

# PROJECTS IN SURFACE PHYSICS: THE THEORY HANDBOOK

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# FOURIER TRANSFORMS

## INTRODUCTION

Our first object of study is the Fourier transform (FT) - a technique with which you will become increasingly comfortable, vital to the analysis of most problems you will encounter in your study of surface physics. A tremendously *ad hoc* approach, serving little justice to the procedure, would be to state that it “picks out” the constituent frequencies making up a waveform. There are a multiplicity of applications (far beyond those of signal analysis); however, we will not list them in the introduction: there are far too many for it to be a productive affair.

A common complaint that arises when students first meet the FT is to feel frustration at the lack of intuition developed from typical sources: we aim to provide an approach that rapidly builds a deep understanding of how the FT behaves, and how it can be used in the real world. Whilst this chapter is far from comprehensive, it offers a perspective that permits the reader to approach all of the Fourier-based mathematics later in this handbook with ease, along with that which they may encounter when reading recent research.

## THE DEFINITION OF THE FT

Unfortunately, it is difficult to develop an intuition for the Fourier transform. It is significantly more nuanced than other operations met near the start of a typical undergraduate course, and such, it is easy to overlook. To better understand what this means, consider the example of a novel student of calculus, who may, quite reasonably for introductory calculus, treat differentiation and integration as the tasks of finding gradients and areas under curves. In introducing the Fourier transform, no primitive explanation with similar simplicity can be given. We must resort to the more abstract notion of the “picking out frequencies” approach, which is not so straightforward to interpret. Thus our first two tasks are to provide a mathematical definition of the FT, and to interpret it.

### FT of a Continuous Function

We define the Fourier transform  $F(k)$  of a continuous function  $f(x)$  first with the operator  $\mathcal{F}$ , such that:

$$F(k) = \mathcal{F}[f(x)],$$

which takes the form of

$$F(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(x) e^{-ikx} dx.$$

At first, it is not clear what this can be interpreted as. Soon, it will be clear why the FT is quite so incredible. We also define the inverse Fourier transform  $\mathcal{F}^{-1}$  with

$$F(k) = \mathcal{F}^{-1}[f(x)] = \int_{-\infty}^{\infty} f(x) e^{ikx} dx.$$

There is a small note we must make at the end of this section. Different authors will use different coefficients for the FT, but “overall”, it must be  $1/2\pi$ . There are also a few different notations for the transformed function: the most common alternative to  $F$  being  $\tilde{f}$ .

### FT of a Dirac Delta

To successfully understand the intuition of the Fourier transform, it is necessary to understand the behaviour of the Dirac delta when operated on by the Fourier transform; fortunately, this is not difficult to calculate - but requires the reader to know what a Dirac delta function is. We define this delta  $\delta$  as the function with the properties:

$$\begin{aligned} \delta(x - a) &= 0, & x &\neq a; \\ \int_R f(x) \delta(x - a) dx &= \begin{cases} 0 & a \notin R; \\ f(a) & a \in R, \end{cases} \end{aligned}$$

the second line of which, with some thought, should indicate to the reader the effect of the Fourier transform on the Dirac delta function. We can immediately write that:

$$\mathcal{F}[\delta(x - a)] = e^{-ika},$$

which also tells us what the FT of any constant complex exponential looks like! We will use this in the next section.

### Interpretation

To yield a good understanding of the Fourier transform, the author’s preferred approach is to consider the effect of performing the FT on

a sinusoid. Why is this? One can construct a Fourier series for any function, and then FT the *Fourier series*. This naturally leads to the approach of considering the constituent frequencies of the function.

What is our starting point? We can set the function  $f(x)$  as a pure sine function, and then transform it. Let

$$f(x) = \sin(2\pi Cx),$$

where  $C$  is an arbitrary constant. The Fourier transform is:

$$F(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \sin(2\pi Cx) e^{-ikx} dx,$$

which can be more conveniently written as:

$$F(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} (0.5ie^{-2\pi i Cx} - 0.5ie^{2\pi i Cx}) e^{-ikx} dx,$$

which yields the result

$$\mathcal{F}[\sin(2\pi Cx)] = \frac{1}{2i} [\delta(k - C) - \delta(k + C)].$$

Do let this sink in. The Fourier transform of a sinusoid is a collection of two Dirac delta functions. These are located at coordinates symmetrical about the origin in reciprocal space, which are proportional to the frequency of the sinusoid.

There is an equivalent expression for a cosine function. We will state it without proof; however, the proof is elegant enough for the reader to go through in their head. This is that

$$\mathcal{F}[\cos(2\pi Cx)] = \frac{1}{2} [\delta(k + C) + \delta(k - C)].$$

The tools we have just developed are of immense power. To see why, consider the Fourier series of a periodic function  $f(x)$ . This is:

$$f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} \left( a_n \cos \frac{n\pi x}{L} + b_n \sin \frac{n\pi x}{L} \right),$$

where  $a_0$ ,  $a_n$  and  $b_n$  are constants, and  $L$  is the half period of the function. Ignoring the constant term at the start, it is clear that the Fourier transform of a Fourier series is a collection of Dirac deltas at the frequencies of the constituent frequencies, scaled by the coefficients in the Fourier series.

There is one major flaw in this treatment; very few functions are periodic, and so this interpretation is not exact for non-periodic functions. However, since a Fourier transform does not care for whether or not the function is periodic, the treatment above is approximate - it leads to the Fourier transform being (usually) continuous, rather than a discrete collection of delta functions.

## SUMMARY

This chapter has provided an intuitive background into the Fourier transform. The reader should note this is as brief as introductions into the topic are likely to be; most authors jump straight into producing a table of transformed functions, with little regard for the reader's understanding for the topic.

## FURTHER READING

See any undergraduate text on mathematical physics for a discussion of Fourier series, if this is unfamiliar to you. Parseval's theorem. Glance over, but do not memorise, a Fourier transform table.

## PROBLEMS

1. The function  $f(x)$  is defined such that  $f(x)$  is normally distributed, with standard deviation  $\sigma$ .
  - a) Find the Fourier transform  $F(k)$ .
  - b) Show that the product of the standard deviations of  $F(k)$  and  $f(x)$  is unitary.
  - c) Describe, in words, the breadth of the Fourier transformed function  $F(k)$  relative to  $f(x)$ .
2. The function  $f(x)$  is defined to be a "comb" of delta functions. This has the formula:

$$f(x) = \sum_i c_i \delta(x - a_i),$$

where  $c_i$  and  $a_i$  are constants. Find the Fourier transform  $F(k)$ . Can you think of a physical interpretation of this formula and its transform?

3. A generic function  $f(x)$  is Fourier transformed, giving a function  $F(k)$ .
  - a) What is the inverse Fourier transform of  $F(k)$ ?
  - b) Is this the same, for all valid definitions of the FT?

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# CONVOLUTION

## INTRODUCTION

On many occasions, we may wish to find the overlap between two functions. There is a simple mathematical formulation to calculate this quantity; we will explore this in the current chapter, without using unnecessary detail. As condensed matter physics frequently uses Dirac delta functions in its mathematical framework, our discussion of convolution will focus on the behaviour of the convolution on a so-called delta “comb”. We will also discuss the relation between the Fourier transform and the convolution function.

## THEORY

### Definition

The first task in our discussion of convolution is to provide a mathematical definition of what it is, and how it behaves. Defining the convolution  $f(x) * g(x)$  as the output of an operator, taking an input of *two* functions  $f(x)$  and  $g(x)$ , we can write:

$$f(x) * g(x) = \int_{-\infty}^{\infty} f(y)g(x - y)dy,$$

where  $y$  is a temporary variable. The asterisk between the two functions is a “binary operator” (of which the  $+$ ,  $-$ , and  $\times$  symbols are further examples), so indicates that the operator takes two inputs, and not one!

### Relation to the Fourier Transform

There is a very deep connection between the Fourier transform and the convolution, which we will explore here. Suppose that, again, we have two functions of a single variable. We denote these, again, as  $f(x)$  and  $g(x)$ . Let us consider the fourier transform of the product of these functions (*i.e.* the FT of  $f(x)g(x)$ ).

Noting that the original functions  $f(x)$  and  $g(x)$  are the inverse of



their Fourier transforms  $F(u)$  and  $G(v)$ , we can write:

$$f(x) = \int_{-\infty}^{\infty} F(u) e^{2\pi i u x} du;$$

$$g(x) = \int_{-\infty}^{\infty} G(v) e^{2\pi i v x} dv,$$

which we can use to find a useful expression for the product. It is important to note that the form of the FT used here is a little different to that used in the chapter § *Fourier Transforms*; however, they are equivalent in interpretation. The can be summarised with the process:

$$f(x)g(x) = \int_{-\infty}^{\infty} F(u) e^{i2\pi u x} du \int_{-\infty}^{\infty} G(v) e^{i2\pi v x} dv;$$

$$= \int_{-\infty}^{\infty} F(u) \int_{-\infty}^{\infty} G(v) e^{i2\pi(v+u)x} dv du,$$

which, with the substitution  $y$  as the sum of  $u$  and  $v$ , the most recent line becomes:

$$\int_{-\infty}^{\infty} F(u) \int_{-\infty}^{\infty} G(y-u) e^{i2\pi y x} dy du = \int_{-\infty}^{\infty} \left( \int_{-\infty}^{\infty} F(u) G(y-u) du \right) e^{i2\pi y x} dy,$$

which is the inverse Fourier transform of the convolution! Thus it is clear that:

$$\mathcal{F}[f(x) * g(x)] = \mathcal{F}[f(x)] \mathcal{F}[g(x)],$$

which is more commonly known as the *convolution theorem*. It should be noted that  $\mathcal{F}$  represents the Fourier transform, in operator form. There is an additional expression in the convolution theorem. We can also show that

$$\mathcal{F}[f(x)] * \mathcal{F}[g(x)] = \mathcal{F}[f(x)g(x)].$$

Why is the convolution theorem useful? It is often an unpleasant task to manually calculate the convolution of two functions. The convolution theorem allows us to bypass this issue, by multiplying together the FT of each of the two functions.

## PROPERTIES

With the convolution of two functions being a more abstract operator than those with which you may be familiar, it is best that we briefly list the key properties; this list is non-exhaustive, but summarises what you need to know to use the convolution of functions in solid state physics. The following are some important properties:

1. **Commutativity:**  $f * g = g * f$
2. **Associativity:**  $f * (g * h) = (f * g) * h$
3. **Distributivity:**  $f * (g + h) = f * g + f * h$
4. **Identity:**  $f * \delta = f$

## INTUITION

It is important to understand what a mathematical process does; otherwise, you will be unable to know when it feels “right” to use it. We will build an intuition using three very simple examples. As unlikely as this sounds, it is enough to understand what happens during convolution!

Before this discussion, we must realise what a convolution would look like, if we were to animate it. Using the typical  $f(x)$  and  $g$  notation, we examine the formula defining convolution. The convolved function, at any  $x$ , is the area under the product of  $f(y)$ , and  $g(x - y)$ . The first of these functions is clear, as we take having it for granted. But what about  $g(x - y)$ ? This is the original shape, but translated by  $x$ , and reflected along the vertical!

### Step Function & Delta Function

For all three cases, we will make an *a posteriori* argument using the figure; the mathematics is tedious, and will not be a worthwhile use of space. First, we have a delta function (red), and a step function (violet). What is the convolution of these functions? To understand what occurs, note how the convolution at  $x$  depends on the separation of the functions. If they are too far separated, the overlap is minimal; this causes the convolution at this value of  $x$  to be small! If the separation is small, the overlap is large. This would give a large convolution.

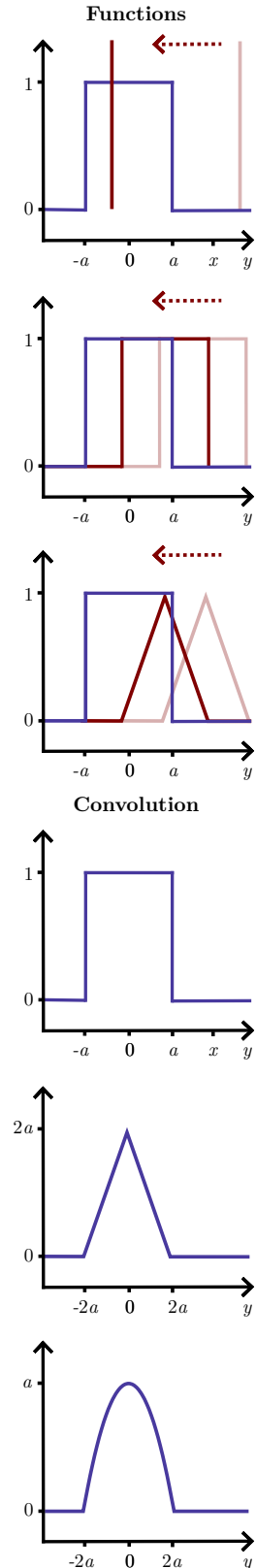
With the case of a delta function, our problem is dramatically simplified: it just picks out the value of  $f$ . No change occurs.

