in radians
8     %                 - G is a vector of (moduli of) allowed
9     %                   reciprocal lattice vectors
10    %                 - outAngle is variable
11    %                 - Scattering is elastic and the Laue
12    %                   condition is satisfied
13    % POSTCONDITION:
14    %                 - k_iz is a scalar
15    %                 - k_Gz is a vector where each element k_Gz(i)
16    %                   is an allowed component corresponding to a reciprocal
17    %                   vector of modulus G(i)
18
19    % Reduced Planck's Constant in units such that k_i is in A
20    %   ^{-1}
21    hbar = 2.05;
22
23    % Incident beam wavevector /A^{-1}
24    k_i = sqrt(2*mass*energy)/hbar;
25
26    % Laue Condition || surface + elastic collision => k_i(sin(
27    %   outAngle)-sin(inAngle)) = G
28    outAngle = asin(G/k_i + sin(inAngle));
29
30    % Perpendicular component
31    k_iz = -k_i*cos(inAngle);
32    % Elastic collision => |k_i|=|k_G| for all G.
33    k_Gz = k_i*cos(outAngle);
34 end
35 %-----
36 %-----

```

Now that we have defined this function, the task reduces to applying the equation for the Eikonal approximation of the scattered amplitude. We will need to integrate to find  $P(\mathbf{G})$  for each considered reciprocal vector  $\mathbf{G}$ . However, in this case we consider only the first three reciprocal lattice vectors (as in question 1). For simple systems this should provide a reasonable approximation since the distribution over  $G$  has a sharp peak at the specular  $G = 0$  beam that decays to smaller intensity contributions for larger  $G$ .

We begin by defining our scattering parameters and passing them into the `beamprops_1()` function. It is assumed that the parameters defined in the previous question are still stored in the workspace.

```

1 %-----
2 % define scattering parameters and compute the wavevector
3 %   components for each scattering azimuth
4 %-----
5 % Incident energy /meV
6 E = 25;
7
8 % Probe particle mass /amu
9 m = 4;
10
11 % Incident angle /rad

```



```

12 theta_i = 0;
13
14 % BEAM PROPAGATION:
15 [k_iz, k_Gz] = beamprops_1(E, m, theta_i, Gx); % We pass in Gx
           here b/c all Gy(i)=0
16
17 % area of unit cells considered
18 S = numCells^2 * norm(cross([a1 0], [a2 0]));
19
20 %-----
21 %-----

```

We then iterate over the set of 7 moduli of the reciprocal lattice vectors  $\mathbf{G}$ , using the Eikonal formula and kinematic correction to calculate the intensity for each momentum transfer (and thus each outgoing angle).

```

22 %-----
23 % diffraction intensity calculation
24 %-----
25
26 for n=1:length(Gx)
27     % amplitude from single scattering center, j, for a given G:
28     A_j = exp(1i*(Gx(n)*x+Gy(n)*y+(k_Gz(n)-k_iz)*zeta));
29
30     % Integrate over unit cell to obtain total amplitude for the
        given G:
31     A = 1/S * trapz(y(:,1),trapz(x(1,:),A_j,2));
32
33     % Total intensity for given G:
34     P(n) = abs(k_Gz(n)/k_iz) * abs(A)^2;
35 end
36
37 %-----
38 %-----

```

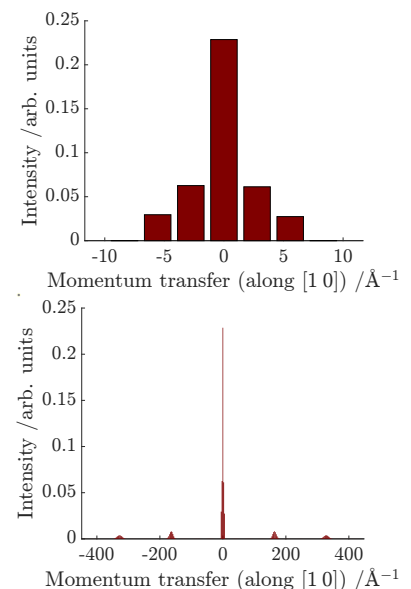
As mentioned in the theoretical background, it can be useful to check the unitarity of intensities to verify the validity of any modelling assumptions. Of course, since we only included the first three non-specular beams, this sum will be well below unity. However, the *relative* intensities can be shown to still be accurate even for poor unitarity, so the qualitative shape of the distribution is still useful.

