

# ASSIGNMENT 4: THE EIKONAL APPROXIMATION

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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