### Two Step Functions

By considering the same process, we can realise that the overlap between the functions starts at 0. It then increases to a maximum when the step functions are perfectly aligned, then decreases back to 0. What shape does the convolution take? It will be a triangular function!

### Step Function & Triangular Function

This case illustrates how the relative shape of the functions affects the shape of the convolution. When a saw-tooth moves over a step function, it traces out a quadratic convolution function! Convince yourself of why this is.



**Figure 1** | The convolution of functions in 3 different scenarios.

## SUMMARY

The convolution of two functions is:

$$f(x) * g(x) = \int_{-\infty}^{\infty} f(y)g(x-y)dy,$$

which obeys the convolution theorem, given by

$$\mathcal{F}[f(x) * g(x)] = \mathcal{F}[f(x)]\mathcal{F}[g(x)].$$

## FURTHER READING

Convolution is a mathematical tool that has a wide range of applications in different areas of physics. For a more detailed discussion, there are many authors writing at a level suitable for first year students. This includes Riley, Hobson & Bence's textbook.

## PROBLEMS

1. Quickly write down and convince yourself the four properties of convolution.
2. Given a finite sum of delta functions  $f(x)$  and a function  $g(x)$ , where:

$$f(x) = \sum_i \delta(x - x_i);$$
$$g(x) = e^{-x^2},$$

find the convolution  $f(x) * g(x)$ .

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# CRYSTAL STRUCTURES

## INTRODUCTION

While it is appealing to describe physical phenomena using words, it is necessary to quantify them; in the case of solid state physics, the start of the process to achieve this is an understanding of the mathematics behind a crystal lattice. In this chapter, we will begin to explore the necessities for the mathematical background of crystal structures, in order to approach problems in surface physics.

## THEORY: REAL SPACE LATTICES

The theory used in crystallography is well-established, and has resulted in the awarding of numerous Nobel prizes. Needless to say, it is an important field of study, and one with which the reader must be well acquainted; otherwise, they will be unable to understand more advanced theory, and will be unable to read most relevant papers. The most intuitive approach is to discuss first what a lattice is, and then some simple examples of them.

### Definition

It is a surprisingly difficult task to define what a lattice is, and one we must approach carefully - we must distinguish it from a crystal structure (the distinction will be explored soon). Hoffman [1] defines a lattice as “a set of regularly spaced points with positions defined as multiples of generating vectors”, which is a good start to describing a lattice. However, this approach does not capture the symmetry of the lattice; it is equally acceptable to allow any so-called “lattice point” to be the origin of the coordinate system. The lattice repeats over an infinite distance, so all points are effectively equivalent. Quantitatively, this is:

$$\mathbf{r} = h\mathbf{a}_1 + k\mathbf{a}_2 + \ell\mathbf{a}_3,$$

where:

1.  $\mathbf{r}$  is the position vector.
2.  $h$ ,  $k$  and  $\ell$  are constants. These will usually be integers.

3.  $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$  are the basis vectors for the lattice.

### Simple Cubic

For illustrative purposes, we will give the example of a simple cubic lattice. In such case, the  $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$  vectors are given in terms of the cartesian unit vectors as:

$$\mathbf{a}_1 = a\hat{\mathbf{x}};$$

$$\mathbf{a}_2 = a\hat{\mathbf{y}};$$

$$\mathbf{a}_3 = a\hat{\mathbf{z}},$$

where  $a$  is the lattice parameter. You should be able to work out what “lattice parameter” means from the lattice vectors; it is the length between adjacent lattice points along a particular basis direction. The reader should note, that despite its simplicity, the simple cubic structure is not very common! The reason why is due to how efficiently atoms can be arranged. The maximum possible packing efficiency arises from the “cubic close packed” (a variant of face centred cubic) and “hexagonal close packed” structures. Simple cubic is not even comparable - so is generally not favourable to form.

### Face Centred Cubic

In the case of a face centred cubic structure, the lattice vectors are:

$$\mathbf{a}_1 = a\hat{\mathbf{x}} + a\hat{\mathbf{y}};$$

$$\mathbf{a}_2 = a\hat{\mathbf{y}} + a\hat{\mathbf{z}};$$

$$\mathbf{a}_3 = a\hat{\mathbf{x}} + a\hat{\mathbf{z}},$$

For this lattice, the lattice parameter is the distance to the centre of a face, from a corner on the same face.

### Body Centred Cubic

The lattice vectors for a body centred cubic lattice are:

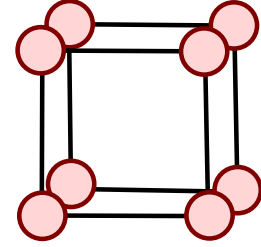
$$\mathbf{a}_1 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}});$$

$$\mathbf{a}_2 = \frac{1}{2}a(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}});$$

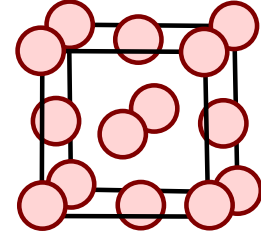
$$\mathbf{a}_3 = \frac{1}{2}a(\hat{\mathbf{x}} - \hat{\mathbf{y}} + \hat{\mathbf{z}}),$$

where the lattice parameter is the distance to the centre of the cube from a vertex on it.

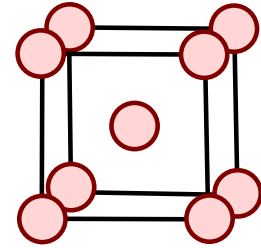
Simple Cubic



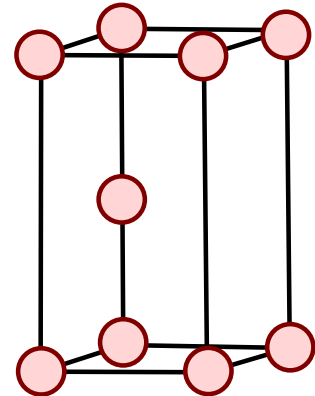
Face Centred Cubic



Body Centred Cubic



Hexagonal



**Figure 1** | The four most useful types of lattice.

## Hexagonal

The lattice vectors for a hexagonal lattice are:

$$\begin{aligned}\mathbf{a}_1 &= \frac{1}{2}a\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}a\hat{\mathbf{y}}; \\ \mathbf{a}_2 &= \frac{1}{2}a\hat{\mathbf{x}} - \frac{\sqrt{3}}{2}a\hat{\mathbf{y}}; \\ \mathbf{a}_3 &= c\hat{\mathbf{z}},\end{aligned}$$

where  $a$  is the side length of the hexagon, and  $c$  is the height of the unit cell.

## LATTICE COORDINATES

It is often useful to specify the positions of atoms in a structure. For this reason, *lattice coordinates* are used. These are coordinates, written as a trio of numbers, that represent the position of an atom as fractions of the distances along the axes of a unit cell.

## MILLER INDICES

In all typical crystal structures, it is intuitive to anticipate the existence of “planes” within the crystal. These are constructs that are very useful: they allow us to describe the crystal structure with greater clarity, and allow us to better quantify what we investigate in experiments. How do we describe the planes in a crystal? We use the notation  $(hkl)$  for a family of planes, which are known as the “miller indices” of the plane. What do we mean by a “family of planes”? These are all planes that are related by symmetry.

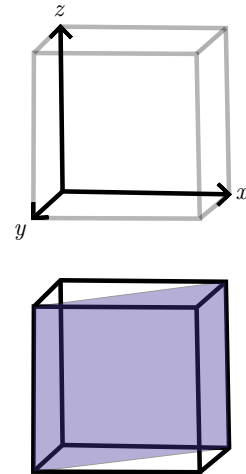
There is a very simple process to find the miller indices for a plane. This is listed below.

### Cubic Crystals

- Write down the 3 values of the coordinates at which the plane intersects the coordinate axes. If these are  $x_0$ ,  $y_0$  and  $z_0$ , then write down  $x_0$ ,  $y_0$ ,  $z_0$ . This is not the finished set of miller indices! Do not confuse it with such.
- Find the reciprocal of each coordinate above. To continue our example, this gives

$$\frac{1}{x_0}, \frac{1}{y_0}, \frac{1}{z_0}.$$

- Multiply the set by the smallest integer that makes each of the coordinates an integer. These are the miller indices  $(hkl)$ .



**Figure 2** | An example for finding the Miller index of a plane in a cubic structure. This plane is from the family  $(110)$ .

## Hexagonal Crystals

For hexagonal crystals, it is occasionally the case that the 3 indices used in the “miller indices” above do not reflect the symmetry of the crystal well. For this reason, there is an alternative notation for hexagonal crystals, using 4 numbers. What does this mean? The first three indices correspond to the ‘in the plane’ coordinates, as seen in figure 3, and the fourth index corresponds to the coordinate along the vertical. We can summarise this as

$$(h \ k \ - (h + k) \ l),$$

which we can easily calculate using the miller indices for cubic crystals.

There is an equivalent version of the lattice coordinates for hexagonal crystals, using four numbers! Try to work out what the additional number will represent. Check against online sources if you are unsure.

## CRYSTALS

We now have all the tools we need to understand the formalism of a crystal structure! The most simple definition of a crystal structure, distinguishing it from a lattice, is to state it is the “convolution of a lattice and a motif”. What does this mean? This section will explain this in greater detail, without going into unnecessary detail.

## Lattices & Delta Combs

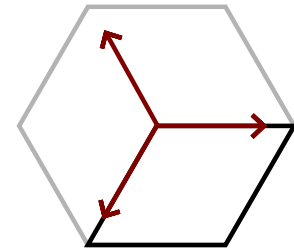
Our first task is to provide a formula that “describes” the lattice. Before we even state it, the reader should note that this description is entirely non-physical, as a delta function cannot exist in nature. Regardless, the lattice can be described as

$$\sum_i \delta(\mathbf{r} - \mathbf{r}_i),$$

where  $\mathbf{r}_i$  are the positions of the lattice points, and  $\mathbf{r}$  is a position vector. In rather poor style, we will abruptly switch to a new section. However, this is no excuse to dodge the physical interpretation of the formula! Realise that the formula returns the sum of the function of each position, when convolved with a function.

## Motif

What do we do now? We recall that we wish to provide a framework that describes a crystal lattice. It is possible to define a “motif” (or



**Figure 3** | An illustration of the three sources of high symmetry in a hexagonal lattice. An additional index is used, to ensure the overall symmetry of the crystal can always be described. A birds' eye view of the typical unit cell is in solid black. The two azimuths along the unit cell are assigned numbers corresponding to  $h$  and  $k$ .

“basis”), describing the atomic density around a lattice point. This does not include terms relating to all of the atoms in the entire crystal! By only including the atoms around a single lattice point, it becomes natural to find the convolution of the motif with the lattice, picking out the atomic density  $\rho$  for the entire crystal! This is what we desire.

How do we do this? The general case is quite abstract. By considering the example of the sodium chloride structure, we should be able to elucidate the procedure. We introduce an example motif as:

$$\rho_{\text{Na}}\delta(\mathbf{r}) + \rho_{\text{Cl}}\delta(\mathbf{r} - \frac{1}{2}\hat{\mathbf{x}} - \frac{1}{2}\hat{\mathbf{y}} - \frac{1}{2}\hat{\mathbf{z}}),$$

where  $\rho_{\text{Na}}$  and  $\rho_{\text{Cl}}$  are constants, corresponding to finding a sodium or chlorine atom at that position. What is the interpretation of this? By considering the argument of the delta functions, it is evident that there is a sodium atom at the origin, and a chlorine atom at the centre of the unit cell. Convolving with a face centred cubic lattice, we obtain:

$$\begin{aligned}\rho &= \sum_i \delta(\mathbf{r} - \mathbf{r}_i) * \left( \rho_{\text{Na}}\delta(\mathbf{r}) + \rho_{\text{Cl}}\delta(\mathbf{r} - \frac{1}{2}\hat{\mathbf{x}} - \frac{1}{2}\hat{\mathbf{y}} - \frac{1}{2}\hat{\mathbf{z}}) \right); \\ &= \sum_i \rho_{\text{Na}}\delta(\mathbf{r} - \mathbf{r}_i) + \rho_{\text{Cl}}\delta(\mathbf{r} - \frac{1}{2}\hat{\mathbf{x}} - \frac{1}{2}\hat{\mathbf{y}} - \frac{1}{2}\hat{\mathbf{z}} - \mathbf{r}_i),\end{aligned}$$

which looks like gibberish. However, carefully considering what each term represents, we can see that it does correctly represent the sodium chloride crystal structure!