```

39 %-----
40 % check validity of model and plot intensity distribution
41 %-----
42
43 % Sum of all intensities
44 U = sum(P, 'all')
45
46 % Bar graph plot
47 fig3 = figure; hold on
48 bar(Gx,P)
49 %-----
50 %-----

```

We can explore more of the diffraction pattern by redefining  $G_x$  to the larger range  $[-160*dG_x:dG_x:160*dG_x]$ . This is given in the margin.



**Figure 2** | The intensity of the scattered beam as a function of the parallel momentum transfer. The bottom figure uses a wider range of reciprocal lattice vectors than the top figure. Hence the bottom figure accounts for a wider range of momentum transfers.

### Task 3: Question

The scattering angle  $\delta$  is a variable. Explore the effect of varying the incident angle, the beam energy, and the corrugation. What do you observe? Repeat the above with  $^3\text{He}$ . What do you notice?

### Task 3: Solution

This is a task for you to explore on your own - however, there are a few general trends that are worth mentioning. Clearly varying the energy and mass have the same effect, causing all peaks to broaden, and causing unusual behaviour in the central peak. Varying the incident angle skews the distribution, so the peak in intensity moves from away from  $G_x = 0$  (*i.e.* moves away from the specular peak).

### Task 4: Question

The scattering angle is fixed at  $\delta = 95.8^\circ$ . The incident angle  $\theta_i$  is now a variable. Compare your code with that in [2] - it should produce similar results.

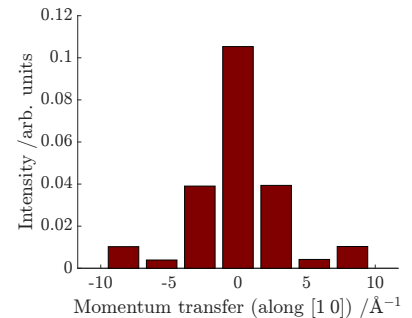
### Task 4: Solution

The only necessary change to our existing code is to switch to a new function, denoted `beamprops_2()`. This finds the normal component of the wavevector for the incoming and scattered waves. The majority of the function is the same. Explicitly, the new function is:

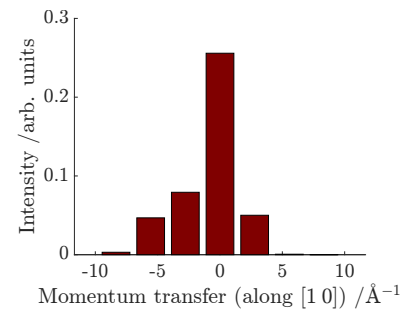
```

1 %-----
2 % define a function beamprops_2 to solve the problem
3 %-----
4 function [k_iz, k_Gz] = beamprops_2(energy, mass, sctAngle, G)
5     % PRECONDITION: - energy in meV
6     %                 - mass in atomic mass units
7     %                 - sctAngle is known and in radians
8     %                 - G is a vector of (moduli of) allowed
9     %                   reciprocal lattice vectors
10    %                 - inAngle is variable
11    %                 - Scattering is elastic and the Laue
12    %                   condition is satisfied
13    % POSTCONDITION: - k_iz is a scalar
14    %                 - k_Gz is a vector where each element k_Gz(
15    %                   i) is an allowed component corresponding to reciprocal
16    %                   vector G(i)
17
18    % Reduced Planck's Constant in units such that k_i is in A
19    %                   ^{-1}
20    hbar = 2.05;
21
22    % Incident beam wavevector /A^{-1}
23    k_i = sqrt(2*mass*energy)/hbar;

```



**Figure 3** | Plot of scattering intensity against momentum transfer as previously, with an energy of  $E = 50$  meV.



**Figure 4** | Plot of scattering intensity against momentum transfer as previously, with an incident angle of  $\theta_i = \pi/6$ .

The difficult part of the problem arises in solving the Laue equation

$$\frac{G}{k_i} = \sin(\delta - \theta_i) - \sin(\theta_i).$$

The easiest way to solve this is to expand rewrite the trigonometric functions as

$$\begin{aligned} \frac{G}{k_i} &= \sin \delta \cos \theta_i - (1 + \cos \delta) \sin \theta_i; \\ &= R \cos(\theta_i + \phi), \end{aligned}$$

where  $R$  and  $\phi$  are constants. This yields the constants as:

$$\begin{aligned} R &= 2 \cos(\delta/2); \\ \phi &= \tan^{-1}(\cot(\delta/2)); \\ &= \frac{\pi - \delta}{2}. \end{aligned}$$

```

19 % Laue Condition || surface + elastic collision
20 theta_i = acos(G/(1.34085*k_i)) - 0.73478;
21
22 % Perpendicular component
23 k_iz = -k_i*cos(theta_i);
24 % Elastic collision => |k_i|=|k_G| for all G.
25 k_Gz = k_i*cos(sctAngle-theta_i);
26 end
27 %-----
28 %-----

```

We then need only switch the function used in our main code, since the angles aren't directly used in our calculation - the rest is precisely the same.