## RECIPROCAL SPACE

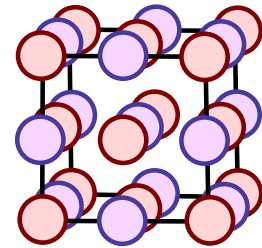
This section concerns the seemingly omnipresent so-called “reciprocal lattice”, encountered throughout the study of solid state physics. To explicitly define it, the reciprocal lattice is the Fourier transform of a real space lattice.

### Brillouin Zones

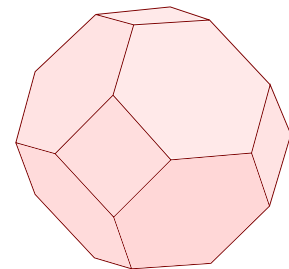
It is likely you will encounter a region known as a “Brillouin zone” when reading papers: this is a concept that can make some theory clearer. What is it? The “first Brillouin zone” is defined as the unique primitive unit cell around a lattice point, where a “primitive” unit cell contains only one lattice point, and wholly encloses it.

## SUMMARY

A lattice is a periodic array of points, repeating over an infinite distance. A motif is the collection of atoms placed on each lattice point,



**Figure 4** | The sodium chloride crystal structure.



**Figure 5** | The first Brillouin zone for an FCC structure. It is no easy task to find these in 3D!



which would generate the crystal structure desired for a given context. A reciprocal lattice is the Fourier transform of the real space lattice.

## REFERENCES

1. Hoffman, P. *Solid State Physics*. Chapter 1 (2015)

## FURTHER READING

Crystallography

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# VERLET INTEGRATION

## INTRODUCTION

On many occasions, the reader will encounter differential equations that describe a physical process. However, it is clear that these differential equations are not always easy to solve; in many cases, no analytical solution exists, so we must attempt to solve the system using another approach. It is often simple to provide a computational solution through many different approaches. In this chapter, we focus on the use of *Verlet integration* [1] to provide numerical solutions to differential equations.

## GENERALISED APPROACH

The essence of the Verlet integration algorithm relies on a process with which, regardless of whether you have realised it, you will be familiar: it has been used extensively in your prior studies. We first make a comment on the order of the differential equations you are likely to encounter (for reasons that will soon be clear) - being that it is unusual for a differential equation to be higher than second order in physics: classical equations use no higher time derivatives than acceleration (as an example), and modern physics has its analogous quantities. Thus these notes almost entirely focus on solving second order equations.

### ***n*th Order Differential Equations**

For the remainder of these notes, we will consider only the *n*th time derivatives of position. Should the reader wish, there is ample information in these notes to trivially bridge the gap to different quantities. The time derivatives of position will be familiar to you, but to state them explicitly, are the velocity and the acceleration. It cannot be emphasised enough that these are vector quantities, and not scalars! In addition, the derivatives of position can be resolved into (independent) components; these can be analysed separately, and by extension, can be programmed separately.

How do we start? After making a couple of assumptions, we have

enough information to make some very reasonable algorithms. Assume that, between times  $T$  and  $T + \delta t$ , where  $\delta t$  is a small increment, the  $n$ th derivative of position is approximately constant. We are interested in the solution to the equation:

$$\mathbf{r}^{(n)} = \mathbf{A}(\mathbf{r}),$$

*i.e.* an equation that contains only the  $n$ th derivative of a vector, and a function of the original vector. Note that the function  $\mathbf{A}$  projects a vector onto another vector. Why is this useful? Assuming linearity, we can form a solution to any  $n$ th order linear differential equation (but this is complicated, and you would likely be better off using a different algorithm for most orders).

How do we solve the equation? We can form an algorithm to iterate through, with our desired precision, the entire range of the input variable we wish to consider. To do this, it is important to consider the Taylor expansion of  $\mathbf{r}$ ; remembering  $\mathbf{r}$  is indeed continuous, we can Taylor expand the variable  $\mathbf{r}$  about the time  $n\delta t$  (where  $n$  is an integer - this will be discussed later) with respect to  $t$  to write the position as:

$$\mathbf{r}(t) = \mathbf{r}(n\delta t) + \mathbf{r}'(n\delta t)(t - n\delta t) + \frac{1}{2}\mathbf{r}''(n\delta t)(t - n\delta t)^2 + O(t^3),$$

where all of the symbols have been previously defined [2]. The  $t^3$  terms are ignored in anticipation of later results. What can we do with this? Substituting  $(n + 1)\delta t$  in place for  $t$  gives:

$$\mathbf{r}((n + 1)\delta t) = \mathbf{r}(n\delta t) + \mathbf{r}'(n\delta t)\delta t + \frac{1}{2}\mathbf{r}''(n\delta t)(\delta t)^2 + O((\delta t)^3),$$

which clearly has a very rich interpretation: using a fixed time interval  $\delta t$  gives a quantisation in an integer  $n$  that can be used to form an algorithm. Hopefully it is clear that if we denote the variable  $\mathbf{r}$  evaluated at  $n\delta t$  as  $\mathbf{r}_n$ , then we can write the position as the recurrence relation:

$$\mathbf{r}_{n+1} = \mathbf{r}_n + \mathbf{r}'_n\delta t + \frac{1}{2}\mathbf{r}''_n(\delta t)^2 + O((\delta t)^3),$$

which is the most basic step in our algorithm.

How do we proceed? It is not sensible to go any further in this section. The next process we will consider is how to continue working through the algorithm, to provide a useful numerical result.

## 2nd Order Differential Equation

For a 2nd order system, we have a special case: classically, we are briefly calculating the displacement due to a constant acceleration, through a time interval  $\delta t$ . The equations used here should be very

familiar! We can write the small change in position in a small time  $\delta t$  as:

$$\delta \mathbf{r} = \mathbf{u}_T \delta t + \frac{1}{2} \mathbf{a}_T (\delta t)^2,$$

where we have ignored the higher order terms. As you may anticipate:

1.  $\delta \mathbf{r}$  is the displacement from time  $T$  to  $T + \delta T$ .
2.  $\mathbf{u}_T$  is the velocity at a time  $T$ .
3.  $\mathbf{a}_T$  is the acceleration of the particle at a time  $T$ , treated as a constant over the entire duration  $\delta t$ .

At this point, it is useful to pause in thought. We must use the information above to create a suitable algorithm for solving the differential equation. How do we achieve this? We have enough knowledge to reduce the equation to an iterative process, using a time step of  $\delta t$ . It is simple to use an index  $n$  (an integer), to split up a time variable into  $n$  steps of  $\delta t$  from an initial time (set as 0, for simplicity). Using this notation, the time variable is quantised according to the chunks:

$$t = n \delta t,$$

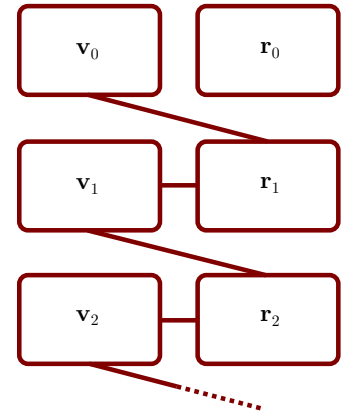
*i.e.* no other time than that specified by this equation is of interest to us. It is natural to then consider the variable previously assigned the letter  $T$ , and to set it as  $n \delta t$ . Changing the subscript from  $T$  to  $n$ , it is evident that:

$$\mathbf{r}_{n+1} = \mathbf{r}_n + \mathbf{u}_n \delta t + \frac{1}{2} \mathbf{a}_n (\delta t)^2,$$

where all of the symbols should be clear from previous definitions. Nothing in this equation should be unexpected; it represents the distance moved under an approximately constant acceleration. Making an algorithm with this is not challenging - it is entirely feasible that the acceleration at any given time can be specified by additional degrees of freedom (use Newton's second law to relate the acceleration to a force). The velocity presents an additional difficulty, in that it is not clearly specified here how  $\mathbf{u}_n$  evolves with increasing  $n$  - fortunately,  $\mathbf{u}_n$  follows from the definition of acceleration as

$$\mathbf{u}_{n+1} = \mathbf{u}_n + \mathbf{a}_n \delta t.$$

There is a common error with this step. Why not use the velocity as rate of change of position? Surely this will work? The reader should take care to not destroy any information in their algorithm. The recurrence relation for the position yields an operation that propagates the position, given a set of velocities; thus to ensure the algorithm works, an additional step is required to propagate the velocity between two time steps. This is achieved with the recurrence relation above - using the velocity as change in position divided by time yields no additional information, and will cause the algorithm to fail.



**Figure 1** | A flowchart depicting the steps in the Verlet algorithm, to solve a second order differential equation.

In discussing the Verlet algorithm for integration, it is not necessary to include any more information than is given in the previous paragraph. If the reader is comfortable with the most recent paragraph (including the full interpretation of it), then they are in an excellent position to use the Verlet algorithm in simulations.

## APPLICATIONS

Verlet integration is used frequently in molecular dynamics simulations [3, 4, 5]. It provides a rapid way to evaluate a large number of steps, without requiring excessive computing capabilities.

## SUMMARY

The Verlet algorithm can be used to find numerical solutions to differential equations. Using an integer  $n$  to quantise time, the evolution of a second order differential equation has a solution numerically computed using the iterative algorithm:

$$\mathbf{r}_{n+1} = \mathbf{r}_n + \mathbf{u}_n \delta t + \frac{1}{2} \mathbf{a}_n (\delta t)^2,$$

where:

1.  $\mathbf{r}_n$  is the position of a particle at a time corresponding to an index  $n$ ,
2.  $\mathbf{u}_n$  is the velocity of a particle at a time corresponding to an index  $n$ ,
3.  $\mathbf{a}_n$  is the acceleration of a particle at a time corresponding to an index  $n$ ,
4.  $\delta t$  is the time step used in the algorithm. The time difference between indices  $n$  and  $n + 1$  is always  $\delta t$

The acceleration is determined by additional degrees of freedom, and the velocity evolution is determined iteratively by

$$\mathbf{u}_{n+1} = \mathbf{u}_n + \mathbf{a}_n \delta t.$$

$\mathbf{u}$  and  $\mathbf{r}$  are subject to the boundary conditions  $\mathbf{u}_0$  and  $\mathbf{r}_0$  for when  $n$  is set as 0. The physical interpretation of this is that the particle begins at rest at the origin. However, other boundary conditions may be used, if appropriate.

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## FURTHER READING

Leapfrog integration.

## PROBLEMS

1. A particle is attached to a spring, and is confined to move along the  $x$  direction. The spring is ideal, with a spring constant  $k$ . No other forces are present. The particle initially has a velocity of  $v_0$  at a position  $x_0$ .
  - a) Write down an equation of motion for the particle.
  - b) Write down a Verlet algorithm to integrate the equation of motion.
  - c) Write this as a program in MATLAB. Execute it, and check it gives the analytical result you expect.
2. Assume the particle is allowed to move in two dimensions. Repeat the task above, with a boundary condition of a velocity of  $\mathbf{v}_0$  at  $\mathbf{r}_0$ .
3. The particle now experiences a drag force, proportional to its velocity. This has a constant of proportionality  $m\eta$ , where  $m$  is the mass of the particle, and  $\eta$  is a positive constant. Repeat task 1 for the setup in task 2, with this additional constraint.

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# LANGEVINS

## INTRODUCTION

An active area of research within surface physics is the use of theoretical models to describe the diffusion of adsorbate atoms (adatoms) across a surface (known as a substrate). There is an inherent difficulty in such models: the function describing coupling between adatoms and their substrate is complicated, and there is a term representing random kicks of force. To work around this issue, there are a range of approaches used to obtain approximate descriptions of surface diffusion. The approach we will discuss here is known as the Langevin equation of motion.

## THE LANGEVIN EQUATION OF MOTION

Simulations in surface physics will frequently use an equation, known as the “Langevin”, to describe the trajectories of particles on surfaces. The basic approach behind these simulations is to integrate the Langevin equation of motion. For an atom labelled  $i$ , this equation can be written as:

$$m_i \ddot{\mathbf{r}}_i = -\nabla V - \eta m_i \dot{\mathbf{r}}_i + \xi(t) + \sum_{j \neq i} \mathbf{F}(\mathbf{r}_j - \mathbf{r}_i),$$

where:

1.  $\mathbf{r}_i$  is the position of the  $i$ th adsorbate,
2.  $m_i$  is the mass of the  $i$ th adsorbate ,
3.  $V$  is the substrate-adsorbate potential as a function of the position of each adsorbate (*i.e.* the potential of the system evaluated when each adatom is at some fixed point),
4.  $\eta$  is a friction coefficient,
5.  $\xi(t)$  is a stochastic force, described by a vector quantity;
6.  $\mathbf{F}(\mathbf{r}_j - \mathbf{r}_i)$  is the force experienced by the  $j$ th adsorbate due to the  $i$ th adsorbate [1].