```

1 %-----
2 % SCATTERING PARAMETERS:
3 %-----
4
5 % Incident energy /meV
6 E = 25;
7
8 % Probe particle mass /amu
9 m = 4;
10
11 % Scattering angle /rad
12 delta = 95.8 * pi/180;
13
14 %-----
15 %-----
16
17 % We use zeta_1 as defined and scaled (to a depth of 1A) in the
   hard wall potentials tutorial.
18
19 % BEAM PROPAGATION:
20 [k_iz, k_Gz] = beamprops_2(E, m, delta, Gx);
21 ...

```

This demonstrates the usefulness of separating your code into separate functions with different behaviour. You may notice that both the functions also shared a lot of code. If you wish, you may try looking into overloaded functions, and think how this might allow you to do even less work! Beware of over-engineering your code!

Note how fixing the scattering angle causes the distribution to become skewed. This distribution is of interest for measuring devices that have a fixed angle between the source and detector.

## ADLAYERS: MAIN TASKS

These tasks focus on applying the Eikonal approximation to adlayers.

### Task 1: Question

Assuming the surface is as described in the theoretical background, write the Eikonal formula for the diffraction amplitude as the Fourier transform of two phase factors, one for each of the corrugation functions. Note we are still assuming that the scattering centres are continuously distributed across the surface so it is reasonable to apply the integral formulation for the scattering amplitude.

### Task 1: Solution

From the hard wall potential tutorial, the Eikonal formula for the scattering amplitude from a surface is given by

$$A(\mathbf{G}) = -\frac{1}{S} \int_S e^{i(k_{Gz} - k_{iz})\zeta(\mathbf{R})} \cdot e^{i\mathbf{G} \cdot \mathbf{R}} d^2\mathbf{R}.$$

Assuming that the Eikonal assumptions hold for both corrugation terms  $\zeta_a$  and  $\zeta_s$  individually, the Eikonal approximation for the amplitude can be separated as:

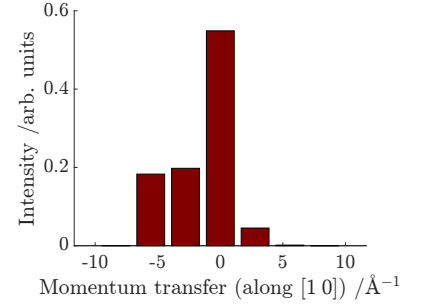
$$\begin{aligned} A(\mathbf{G}) &= -\frac{1}{S} \int_S e^{i(k_{Gz} - k_{iz})\zeta_a(\mathbf{R})} \cdot e^{i(k_{Gz} - k_{iz})\zeta_s(\mathbf{R})} \cdot e^{i\mathbf{G} \cdot \mathbf{R}} d^2\mathbf{R}; \\ &= -\frac{4\pi^2}{S} \mathcal{F} [e^{i(k_{Gz} - k_{iz})\zeta_a(\mathbf{R})} \cdot e^{i(k_{Gz} - k_{iz})\zeta_s(\mathbf{R})}]; \\ &= -\frac{4\pi^2}{S} \mathcal{F} [\phi_a \cdot \phi_s]. \end{aligned}$$

### Task 2: Question

Using the convolution theorem, show that the total scattering amplitude can be written as:

$$A(\mathbf{G}) = \mu(A_a + A_s),$$

for some constant  $\mu$ . Calculate the value of  $\mu$  required for this equality.



**Figure 5** | Plot of scattering intensity against momentum transfer as previously, with an fixed scattering angle of  $\delta = 95.8^\circ$ .

### Task 2: Solution

The convolution theorem states that, for arbitrary functions  $f$  and  $g$ :

$$\begin{aligned}\mathcal{F}[f * g] &= \mathcal{F}[f] \cdot \mathcal{F}[g]; \\ \mathcal{F}[f \cdot g] &= \mathcal{F}[f] * \mathcal{F}[g].\end{aligned}$$

Applying the second identity to the formula for  $\hat{A}(\mathbf{G})$  derived in task 1, we obtain:

$$\begin{aligned}A(\mathbf{G}) &= -\frac{4\pi^2}{S} \mathcal{F}[\phi_a \cdot \phi_s]; \\ &= -\frac{4\pi^2}{S} \mathcal{F}[\phi_a] * \mathcal{F}[\phi_s].\end{aligned}$$

Writing the components of the scattered amplitude as

$$\begin{aligned}A_a(\mathbf{G}) &= -\frac{4\pi^2}{S} \mathcal{F}[\phi_a]; \\ A_s(\mathbf{G}) &= -\frac{4\pi^2}{S} \mathcal{F}[\phi_s],\end{aligned}$$

both with the same constant of proportionality as  $A(\mathbf{G})$ , the scattered amplitude becomes:

$$A(\mathbf{G}) = -\frac{1}{(2\pi)^2} \frac{S_a S_s}{S} (A_a * A_s),$$

where  $S$  is the area of a unit super cell, defined by the periodicity of both the substrate and adsorbates.

### Task 3: Question

Calculate the intensity distribution of diffraction from a complete adsorbate layer with hexagonal symmetry of  $(3 \times 3)R\frac{\pi}{6}$  on a hexagonal Cu(111) surface using the corrugation functions (and much of the code) from previous. You should make use of the information in [1]. Assume the incident conditions of the beam are the same as in the task above.

### Task 3: Solution

Cu has the face-centred cubic structure, with its close-packed hexagonal planes having Miller indices of {111}. Thus, the corrugation is exactly the same as in tutorials 2.1 and 2.2 but with a lattice parameter of  $a = 3.61/\sqrt{2} \text{ \AA} \approx 2.55 \text{ \AA}$ . This lattice is defined by the symmetry  $(1 \times 1)R\frac{\pi}{6}$ .

The adsorbate layer, then, has an effective lattice parameter 3× that of the substrate. Considering the figure in [1], it is clear that some

adatoms lie on top sites on the underlying lattice. We take one of these sites to be our origin in the plane.

In the following solution we compile code from the first two parts as a summary of this tutorial.

We begin by defining our scattering parameters, as well as the set of moduli for the reciprocal lattice vectors along the  $[1\ 0]$  azimuth, denoted  $G_x$ . The `beamprops_1()` function as defined in the appendices, which calculates the incident wavevector and the set of allowed outgoing wavevectors.