## THE ADSORBATE-SUBSTRATE POTENTIAL

The potential between the adsorbate and the substrate  $V$  is no simple function: it is affected by the surface corrugation, and surface thermal vibrational modes. [2] For reasonably “flat” surfaces, it is commonplace to ignore the gradient of the potential term in the Langevin - the rate of change of the potential function is very small. This simplifies our equation! There will be fewer calculations in the simulation, as the result of this.

## THE STOCHASTIC FORCE

Within our model, the frictional force removes energy from the adatom. This decreases its kinetic energy, consequently reducing the temperature of the adatom. Why does this matter? The average temperature of the adatoms must remain constant, otherwise our system is not in equilibrium. For our simulation to be useful, it must reach a steady state! How do we correct for this loss of energy? On this assumption of thermal equilibrium with a reservoir, a “stochastic force”  $\xi$  is needed to transfer energy back to the adatom, and therefore keep it in thermal equilibrium. This corresponds to “white noise” from collisions with electrons and atoms making up the surface of substrate.

How do we quantify the so-called stochastic force? We desire a Gaussian source of white noise that causes a behaviour like Brownian motion. Writing the stochastic force as:

$$\xi = \xi_x \hat{x} + \xi_y \hat{y},$$

the components can be clearly discussed. What can we say about the value the stochastic force takes? This arises from the moments of the stochastic force. These so-called moments are:

$$\begin{aligned} \langle \xi_i(t) \rangle &= 0; \\ \langle \xi_i(t_1) \xi_j(t_2) \rangle &= 2m\eta k_B T_s \delta_{ij} \delta(t_2 - t_1), \end{aligned}$$

where:

1.  $m$  is the mass of the adatom,
2.  $k_B$  is the Boltzmann constant,
3.  $T_s$  is the temperature of the reservoir [1].

The constant arising in the second equation is a result of the fluctuation-dissipation theorem.

It is possible to find the standard deviation in the stochastic force. In the appendices, we find a result for the standard deviation in the *impulse* generated by the stochastic force in a small time  $\delta t$  in one dimension. Dividing this by the time interval  $\delta t$ , we obtain the standard

deviation in the stochastic force  $\sigma$  over the same time period. This is:

$$\sigma = \sqrt{2k_B T_s m \eta \frac{1}{\delta t}},$$

where all symbols have been previously defined. Note the dimensions of this quantity! This represents the force, and not the impulse. The derivation for this is quite involved, so do not attempt to follow it unless you have plenty of time; it is not necessary to read through to build an intuition of what is going on (although still beneficial).

## ADSORBATE-ADSORBATE INTERACTIONS

For the simulation to be completed in a realistic time, the adsorbate-adsorbate interactions  $\mathbf{F}(\mathbf{r}_j - \mathbf{r}_i)$  must be neglected. When can this occur? If the adsorbates are sparsely populated on the surface of the solid, then the forces between the adsorbates must be miniscule, and the  $\mathbf{F}(\mathbf{r}_j - \mathbf{r}_i)$  term does indeed vanish. Continuing without this sum is known as the “single adsorbate approximation”. In such a case, the dynamics of the diffusion are fully characterised by studying the dynamics of isolated adsorbates on the surface [3] - meaning considering single particles, without any reference to other particles, leads to an accurate model for the diffusion.

## THE SIMPLIFIED LANGEVIN

With the approximations discussed above, our typical simulation has been simplified: only the terms related to the frictional force  $\eta$  and the stochastic force  $\xi$  remain. We explicitly write this as:

$$m_i \ddot{\mathbf{r}}_i = -\eta m \dot{\mathbf{r}}_i + \xi(t),$$

which we note is in the form of an equation that can be easily solved with Verlet integration! Also note that the derivation for several aspects of the stochastic force depends on the Langevin being in this form.

## SUMMARY

A particle diffusing on a surface can be modelled using the Langevin equation of motion, given by:

$$m_i \ddot{\mathbf{r}}_i = -\nabla V - \eta m \dot{\mathbf{r}}_i + \xi(t) + \sum_{i \neq j} \mathbf{F}(\mathbf{r}_j - \mathbf{r}_i),$$

where the stochastic force  $\xi(t)$  is normally distributed, with a standard deviation  $\sigma$ , in each dimension, of

$$\sigma = \sqrt{2k_B T_s m \eta \delta t}.$$

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2. Martínez-Casado, R et al *Quasi-elastic peak lineshapes in adsorbate diffusion on nearly flat surfaces at low coverages* J. Phys. Condens. Matter, 19, 176006 (2007)
3. Martínez-Casado, R et al *Quantum Markovian activated surface diffusion of interacting adsorbates*. J. Chem. Phys., 129, 184704 (2008)
4. Kramers, H.A. *Brownian motion in a field of force and the diffusion model of chemical reactions*. Physica, 7, 4, pp284-304 (1940)

## FURTHER READING

There are many instances of authors using more complicated forms of Langevin equations to describe physical systems. A thorough discussion is given in [4].

## PROBLEMS

This chapter aims to briefly introduce a background into the type of equation used in molecular dynamics simulations, and so there are no problems *per se*; however, it is essential the reader understands that it is reasonable to use the simplified version of the Langevin mentioned in the main body of the text. Consult additional literature if this does not make sense to you.

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# BULK SCATTERING

## INTRODUCTION

The principles of scattering are central to the study of surface physics, as they form the basis of a range of experimental techniques. Of special interest is the scattering of neutral atoms (especially helium), as their properties have enabled methods, including helium spin echo spectroscopy and helium microscopy, to probe previously inaccessible timescales and lengthscales. The chapter discusses an approach towards scattering, which is indicative of scattering in the bulk lattice of a material.

## DIFFRACTION: THE LAUE CONDITION

In many cases, we are interested in the diffraction of waves in crystal lattices. Our first task is to investigate the conditions under which waves will diffract.

We will construct the “Laue condition” for a scattering event. This relates the incoming and outgoing wavevectors of a wave, undergoing diffraction through a crystal lattice - giving the condition for a maximum in intensity.

### Definitions

We start by defining some quantities: let  $\mathbf{a}$ ,  $\mathbf{b}$  and  $\mathbf{c}$  be the real-space basis vectors of a crystal lattice, and let  $\mathbf{A}$ ,  $\mathbf{B}$  and  $\mathbf{C}$  be their respective basis vectors in reciprocal space. Assume two occupied lattice points are separated by a displacement vector  $\mathbf{r}$ ; a general form of which is:

$$\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c},$$

where each of the coefficients are integers.

### Derivation

We intend to produce an *a priori* criterion for the position of a maximum in intensity of a diffracted wave. For a maximum in intensity,

we require two diffracted waves to constructively interfere. This is easy to express quantitatively; setting the phase difference between the diffracted waves as  $\phi$ , any first year student will know that:

$$\begin{aligned}\phi &= \Delta \mathbf{k} \cdot \mathbf{r}; \\ &= 2\pi n,\end{aligned}$$

for any integer  $n$ , where  $\Delta \mathbf{k}$  is the difference between the wavevectors of the incident and final waves. Fortunately, we already have a mathematical construct that allows us to solve this problem with ease: the reciprocal lattice! For any reciprocal lattice vector  $\mathbf{G}$  given by:

$$\mathbf{G} = h\mathbf{A} + k\mathbf{B} + \ell\mathbf{C},$$

where  $h, k$  and  $\ell$  are integers, we have:

$$\begin{aligned}\mathbf{G} \cdot \mathbf{r} &= 2\pi(uh + ck + w\ell); \\ &= 2\pi n.\end{aligned}$$

The right hand side of this equation is the required condition for constructive interference! Therefore we can write the Laue condition in the form:

$$\begin{aligned}\Delta \mathbf{k} &= \mathbf{k}_f - \mathbf{k}_i; \\ &= \mathbf{G},\end{aligned}$$

where  $\mathbf{k}_i$  and  $\mathbf{k}_f$  are the wavevectors before and after scattering. This condition allows for an incident beam to be diffracted in infinitely many directions!

### Bragg's Law

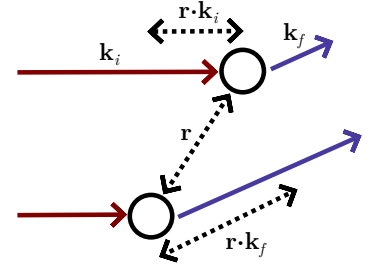
For the case of perfectly elastic scattering, we can manipulate the Laue condition to yield a more familiar form, with which you may already be familiar. In this case, conservation of energy requires that

$$|\mathbf{k}_f|^2 = |\mathbf{k}_i|^2.$$

Taking square moduli, we rewrite the Laue condition in the equivalent form:

$$\begin{aligned}\mathbf{k}_i &= \mathbf{k}_f - \mathbf{G}; \\ |\mathbf{k}_i|^2 &= |\mathbf{k}_f - \mathbf{G}|^2; \\ |\mathbf{k}_f|^2 &= |\mathbf{k}_f|^2 - 2\mathbf{k}_f \cdot \mathbf{G} + |\mathbf{G}|^2.\end{aligned}$$

It should be clear how the first line was generated. The second line arises from taking the square modulus of both sides. To finish off, we



**Figure 1** | A sketch of the origin of the Laue condition.

apply the condition that occurs during purely constructive interference. Simplifying this equation suggests the more elegant form:

$$2\mathbf{k}_f \cdot \mathbf{G} = |\mathbf{G}|^2,$$

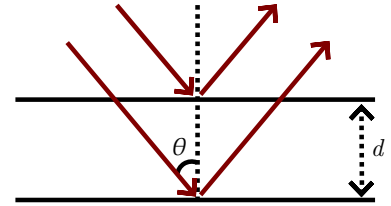
which, with a little algebra (don't bother deriving it), gives Bragg's law:

$$2d \sin(\theta) = n\lambda,$$

where:

1.  $d$  is the spacing between the planes given by the miller index  $(hkl)$ ,
2.  $n$  is an integer,
3.  $\theta$  is the angle of incidence,
4.  $\lambda$  is the wavelength of the diffracting wave.

Note that  $d$  is the interplanar spacing corresponding to the reciprocal lattice vector  $\mathbf{G}$ . This has a shockingly deep interpretation: in the context of diffraction, each point in reciprocal space corresponds not to a point in real space, but to an entire plane! Light diffracts according to the spacing between this plane, in a manner predictable using basic physics.



**Figure 2** | The interpretation of Bragg's law.

## SUMMARY

The Laue condition for diffraction is:

$$\Delta\mathbf{k} = \mathbf{k}_f - \mathbf{k}_i = \mathbf{G},$$

for elastic scattering, this reduces to Bragg's law:

$$2d \sin(\theta) = n\lambda,$$

where:

1.  $\Delta\mathbf{k}$  is the difference in wavevector between the incident and scattered wave,
2.  $\mathbf{k}_i$  is the wavevector of the incident wave,
3.  $\mathbf{k}_f$  is the wavevector of the scattered wave,
4.  $\mathbf{G}$  is a reciprocal lattice vector,
5.  $d$  is the interplanar spacing,
6.  $\lambda$  is the wavelength of the wave,
7.  $n$  is an integer,
8.  $\theta$  is the angle of incidence.

## FURTHER READING

X-ray crystallography.

**PROBLEMS**

1. Bragg's law can be used to investigate some types of scattering.  
Why is Bragg's law inappropriate for inelastic scattering?
2. Predict how the Laue condition for scattering in the bulk lattice can be adapted to scattering from surfaces.

---

# SURFACE SCATTERING

## INTRODUCTION

In the previous chapter, our general treatment was to consider the behaviour of diffracted waves from the bulk lattice of a crystal. The natural progression is to pursue an understanding of how waves behave when they diffract from a surface, without interacting with particle below the surface level of the crystal; this is achieved with again considering the Laue criterion. Our main change, with our surface being a two dimensional entity, is that the reciprocal “lattice” is now a two dimensional object.

## NOTATION: ADAPTING TO SURFACES

For analysis of diffraction from surfaces, it is suitable to slightly adjust the notation we use - allowing us to have a more convenient mathematical framework. Let the  $xy$  plane as the scattering plane. Let the  $z$ -axis be the axis normal to the scattering plane, which points towards the incident atoms. Using this new notation, it is trivial to write any position vector about an origin as:

$$\mathbf{r} = \mathbf{R} + z\hat{\mathbf{z}},$$

where  $\mathbf{R}$  is a vector in the  $xy$  plane,  $\hat{\mathbf{z}}$  is a unit vector along the  $z$ -axis, and  $z$  is the coordinate along the  $z$ -axis. We can give this the coordinate  $(\mathbf{R}, z)$ . Conveniently, this allows the incident wavevector  $\mathbf{k}_i$  and final wavevector  $\mathbf{k}_f$  of the scattering atom to be written in the form of the new coordinates! These are summarised as:

$$\begin{aligned}\mathbf{k}_i &= (\mathbf{K}_i, k_{iz}); \\ \mathbf{k}_f &= (\mathbf{K}_f, k_{fz}),\end{aligned}$$

where it should be clear that the symbols used represent an in-plane vector, and a component along  $z$ .