```

51 %-----
52 % scattering parameters
53 %-----
54
55 % hexagonal plane lattice constant
56 a = 2.55;
57
58 % Incident energy /meV
59 E = 25;
60
61 % Probe particle mass /amu
62 m = 4;
63
64 % Incident angle /rad
65 theta_i = 0;
66
67 % Substrate corrugation depth /A
68 hs = 1;
69
70 % Adsorbate corrugation depth /A
71 ha = 1;
72
73 %-----
74 %-----
75
76
77
78
79 %-----
80 % define reciprocal lattice vectors of interest and calculate
    corresponding wavevector components
81 %-----
82
83 % define reciprocal lattice vectos for [10] azimuth o surface (
    actually [110] in 3D lattice but we assume an in-plane basis
    ):
84
85 % reciprocal point spacing along [10]
86 dGx = 2*pi/(a/2);
87
88 % set of first three x-components in either direction, plus
    zeroth
89 Gx = [-3*dGx:dGx:3*dGx];
90
91 % y-component zero along [10] azimuth
92 Gy = zeros(size(Gx));
93
94 % beam propagation
95 [k_iz, k_Gz] = beamprops_1(E, m, theta_i, Gx);

```

96

97 %-----

98 %-----

We then define unit cell vectors for the substrate and adsorbate, since both lattices have different lattice parameters and orientations. We additionally define a third “redundant” reciprocal lattice vector for both lattices, since this will allow us to use three Fourier components in our corrugation functions.

99 %-----

```
100 % define unit cell vectors and reciprocal vectors for substrate
    and adsorbate layers
```

101 %-----

102

103 % substrate vectors

```
104 [a1s, a2s, b1s, b2s] = auxCls.unitCellVecs(1,a,0);
```

105

106 % adsorbate layers &gt; 3x the lattice parameter

```
107 [a1a, a2a, b1a, b2a] = auxCls.unitCellVecs(1,3*a,30);
```

108

```
109 % define third 'redundant' reciprocal lattice vectors for both
    substrate and adsorbate
```

```
110 b3s = b2s - b1s;
```

```
111 b3a = b2a - b1a;
```

112

113 %-----

114 %-----

The following code generates a meshgrid for a square of  $7\sqrt{3} \times 7\sqrt{3}$  substrate unit cells. This factor is chosen since these are the dimensions of the so-called ‘supercell’, which encapsulates the periodicity of *both* the substrate and adsorbate lattices. There is no need to generate a meshgrid for the adsorbate lattice since we can simply use the same one.

115 %-----