There is one final piece of notation to consider. Given we are generally interested in the waves for which constructive interference occurs, it is useful to assign a symbol to indicate this criterion is met. For this



purpose, we use the vector  $\mathbf{k}_G$ , with components  $\mathbf{K}_G$  and  $k_{Gz}$ , to denote the scattered wavevectors which satisfy the Laue condition for surface scattering. Recall that the Laue condition is:

$$\Delta\mathbf{K} = \mathbf{G},$$

where  $\mathbf{G}$  is a reciprocal lattice vector in the scattering plane. The Laue condition is not applied to the normal component of the wavevector, as the crystal symmetry is “broken” in that direction.

## THE CORRUGATION FUNCTION

When atoms are incident on a surface and scatter, it is necessary to know the position at which this scattering occurs; modelling the substrate atoms as point charges, we can approximate this scattering point with the classical turning point for a charged particle: which gives a reasonable result, while ignoring quantum effects.

How do we quantify this? We define a locus of points at which an incident atom of a particular energy will begin to move in the other direction. If the incident atoms start from far away, it is reasonable to approximate their initial potential energy as 0. From this it is clear that:

$$V(\mathbf{R}, z) = E_{iz},$$

where  $V(\mathbf{R}, z)$  is the adsorbate-substrate potential, and  $E_{iz}$  is the kinetic energy of the incident particle along the  $z$  axis. The value of  $z$  for which solvation occurs is defined as the *corrugation function*  $\zeta$ , which we can write (in the most general form) as

$$z = \zeta(\mathbf{R}, E_{iz}).$$

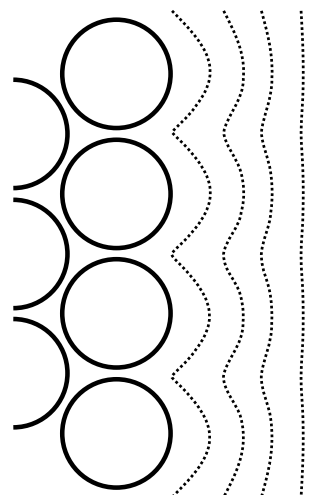
The  $E_{iz}$ -dependence is not usually included; it is assumed all incident atoms have the same kinetic energy and direction.

## SUMMARY OF SURFACE SCATTERING BEHAVIOUR

We first seek a qualitative understanding of the different possible scattering modes. In general, a particle incident on a given surface can scatter in many different ways; fortunately, we can broadly classify these into two main categories: *multiple scattering* events, and *single scattering* events. These classifications will be individually discussed in this section.

### Multiple Scattering

Multiple scattering is a surprisingly intuitive process, in which, as easily anticipated, a wave scatters from a surface more than once before



**Figure 1** | A comic depicting equipotentials around a surface, which constitute the so-called “corrugation function”.

“returning” into the space outside of the solid. For “strong” corrugation, the function  $\zeta$  varies significantly with the position  $\mathbf{R}$ . In such cases, multiple scattering can be significant, if the angle of incidence is large enough to permit it. However, multiple scattering events are difficult to model in a computationally efficient manner; near the surface there is an attractive potential between the adsorbate and substrate; this further distorts the paths, and introduces many more steps than can be considered simple. Thus we tend to restrict our attention to weak corrugation, and particles in near-normal incidence.

### Single Scattering

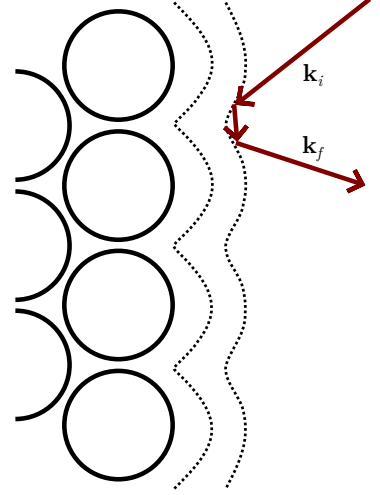
Even if we restrict attention to single scattering, there are many different ways in which an incident atom can scatter:

1. Elastic scattering. There is no energy exchange with the substrate (surface). The scattered wave can correspond to the mechanism of “specular” scattering (meaning the incident angle and final angle are the same), or that by which an assortment of final angles are possible. The latter of these cases arises from an exchange of momentum with the substrate; symbolically, this can be quantified as:

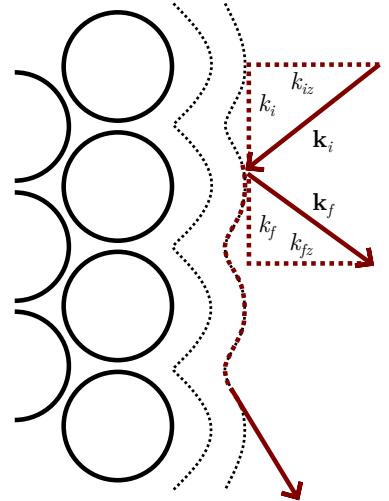
$$\Delta\mathbf{K} = \mathbf{G} \neq 0,$$

(i.e. there is a non-momentum exchange satisfying the Laue criterion) where all symbols have been previously defined.

2. Inelastic Scattering. Incident particles create phonons in the crystal, which have an associated energy. This will be removed from the kinetic energy of the particle, causing the collision to be “inelastic”. This process of creating phonons gives rise to a selection of peaks with discrete intensity levels, from single-phonon energy transfers, with roughly continuous background from multi-phonon scattering events.
3. Selective Adsorption Resonance. This process is a little more confusing, so the authors recommend that the reader first looks at the figure in the margin: noting one of the paths of the probe particle appears to trace out along a section of the equipotential, an intuition for what “selective adsorption resonance” constitutes can be built. The incident atom scatters into a path where it moves along an energy level of the potential well, until another diffractive process scatters it. This phenomenon is also known as “resonant scattering”; the wave from elastic scattering is coherent with the selective adsorption resonance wave, so can produce strong interference effects.



**Figure 2** | Multiple scattering events can occur for particles at a large enough angle of incidence, on a strongly corrugated potential surface.



**Figure 3** | The types of scattering mentioned in the main body of the text.

## INELASTIC SCATTERING

We have briefly mentioned inelastic scattering in the previous section. We will now introduce a slightly more detailed discussion, so the process of inelastic scattering can be better understood. The consideration of inelastic scattering is very similar to that of elastic scattering, however we allow transfer of energy (and thus momentum) to phonons on the surface; any change in the normal component of momentum moves the entire crystal, and parallel momentum changes are transferred to phonons. This is easy to quantify - writing in terms of momentum and energy conservation, we obtain the equations (recalling the momentum of a particle is  $\hbar k$ ):

$$\mathbf{K}_i - \mathbf{K}_f = \mathbf{Q} + \mathbf{G};$$

$$E_i - E_f = \frac{\hbar^2}{2m}(k_i^2 - k_f^2) = \hbar\omega_q,$$

where:

1.  $\mathbf{K}_i$  and  $\mathbf{K}_f$  are the incident and final wavevectors of the probe particle parallel to the surface,
2.  $\mathbf{Q}$  is the wavevector of the phonon,
3.  $\mathbf{G}$  is the reciprocal lattice vector,
4.  $m$  is the mass of the probe particle,
5.  $k_i$  and  $k_f$  are the incident and final particle wavevectors,
6.  $\omega_q$  is the frequency of the phonon.

These relations hold because the  $n$ th eigenstate of a phonon has an energy level  $E_q$  given by:

$$E_q = (n + \frac{1}{2})\hbar\omega_q,$$

where  $n$  is an integer greater than or equal to 0. Note that the reciprocal lattice vector  $\mathbf{G}$  in the first equation not only encodes the Laue condition, but also accounts for phonons which lie outside the first Brillouin zone.

The study of inelastic scattering is essential to experiments in surface scattering, and will be discussed in more detail later.

## SUMMARY

The Laue criterion applies to a reciprocal lattice generated from a 2D plane. The corrugation function  $\zeta(\mathbf{R})$  is the height at which atoms are scattered. A variety of outcomes can occur when an atom scatters from a surface.

## FURTHER READING

Quasi-elastic scattering.

## PROBLEMS

1. Why can multiple scattering events occur?
2. Why are some scattering events inelastic?
3. What do you think *quasielastic* scattering might be? Compare your guess to an accepted definition, in the context of atom scattering.

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# ADSORBATES

## INTRODUCTION

The study of adsorbate motion on surfaces is of immense importance to the analysis of surface scattering experiments, and to industry - one of the most prominent areas of which is the development of catalysts. In this chapter, we will seek a quantitative classical understanding of how the intensity of static, isolated adsorbates on a flat surface varies with coverage. We then extend this model to strongly-corrugated surfaces. We briefly discuss the interactions between adsorbates, and how they can lead to the condensation of the so-called “islands” on the surface, and even the condensation of complete adlayers.

We conclude with a return to the discussion of isolated adsorbates, deriving an expression for the quantum differential scattering cross-section (QCDS): demonstrating that it is, under a small set of assumptions, completely equivalent to the classical model.

## COVERAGE

In this chapter, we will frequently discuss the “coverage”  $\Theta$  of adsorbates on a surface. The coverage  $\Theta$  of adsorbates on a surface is defined as:

$$\Theta = \frac{n}{n_s},$$

where  $n$  is the number of adsorbates per unit surface area on the surface, and  $n_s$  is the number of substrate atoms per unit surface area on the surface. The interpretation of this is trivial.

## SCATTERING CROSS-SECTION

In atom scattering, the “differential cross section”  $d\Sigma/d\Omega$  is defined to be the number of particles scattered into an angle  $(\theta, \phi)$  per unit time, per unit solid angle. For normalisation purposes, this is divided by the flux of the incident beam. This can be written as:

$$\frac{d\Sigma}{d\Omega} = \frac{N}{j_i},$$

where  $N$  is the number of particles scattered in the correct orientation per unit time, and  $j_i$  is the incident flux. Evidently the “total” scattering cross-section, often simply called the scattering cross-section, is found by integrating the expression above. This is usually very involved, so we will not be exploring the mathematical framework here.

## ISOLATED ADSORBATES - CLASSICAL APPROACH

Classically, a given adsorbate on a surface can be modelled as a hard, repulsive core. This core is surrounded by a weak, long-range attractive Van der Waals surface. For probe atoms of sufficiently high energies, the attractive potential can be neglected; the adsorbate can be well-modelled by a single scattering centre (as in the Monte Carlo simulation tutorial). In general this assumption is not valid; the long-range potential causes deviations in the paths of incident atoms, scattering them away from the Bragg peak directions. This introduces noise into the intensity distribution, making measurement more difficult. Since a sample surface in surface scattering experiments will inevitably be covered with adsorbates, despite extensive cleaning, it is important to know the extent to which they affect measurements. The cross-section for scattering from such adsorbates is much larger than would be geometrically expected, due to the effect of the long-range potential.

### Weakly-Corrugated/Flat Surfaces

In the limiting case of a perfectly flat surface, and in the absence of any adsorbates, the intensity distribution of surface scattering is dominated by the specular beam (when the parallel momentum transfer is 0). Put more quantitatively, the intensities of all Bragg peaks, corresponding to a parallel momentum transfer  $\Delta K$ , drop to zero whilst the specular peak approaches 1.

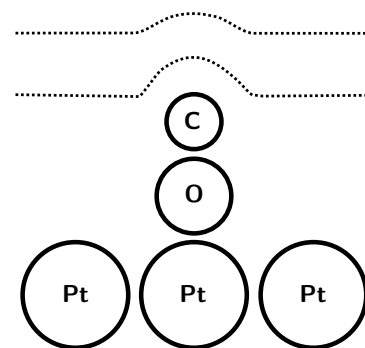
The presence of defects on a flat surface, in the form of adsorbate “steps” and “edges”, cause beams to scatter from this spectral path. This decreases the specular intensity  $I$  to smaller values.

In the low-coverage limit, the scattering cross-section  $\Sigma$  for an isolated adsorbate on a surface is given by:

$$\begin{aligned}\Sigma &= -\frac{1}{n_s} \left. \frac{d(I/I_0)}{d\Theta} \right|_{\Theta=0}; \\ &= -\left. \frac{d(I/I_0)}{dn} \right|_{n=0},\end{aligned}$$

where:

1.  $I$  is the specular intensity with coverage  $\Theta$ ,



**Figure 1** | The potentials generated by a CO admolecule on the Pt(111) surface and the deflection of an incident beam. Note: most metals have flat surfaces for low Miller index planes. This is because the delocalised electrons (which generate the repulsive potential) can spread out to flatten the hard-wall potential in the absence of adsorbates.

2.  $I_0$  is the specular intensity with zero coverage.

Note that this equation neglects double scattering, where beams scatter from both the surface and adsorbate. This process does not occur for small adsorbates; it also significantly complicates analysis, so is ignored throughout this chapter.

To extend the equation above for the scattering cross-section  $\Sigma$  to coverages  $\Theta$  greater than 0, we require that:

- Adsorbates are non-interacting/isolated.
- Adsorbates are randomly distributed.
- Adsorbates have small cross-sections, that do not overlap.

These conditions suggest the equation for the scattering cross-section to be:

$$\Sigma \approx -\frac{1}{n_s} \frac{d(I/I_0)}{d\Theta},$$

leading to the result

$$\frac{I}{I_0} \approx \exp(-\Theta \Sigma n_s).$$

This applies at low coverages. In general, adsorbates do interact at short ranges, so this model is only valid for sparsely distributed adsorbates on the surface. If the interactions between adsorbates are repulsive, then adsorbate cross-sections overlap less, and the effective value of the coverage  $\Sigma$  increases. The opposite applies for attractive interactions. Additionally, on most surfaces, there are preferential lattice sites for adsorption: the randomness condition is not met.

### Strongly-Corrugated Surfaces

On a strongly-corrugated surface, in principle, there are intensity peaks (called “Bragg peaks”) corresponding to all momentum transfers satisfying the Laue condition, which is the parallel momentum transfer  $\Delta \mathbf{K}$  is the same as a reciprocal lattice vector  $\mathbf{G}$ . The question then stands as to whether there exists a simple relation for the intensity of a given Bragg peak in terms of adsorbate cross-sections.

A simple generalisation of the weakly-corrugated case was proposed by Armand *et al.* This takes the form:

$$\Sigma_{\mathbf{G}} = -\frac{1}{n_s} \frac{d(I_{\mathbf{G}}/I_{0\mathbf{G}})}{d\Theta} \bigg|_{\Theta=0},$$

such that each adsorbate has a different cross-section for each reciprocal lattice vector. For this equation to be useful, there must be a simple relation between the components  $\Sigma_{\mathbf{G}}$ , however it was shown by Farias *et al* that no such relation generally exists.

Instead, a more general approach is to sum across all Bragg peaks



to obtain a single cross-section as follows:

$$\Sigma_{\text{corr}} = \frac{1}{n_s} \sum_{\mathbf{G}} \left. \frac{d(I_{\mathbf{G}}/I_{0\mathbf{G}})}{d\Theta} \right|_{\Theta=0},$$

where  $I_{\mathbf{G}}$  and  $I_{0\mathbf{G}}$  represent the measured intensities at the Bragg peak corresponding to reciprocal lattice vector  $\mathbf{G}$  at coverages of  $\Theta$  and 0 respectively.

### Measuring the Cross-Section

In experimental applications, it is often desirable to measure the cross-section of a given adsorbate species on a surface. The process for this is rather simple:

1. Measure the specular intensity with zero coverage  $I_0$  on a clean surface.
2. Abruptly increase the partial pressure of adsorbates surrounding the surface at  $t = 0$ . This will increase the rate of adsorbant impingement on the surface, and therefore the rate of adsorption.
3. The intensity  $I$  is measured over time to give a curve  $I(t)$ .
4. Using the curve, estimate the value

$$\left. \frac{dI}{dt} \right|_{t=0}.$$

5. Since:

$$\frac{dn}{dt} = v(t)s(t),$$

for small  $t \approx 0$  we have that

$$n(t) = n_s \Theta(t) \approx v_0 s_0 t.$$

Thus we can calculate the cross-section as

$$\Sigma = -\frac{1}{n_s I_0} \left. \frac{dI}{d\Theta} \right|_{\Theta=0} = -\frac{v_0 s_0}{I_0} \left. \frac{dI}{dt} \right|_{t=0}.$$

This method requires prior knowledge of both constants  $v_0$  and  $s_0$ . While  $v_0$  can be calculated from the (known) partial pressure of adsorbates around the surface,  $s_0$  must be determined experimentally.

## INTERACTING ADSORBATES

In general, the interactions between adsorbates on a surface are very complex, and non-negligible (due to their large cross-sections). It is crucial that these interactions can be investigated. A quantitative description of adsorbate interactions themselves is neglected here, in favour of a qualitative description of their effects.

## The Overlap Approach

A consequence of the large cross-sections  $\Sigma$  of adsorbates is that there will be significant cross-section overlap between adsorbates, even for low coverages. This overlap causes the effective cross-sections of adsorbates to decrease, departing from the above model, and depends both on the coverage and the distribution of adsorbates on the surface.

A simple model, called the “overlap approach”, assumes that the cross-section overlap is purely geometrical (so the potentials aren’t distorted in any way, they simply overlap). For perfectly diffuse adsorbates, distributed randomly on the surface, the intensity is given by the “lattice gas formula”:

$$\frac{I}{I_0} = (1 - \Theta)^{n_s \Sigma},$$

where it is understood that  $\Sigma$  is the (fixed) cross-section without overlap. The formula is named as such as it models adsorbates as a (discrete) two-dimensional gas on the surface. If occupying nearest-neighbour sites is forbidden, then this expression becomes:

$$\frac{I}{I_0} = (1 - m\Theta)^{n_s \Sigma/m},$$

where  $\Theta_m = 1/m$  is the maximum coverage for the system (*i.e.*  $m$  is the minimum number of surface substrate atoms to each adsorbate).

Note that these models match with the isolated adsorbate model at low coverages  $\Theta$ , but diverge at higher coverages  $\Theta$  due to restrictions on the closeness of adsorbates (in the 2D lattice gas model, adsorbates cannot occupy the same lattice site).

Deviations of  $I/I_0$  from the first model directly yields the nature of adsorbate-adsorbate interactions. Positive deviations indicate repulsive interactions, since the overlapping regions are smaller than expected (and vice-versa for negative deviations). A reasonable fit can then be provided with the second model (*e.g.* for CO adsorbates, on close-packed planes, setting  $m$  as 3 gives a good fit).

## Adsorbate Condensation

In the case of attractive adsorbate-adsorbate interactions, isolated adsorbates may condense from their two-dimensional gas phase - forming “islands”. This tends to occur at higher coverages, when the distances between adsorbates is small. While, for isolated adsorbates, the intensity decreases exponentially with coverage, for islands it decreases linearly (for small coverages). This is because the adsorbates create a larger, localised distortion, and because double scattering is more likely for islands.

If enough adsorbates condense, they form an “adlayer” (or “monolayer”). In this state, the cross-sections of the adsorbates all overlap, to produce a quasihard-wall potential; this causes the appearance of diffraction effects, as we would expect to see on a clean surface. The overlap effectively forms a second flat surface, which increases the order of the surface, thereby *increasing* the specular intensity.

Assuming that the potentials for both the substrate and adsorbate are purely additive (i.e. neglecting the attractive potentials), then we can easily decompose the total corrugation function for the new surface into an adsorbate and substrate component as

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

Using the Eikonal approximation and the convolution theorem, it can be shown that the total diffraction amplitude  $F$  is a convolution the diffraction amplitudes  $F_a$  from the ordered adlayer, and  $F_s$  from the substrate-induced modulation. This gives

$$F(\Delta\mathbf{K}) = \frac{S_a S_s}{S} (F_a * F_s)(\Delta\mathbf{K}),$$

where  $S$ ,  $S_a$  and  $S_s$  are the surface areas of the super cell (including adsorbates and substrates), adsorbate and substrate unit cells respectively. Thus, whilst full layers of impurities on a sample may obscure study of the surface via scattering experiments, in principle the total corrugation is modulated by the substrate; analysis is still possible for small numbers of complete adlayers.

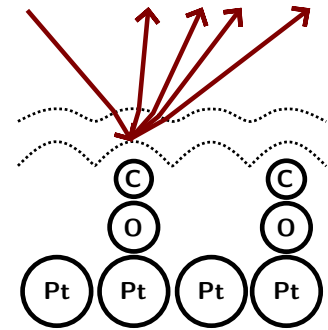
Continued deposition of adsorbates on the surface, when  $\langle \rangle$ , will lead to the formation of successive adlayers; this will cause an oscillation in the measured specular intensity as the order of the surface oscillates. Each cycle corresponds to the deposition of a full layer. Graphs of intensity on coverage (or exposure) are called “uptake curves” and are especially useful in measuring the sticking probability of adsorbates.

## ISOLATED ADSORBATES - QUANTUM APPROACH

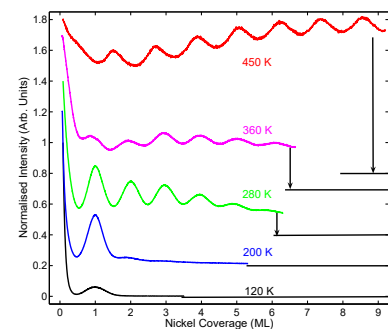
In this section we only consider scatter from a flat surface with a single, isolated defect (which could be an adsorbate).

### The Quantum Differential Scattering Cross-Section

Suppose we have an incident, monochromatic beam of probe particles with wavevector  $\mathbf{k}_i$ . This can be written component-wise in the normal manner, as  $(\mathbf{K}_i, k_{iz})$ . The lateral spread of such a wave in the surface plane can be described by a set of generic quantum states  $|\Psi_{in}\rangle$ . These are denoted  $|\Phi_{\mathbf{R}}\rangle$ . ( $\mathbf{R}$  is its lateral displacement with respect



**Figure 2** | Diagram depicting the potentials generated by an adlayer of CO ad molecules on a Pt(111) surface. This generates a quasihard-wall corrugation at the adlayer surface from which regular surface diffraction as in earlier chapters can occur.



**Figure 3** | An uptake curve for the epitaxial growth of Ni adlayers on Cu(111). There initial linear drop due to random adsorption is sharper at lower temperatures since it takes more time for a full layer to form (the rate of condensation is lower at lower temperatures due to lower thermal energies). For clarity, uptake curves are shifted vertically to avoid overlap and the corresponding zero-intensity positions are indicated by the horizontal lines on the right hand. Reproduced from Huang’s PhD thesis.

to the origin). Upon colliding with the surface, the beam is scattered, in-part by a defect of interest, into a solid angle  $d\Omega$ . The solid angle  $\Omega$  is defined as the area of a segment of the unit sphere. For spherical coordinates, this is

$$d\Omega = \sin \theta d\theta d\phi.$$

Physically, the solid angle  $\Omega$  characterises the angular range into which scattering occurs. The solid angle  $d\Omega$  characterises an infinitesimal range (i.e. a single trajectory) at an angle  $\theta$ . Thus  $d\Omega$  defines a single scattering direction.

We begin with the formal definition of the (time-independent) quantum differential cross-section (QDCS) for 2-body collisions, which we will then extend to surface scattering. First, let  $w(d\Omega \leftarrow \Phi_{\mathbf{R}})$  be the probability that an incident particle wavepacket  $\Phi_{\mathbf{R}}$  emerges after an elastic collision in the solid angle  $d\Omega$ . Note the use of the arrow, which indicates that this only describes the *asymptotic* behaviour of the wavefunction when the projectile and target are far enough apart for their interaction to be negligible. Then the average number of scatterings into a solid angle  $d\Omega$  is given by:

$$\begin{aligned} N_{sc}(d\Omega) &= \sum_i w(d\Omega \leftarrow \Phi_{\mathbf{R}_i}); \\ &\approx n_{inc} \int d^2\mathbf{R} w(d\Omega \leftarrow \Phi_{\mathbf{R}}), \end{aligned}$$

where the sum is taken over all scattering centres.  $n_{inc}$  is the incident density of helium atoms per unit area (i.e.  $n_{inc}$  is the ratio  $N_{inc}/A$  for a unit cell of area  $A$ ). We can then write:

$$N_{sc}(d\Omega) = \frac{N_{inc}}{A} \frac{d\sigma}{d\Omega} d\Omega,$$

where  $d\sigma/d\Omega$ , the differential cross-section, is defined to be:

$$\begin{aligned} \frac{d\sigma}{d\Omega} d\Omega &= \sigma(d\Omega); \\ &= \int_A d^2\mathbf{R} w(d\Omega \leftarrow \Phi_{\mathbf{R}}). \end{aligned}$$

$\sigma(d\Omega)$  is the QDCS, and can be interpreted as a measure of the target area effective in scattering the incident beam to  $d\Omega$ .

Note that the definition of the QDCS excludes the forward direction, since classically we cannot distinguish forward scattering from no scattering. In the context of surface scattering, this means we cannot distinguish specular scatter by a defect from scattering by the flat surface (formally, including this direction would cause the QDCS  $\sigma$  to diverge).

The QDCS is defined if:

- Incident particles have a sharply defined incident momentum  $\mathbf{p}_i$  and are randomly displaced in a plane perpendicular to the incident beam (satisfied for surface scattering since displacements are parallel to the surface).
- Distribution of scatterers is such that we avoid scattering by greater than 2 scatterers (satisfied if defects are distributed very diluted).