```
116 % grid supercell of the ensemble with origin at the centre
```

117 %-----

118

```
119 % scaling factor for the number of cells included in the
    supercell
```

```
120 nCells = 7*sqr(3);
```

121

```
122 % Range along x and y axes -- note, norm(a1+2*a2) is the
    perpendicular height of unit cell
```

```
123 Lx = nCells*[-a/2 a/2]; Ly = nCells*[-norm(a1s+2*a2s)/2 norm(a1s
    +2*a2s)/2];
```

124

```
125 % Linspace across x and y axes
```

```
126 lx = linspace(Lx(1),Lx(2),30*nCells); lx(end) = [];
```

```
127 ly = linspace(Ly(1),Ly(2),50*nCells); ly(end) = [];
```

128

```
129 % meshgrid across range with desired resolution
```

```
130 [x,y] = meshgrid(lx,ly);
```

```
131 R = [x(:) y(:)];
```

132

133 %-----

134 %-----

This allows us to evaluate the corrugations for both lattices using the 3-Fourier component `sample_zeta_2()` function defined in the appendices. Plotting these corrugations using `contourf()` may be useful to check that the scaling and orientation of both lattices are correct.

```

135 %-----
136 % evaluate corrugations for both substrate and adsorbate layers
    then resize to fit meshgrid formulation
137 %-----
138
139 % individual corrugations
140 zeta_s = reshape(sample_zeta_2(R, hs, b1s', b2s', b3s'), size(x)
    );
141 zeta_a = reshape(sample_zeta_2(R, ha, b1a', b2a', b3a'), size(x)
    );
142
143 % total corrugation
144 zeta = zeta_s + zeta_a;
145
146 %-----
147 %-----

```

The problem then reduces to calculating the intensities for each reciprocal lattice vector as before:

```

148 %-----
149 % diffraction intensity calculation
150 %-----
151
152 % area of unit cell
153 S = numCells^2 * norm(cross([a1 0], [a2 0]));
154
155 for n=1:length(Gx)
156     % Amplitude from single scattering centre
157     A_j = exp(1i*(Gx(n)*x+Gy(n)*y+(k_Gz(n)-k_iz)*zeta));
158
159     % Total amplitudes
160     A = 1/S * trapz(y(:,1),trapz(x(1,:),A_j,2));
161
162     % Intensities
163     P(n) = abs(k_Gz(n)/k_iz) * abs(A)^2;
164 end
165
166 %-----
167 %-----

```

Once again, one can calculate the sum of intensities to check the validity of the model, however given that in this tutorial there are additional assumptions on top of the Eikonal assumptions, the unitarity will likely be even worse!

```

168 %-----
169 % check validity of approximation then plot the intensity
    distribution
170 %-----
171
172 % Sum of all intensities
173 U = sum(P, 'all');
174

```



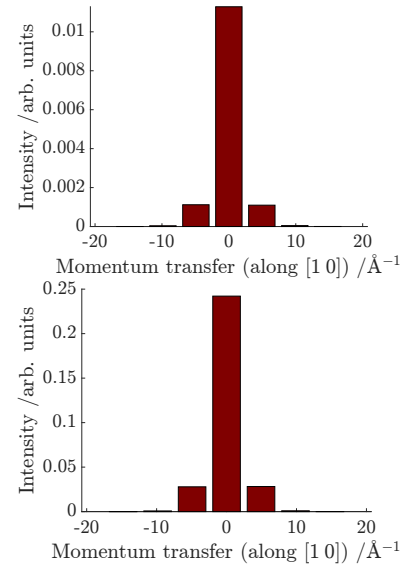
```

175 % Bar graph plot
176 fig3 = figure; hold on
177 bar(Gx,P)
178 %axis([-20 20 0 0.1]) % Useful if you wish to inspect specific
    regions of the graph
179
180 %-----
181 %-----

```

Running the above code gives the figure in the margin.

So the adsorbate layer seems to have the effect of reducing the peak intensity due to the lattice mismatch, but still has the same general distribution since it is an ordered layer. Thus the resultant distribution is of the same general shape as both single distributions. You may wish to investigate how this broadening varies with the corrugation height of the adsorbate layer (assumed 1 Å in the above).



**Figure 6** | Top: plot of scattering intensity against momentum transfer for the first three momentum transfers along the [1 0] azimuth when adsorbates form a complete adlayer on top of the substrate. Bottom: plot of scattering intensity against momentum transfer for the first three momentum transfers along the [1 0] azimuth in the absence of adsorbates.