To show the equivalence of the QDCS formulation to the classical equation, replace  $N_{sc}(\Omega)/N_{inc}$  by  $J(d\Omega)/I_0 d\Omega$  in our equation (with  $J$  being the off-specular intensity,  $I$  the specular/incident intensity with adsorbates and  $I_0$  the specular/incident intensity without adsorbates). This gives:

$$\begin{aligned}\Sigma_{QDCS} &= \int \frac{d\sigma}{d\Omega} d\Omega; \\ &= \frac{A}{I_0} \int J(\Omega) d\Omega.\end{aligned}$$

For a single defect on the surface, we know that the product of that  $dn$  and  $A$  is 1. We also know that  $dI$  is equal to  $I - I_0$  in the limit of small  $n$ . Then our classical definition becomes:

$$\begin{aligned}\Sigma_{class} &= -\frac{1}{I_0} \lim_{n \rightarrow 0} \frac{dI}{dn}; \\ &= \frac{A}{I_0} (I_0 - I); \\ &= \frac{A}{I_0} \int J(\Omega) d\Omega; \\ &= \Sigma_{QDCS}.\end{aligned}$$

We note that  $I_0 - I = \int J(\Omega) d\Omega$ . This is because it is the sum of the intensity of all beams scattered away from the specular direction by the adsorbate.

## SUMMARY

In the low-coverage limit, the scattering cross-section for isolated adsorbates is

$$\Sigma = -\frac{1}{n_s} \lim_{\Theta \rightarrow 0} \frac{d(I/I_0)}{d\Theta}.$$

This implies that

$$\frac{I}{I_0} \approx \exp(-\Theta \Sigma n_s).$$

A simple model for higher coverages, accounting for overlap of cross-sections, is:

$$\frac{I}{I_0} = (1 - m\Theta)^{n_s \Sigma / m},$$

where  $\Theta_m = 1/m$  is the maximum allowed coverage of the surface. At high enough coverages, adsorbates may begin to condense to form

islands or even complete adlayers. Thus, continued exposure to an adsorbate in the atmosphere will cause the buildup of successive adlayers; these cause the specular intensity to oscillate, while the order of the surface oscillates between a disordered 2D-gas and a complete layer.

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# SCATTERING FUNCTIONS

## INTRODUCTION

There are numerous processes in solid-state physics that take place on the surfaces of solids. From this it is clear why many people desire to better study these processes by experiment, and in doing so require novel techniques; most archaic techniques tend to cause significant disruption on surfaces, and so are inappropriate for measurements over incredibly small distances. Similarly, there are challenges emerging when attempting to measure increasingly small time intervals in surface processes: equilibrium processes are usually used for small length scales, which do not offer small time frames alongside this [1].

In recent years a novel technique has emerged, known as helium-3 spin echo spectroscopy ( $^3\text{HeSE}$ ), which uniquely permits the investigation into the order of both Angstrom length scales, and picosecond time scales. This technique measures the “intermediate scattering function” (ISF) [2] as an observable, which will be discussed in this chapter. In doing so, we aim to allow the reader to have an intuition of the behaviour of the ISF in theoretical, computational, and experimental contexts. We will perform a similar discussion for the dynamic structure factor (DSF), which is the observable in QHAS experiments.

## THE VAN HOVE FUNCTION

There is a long history associated with the three functions discussed in this chapter; this history is useful to help to understand the origin of the ISF, and how it behaves. The clear starting point is the van Hove time dependent pair correlation function, first discovered in the 1950s in the context of atom scattering. We denote this function  $G(\mathbf{R}, t)$ , and give it a very satisfying definition: it is the probability that given there was an adsorbate at the origin at a time of 0, there is an adsorbate at  $\mathbf{R}$  at a time  $t$ .

After introducing the van Hove function, most scientific papers will demonstrate how it can be decomposed - and we will do the same. The van Hove function can be written in terms of so-called “self” and “distinct” parts  $G_s$  and  $G_d$ , which correspond to finding the same



particle at  $(\mathbf{R}, t)$  that was at  $(\mathbf{0}, 0)$ , or a different particle at  $(\mathbf{R}, 0)$  to that found at  $(\mathbf{0}, 0)$ . It is reasonable to suggest that the sum of these restores the van Hove function as

$$G(\mathbf{R}, t) = G_s(\mathbf{R}, t) + G_d(\mathbf{R}, t).$$

What use is this? This function allows the scattering of probe particles from surfaces to be analysed. While it is not the direct observable of techniques such as helium spin echo, it is useful in the discussion of its background, by effectively reducing the scattering process to statistical mechanics. The comparison to statistical mechanics arises from the *ab initio* formula for the van Hove function (which we will not discuss here), which is a generalisation of the pair distribution function from fluid dynamics. To illustrate this further, the pair distribution function is a distribution that represents the distances between particles - which is clearly going to be inherently statistical.

The objective of this chapter is to discuss the behaviour and interpretation of the quantities given by Fourier transforming  $G$  in space, and in time. We can easily summarise this with:

$$\begin{aligned} G(\mathbf{R}, t) &= \mathcal{F}[I(\Delta\mathbf{K}, t)]; \\ S(\Delta\mathbf{K}, \Delta\omega) &= \mathcal{F}[I(\Delta\mathbf{K}, t)], \end{aligned}$$

where  $I(\Delta\mathbf{K}, t)$  is the *intermediate scattering function*, and  $S(\Delta\mathbf{K}, \Delta\omega)$  is the *dynamic structure factor*. The first line represents a FT over space, whereas the second line represents a FT over time. The other variables are:

1.  $\Delta\mathbf{K}$ , known as the parallel momentum transfer. This represents the total change in momentum of the probe particle parallel to the surface, before and after scattering. Strictly the  $\hbar$  has been dropped, so the momentum transfer is technically  $\hbar\Delta\mathbf{K}$ , but it is common practice to write it without the  $\hbar$ .
2.  $\Delta\omega$ , representing the energy transfer in the scattering event. Again, the  $\hbar$  has been dropped [1].

We will now explore the two Fourier transformed quantities in more detail.

## INTERMEDIATE SCATTERING FUNCTION

Examining the two FT equations at the end of the previous section, the reader will see a common function being transformed, on both occasions. The somewhat mutual character of this function naturally gives rise to its assigned name, as the *intermediate scattering function*. This function is quite abstract, so requires thorough consideration. Due to its simplistic relation with the van Hove function, it provides

information about the position evolution of species on the surface of a solid.

### Statistical Approach

There is an expression for the intermediate scattering function, that although appearing complicated, is quite elegant in form. This is that:

$$I(\Delta\mathbf{K}, t) = \langle e^{-i\Delta\mathbf{K} \cdot [\mathbf{R}(t) - \mathbf{R}(0)]} \rangle,$$

where  $\langle \dots \rangle$  represents an expectation value taken over the trajectories  $\mathbf{R}$  [3]. Noting that the difference in trajectories is simply the displacement since the initial time, we can form an alternative expression, that represents the same information. This utilises the fact that the displacement is the integral of the velocity, and further simplifies the expression, by removing the perpendicular component. We are left with:

$$I(\Delta\mathbf{K}, t) = \langle e^{-i\Delta\mathbf{K} \int_0^t v_{\Delta\mathbf{K}}(t') dt'} \rangle,$$

where  $v_{\Delta\mathbf{K}}$  is the component of the velocity of the adsorbate along the direction of  $\Delta\mathbf{K}$ , and  $\Delta K$  is the modulus of the parallel momentum transfer  $\Delta\mathbf{K}$ .

### Cumulant Approach

We can also approximate the ISF as a cumulant expansion in  $\Delta\mathbf{K}$ . In this case, we write:

$$I(\Delta\mathbf{K}, t) \approx e^{-(\Delta K)^2 \int_0^t (t-t') C_{\Delta\mathbf{K}}(t') dt'},$$

where the autocorrelation  $C_{\Delta\mathbf{K}}(t)$  is

$$C_{\Delta\mathbf{K}}(t) = \langle v_{\Delta\mathbf{K}}(0) v_{\Delta\mathbf{K}}(t) \rangle$$

[3]. Why is there an approximation sign, and what does this equation represent? What we have written is the *Gaussian approximation* for the ISF. This is the expression that comes increasingly close to the exact value as the velocity correlation, at distinct values of the time  $t$ , becomes vanishingly small. This can be useful in computer simulations.

### Fourier Transform

The attentive reader will have noticed that this section has not referred mathematically back to the van Hove function, or the dynamic structure factor. Do not forget that the ISF can be expressed in terms of Fourier transforms of these functions!

## DYNAMIC STRUCTURE FACTOR

In a very similar spirit to the previous two functions, we introduce another scattering function, known as the *dynamic structure factor* (DSF); this intrinsically represents the same information as the van Hove function, due to the FT relationship the DSF holds with it. Fortunately, this makes the discussion much simpler, because the bulk of the interpretation has been discussed above. It should be noted that the DSF is sometimes referred to as the “linear response function” for interacting particles, or the “scattering law”. Why is the DSF important? It is the observable in time-of-flight type experiments. This means fitting computer simulations to the experimental data can be used to confirm hypotheses.

### Mathematics

To ensure the mathematics is fully understood, we can write an expression that relates the dynamic structure factor to the van Hove function. This is that:

$$S(\Delta\mathbf{K}, \Delta\omega) = \frac{1}{2\pi\hbar} \iint e^{i(\Delta\mathbf{K}\cdot\mathbf{R}-\omega t)} G(\mathbf{R}, t) dt d\mathbf{R},$$

where all symbols have been previously defined [4]. This represents the combination of a Fourier transform over time, and an inverse Fourier transform over space.

## SUMMARY

The van Hove function describes the probabilistic position evolution of adsorbates diffusing on a surface. This is related to the intermediate scattering function and the dynamic structure factor by Fourier transforms, which are observables in surface scattering experiments.

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# SPIN ECHO

## INTRODUCTION

Throughout this document, on numerous occasions, we have mentioned the technique known as “helium-3 spin-echo spectroscopy”. The question naturally arises of how the machine used in this technique operates, and how we can mathematically describe it. These questions can be answered with greater ease than one might expect. The fundamental formalism for the more general “spin-echo” technique for analysing condensed matter was produced by F. Mezei using neutrons as probe particles; this chapter focusses on how this formalism can be adapted, very trivially, for use when the probe particle is not a neutron - but an atom of helium-3.

The content of this chapter is the surface technique with the greatest simultaneous sensitivity for both length and time scales in the world. It has potential for many decades of ground-breaking measurements.

## COMMENT

This chapter is very chunky. It is not a good use of time to memorise it start to finish; consult the appropriate section when it is relevant to what you are doing.

## ORIGIN OF SPIN ECHO

The concept of “spin-echo”, before it was used to analyse matter with neutrons, was developed to be used in nuclear magnetic resonance machines (NMR). What does it mean? While the phrase “spin-echo” seems a little fantastical, it has a simple definition. It is the process by which a magnetic field is used to reorient the direction of the spin of a particle, by applying a magnetic field for a specific amount of time.

In some capacity, the background of this may be familiar to you; the precession of a particle’s magnetic moment in a magnetic field is known as *Larmor precession*, and can be described simply: the so-called “Larmor frequency”  $\omega_L$  of a particle precessing in a magnetic field can

be written as

$$\omega_L = -\gamma B.$$

In this expression,  $\gamma$  is the gyromagnetic ratio for the particle, and  $B$  is the magnetic flux density it experiences.

### Larmor Precession and Spin

It is useful to have an aside discussing the nature of the precession in greater detail; this arises from the spin of the particle, which in turn arises from a relativistic formulation of quantum mechanics, the magnetic moment operator  $\hat{\mu}$  can be written as:

$$\hat{\mu} = \gamma \hat{\mathbf{S}},$$

where  $\gamma$  is the gyromagnetic ratio, and  $\hat{\mathbf{S}}$  is the total spin operator of the particle. Imposing a magnetic flux density  $\mathbf{B}$  along the  $z$ -axis of the system, the definition of the magnetic dipole moment  $\mu$  for orbital angular momentum suggests that the torque operator  $\mathbf{T}$  for the particle is

$$\hat{\mathbf{T}} = \hat{\mu} \wedge \mathbf{B}.$$

However, this is an oversimplification, and so we cannot jump to this conclusion! This equation applies for the orbital angular momentum - we are yet to know what the time evolution looks like for spin. How do we find this time evolution? Like all other observables, we would use the Schrodinger equation. However, finding this similar expression for the spin requires knowing the Hamiltonian for the particle in a magnetic field. This Hamiltonian is:

$$\begin{aligned} \hat{H} &= -\hat{\mu} \cdot \mathbf{B}; \\ &= -\gamma \hat{\mathbf{S}} \cdot \mathbf{B}, \end{aligned}$$

where we have used the fact that  $\hat{\mu}$  can be written as  $\gamma \hat{\mathbf{S}}$ . Applying the time-dependent Schrodinger equation verifies that the time evolution does indeed follow such a similar relation, with angular frequency  $\omega_L$  equal to

$$\omega_L = -\gamma B.$$

The simplest way to solve this uses the time-evolution operator.

## THE CAMBRIDGE APPARATUS

The concept of spin echo has been utilised by the surfaces group at Cambridge to create a machine that can investigate processes occurring on surfaces. It is possible to provide a semi-classical step-by-step description of the inner workings of the Cambridge helium-3 spin-echo spectrometer. There is a prerequisite that we must first discuss - hexapole magnets.

## Hexapole Magnets

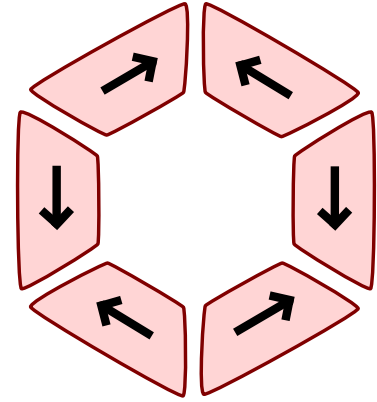
It should be evident to the reader that to produce a beam of atoms, as will be used in this machine, a set of atoms need to be focussed into a collimated cross section. This is achieved with a so-called “hexapole magnet”. Typically used in particle physics, a hexapole magnet consists of a set of six magnetic coils, alternating between pointing in the “North” and “South” directions. This is not all there is to say about hexapole magnets - see [4] for a more detailed review.

## Summary of Steps

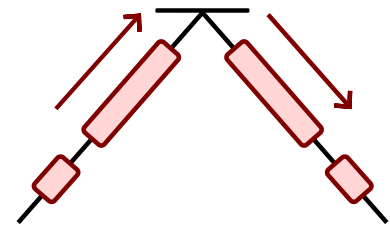
We will now explore the general process involved in the  $^3\text{HeSE}$  spectrometer, between the release of helium-3 atoms, and their detection. There is a lot of information to absorb! Before reading the summary below, briefly look over the diagram. The operation of the Cambridge helium-3 spin echo spectroscopy machine can be summarised with:

1. A set of helium-3 atoms are produced by a source. These pass through a nozzle, and travel towards the polariser. The speeds of the helium atoms are determined by the temperature of the nozzle.
2. The beam is passed through a polarising stage. This consists of the combination of a hexapole magnetic field, as in the diagram above, and a dipole magnetic field. The polariser splits the polarisation components into two: one is transmitted, and the other is dumped into the vacuum.
3. The newly polarised atoms are focussed into a collimated beam. This is then aimed at the sample. There is an important point to note - the collimation prevents the inverse square dissipation that would be expected from a radial source.
4. Before striking the sample, the beam passes through a magnetic field, known as a “precession field”. When passing through this field, the particles each acquire a spin phase  $\phi_1$ .
5. Each atom in the beam is individually incident on the sample. The particles scatter.
6. The particles pass through a second magnetic field, also known as a “precession field”. When passing through this second field, the particles each acquire a spin phase  $\phi_2$ .
7. The beam is then incident on an analysing filter - which is where the key concepts come into play. If the spin phases align in the right way, the particles will pass through the analysing filter. Following this, they either enter the detector (if transmitted), or are dumped into the vacuum (if rejected). This will be explored in greater detail in the full formalism.

The explanation above is quite vague; it is intended to be so, but nonetheless - it is still saturated with information. A thorough ex-



**Figure 1** | A hexapole magnet. Six individual magnets are placed in a hexagonal ring, alternating between North and South oriented poles.



**Figure 2** | A comic of the main elements of a spin-echo spectrometer. A beam of  $^3\text{He}$  atoms pass through a spin polariser. They then pass through a magnetic field, undergoing spin precession, before being incident on a sample. The beam of atoms scatters. It then passes through an equal and opposite magnetic field, and the spin of the atoms will again precess. The beam of atoms is then incident on an analysing filter. If the spins are oriented in the correct orientation, the atoms will pass through the filter, and will reach a detector.

planation of most of these concepts will be proffered in the coming sections.

## SPIN PHASES

In the summary of the operation of the Cambridge machine above, we mentioned that particles moving through the so-called “precession fields” will acquire a spin phase. What does this mean? Like all other vectors, the spin of a particle has direction. Consequently, this leads to the realisation that the direction of the spin can change. When passing through a magnetic field, the direction of the spin precesses, rotating about a set axis. This is surprisingly simple to mathematically describe. Given a Larmor frequency  $\omega_L$  describes the angular frequency of rotation of the spin phase  $\phi$ , it is clear that, in magnitude, the spin phase change with time according to

$$\omega_L = \frac{d\phi}{dt}.$$

What can we do with this? It is straightforward, and natural, to integrate. Thus we can see that the spin phase  $\phi$  can be written as:

$$\begin{aligned}\phi &= \int \omega_L dt; \\ &= \int \gamma B dt.\end{aligned}$$

It is essential to pause at this point, and consider the variables in the integral. While the magnetic flux density  $B$  is stationary with time, the particle will be in different sections of the field at any point (as it moves through the field). Therefore to consider the field as independent with time is misleading in this context - we must substitute a different variable in place of the time  $t$ .

Let the particle travel along the  $z$ -axis. Let the position of the particle be  $z$ . Then to bring clarity to the paragraph above, we can write the magnetic flux  $B$  in a slightly different notation: as the function  $B(z)$ . Then, given  $z$  and  $t$  are not independent, it is evident that the integral above is not straightforward; it is inviting to suggest that substituting  $z$  as the integration variable may simplify the algebra. How can we do this? If we set the velocity of the particle through the magnetic field as  $v$ , then the definition of velocity suggests that:

$$v = \frac{dz}{dt},$$

and so, by substitution, the spin phase accumulated while travelling through the field is:

$$\phi = \frac{\gamma}{v} \int_0^L B(z) dz,$$

where  $L$  is the length of the field region.

The algebra here can be simplified further. It is useful to define a quantity denoted  $B_{eff}$ , which measures the sensitivity of the coil making the magnetic field. This is given by

$$B_{eff} = \int_0^L \frac{B(z)}{I} dz,$$

where  $I$  is the current through the coil making the field. Evidently this allows the spin phase to be rewritten in the more convenient form

$$\phi = \frac{1}{v} \gamma B_{eff} I.$$

Why is this useful? At first glance, it may appear that we have first divided by the current  $I$ , and then multiplied by same current  $I$  (which we have done!). However, using the Biot-Savart law, we can make sense of this equation. We know that the magnetic flux  $B$  (from the equations above) is proportional to the current  $I$  causing it. Therefore dividing by the current gives a constant, represented by  $B_{eff}$ , rather than a variable! This leads us to conclude that the spin phase  $\phi$  accumulated while travelling through a magnetic field is proportional to the current  $I$  causing the field.

### Multiple Coils

In the Cambridge machine, there are two magnetic field regions. Since these are not necessarily identical, the spin phases in each one cannot be considered to be the same entity - we must go through them individually! Let the spin phase accumulated in the first of these coils be  $\phi_1$ , and the phase accumulated in the second be  $\phi_2$ . Then we can write these in terms of the subscripts 1 and 2, denoting the value of the variables in the first and second fields. These are:

$$\begin{aligned} \phi_1 &= \frac{1}{v_1} \gamma B_{eff1} I_1; \\ \phi_2 &= \frac{1}{v_2} \gamma B_{eff2} I_2, \end{aligned}$$

where all of the symbols have been previously defined. There is no new information here! It has all been discussed above.

## THE SPIN ECHO CONDITION

The usefulness of the spin echo machine may not yet be evident to you. Before proceeding further, we must discuss the detection procedure in more detail. How do we do this? We will illustrate the relevant concepts with the example of elastic scattering from the surface. In



this case, the speeds  $v_1$  and  $v_2$  must be the same. Otherwise, if the speed changes, the scattering would be inelastic!

The so-called “spin-echo condition” requires that the spin phase  $\phi$  *after* the particle has passed through both precession fields is 0. However, this only applies for the particles undergoing elastic scattering! It is fortunately very easy to quantify this condition. We can write it as:

$$\begin{aligned}\phi &= \phi_1 + \phi_2; \\ &= 0,\end{aligned}$$

which can be expanded further. With a short amount of algebra, for identical coils, we can see that the spin-echo condition reduces to

$$I_1 = -I_2.$$

## INELASTIC SCATTERING

### Energy States of a Phonon

The energy states of a phonon are given by:

$$E_n = (n + \frac{1}{2})\hbar\omega,$$

where  $n$  is an integer, and  $\omega$  is the frequency of oscillation. This is a very common result - see any condensed matter textbook if this is not familiar to you.

### New Spin Echo Condition

When a particle is incident on a surface, it may impart some energy to the surface. Using the example of surface phonons of frequency  $\omega$ , we can begin to describe how inelastic scattering events may impact the spin phase of the particles when incident on the analyser. Using the conservation of energy, we can relate this imparted energy to previously defined quantities as

$$\hbar\omega = \frac{1}{2}mv_2^2 - \frac{1}{2}mv_1^2.$$

How do we interpret this equation? Noting the difference between the  $n$ th and  $(n + 1)$ th energy levels of a phonon is  $\hbar\omega$ , the expression above represents a phonon being excited by one energy level. What use is this? Defining the mean velocities through the two fields as  $\langle v_1 \rangle$  and  $\langle v_2 \rangle$ , we can calculate the effect of a small change in each of the velocities from their expectation values on the spin phase. In order to do this, there is something we must do first - calculating the mean

value of the spin phase  $\langle\phi\rangle$  after the particles have travelled through the two fields. This is

$$\langle\phi\rangle = \frac{1}{\langle v_1\rangle} \gamma B_{eff1} I_1 + \frac{1}{\langle v_2\rangle} \gamma B_{eff2} I_2.$$

It is possible to relate this to the more spin phase  $\phi$  that is accumulated for velocities  $\langle v_1\rangle + \delta v_1$  and  $\langle v_2\rangle + \delta v_2$ . How do we do this? It is fortunate, that if the two small increments  $\delta v_1$  and  $\delta v_2$  are small enough, then it is reasonable to produce a first-order approximation for  $\phi$ . This is quite a simple procedure. Noting that, for small  $\delta v$ :

$$\frac{1}{\langle v\rangle + \delta v} \approx \frac{1}{\langle v\rangle} \left(1 - \frac{\delta v}{\langle v\rangle}\right),$$

it is straightforward to see that

$$\phi - \langle\phi\rangle = -\frac{\gamma}{\langle v_1\rangle^2} B_{eff1} I_1 \delta v_1 - \frac{\gamma}{\langle v_2\rangle^2} B_{eff2} I_2 \delta v_2.$$

Our next step is to produce a similar expression for the angular frequency  $\omega$ . Recalling that the angular velocity  $\omega$  of the phonon satisfies:

$$\hbar\omega = \frac{1}{2}mv_2^2 - \frac{1}{2}mv_1^2,$$

it is evident that, writing the most general angular velocity  $\omega$  as the sum of its mean  $\langle\omega\rangle$  and a small deviation  $\delta\omega$  from the mean, we can rewrite the above equation as

$$\hbar(\omega) = \hbar(\langle\omega\rangle + \delta\omega).$$

At the first order, we can neglect the squares of the infinitesimals. Then our equation can be approximated as:

$$\hbar(\omega) \approx \frac{1}{2}m\langle v_2\rangle^2 - \frac{1}{2}m\langle v_1\rangle^2 + mv_2\langle v_2\rangle - mv_1\langle v_1\rangle,$$

which conveniently leads to the expression:

$$\omega - \langle\omega\rangle = \frac{m}{\hbar}\langle v_2\rangle\delta v_2 - \frac{m}{\hbar}\langle v_1\rangle\delta v_1,$$

where  $\langle\omega\rangle$  denotes the expectation value of the phonon frequency.

In the case of elastic scattering, the spin echo condition is redefined. We now require that the deviation in the phase  $\phi$  (from the mean) is proportional to the deviation of the frequency of the phonon  $\omega$  from the mean. The constant of proportionality in this relationship is the so-called “spin echo time”, denoted  $t$ . Thus

$$\phi - \langle\phi\rangle = t(\omega - \langle\omega\rangle).$$

How do we solve this system? It is sensible to compare coefficients. This yields the equations:

$$\begin{aligned}\frac{\gamma}{\langle v_1 \rangle^2} B_{eff1} I_1 &= \frac{tm}{\hbar} \langle v_1 \rangle; \\ \frac{\gamma}{\langle v_2 \rangle^2} B_{eff2} I_2 &= \frac{tm}{\hbar} \langle v_2 \rangle.\end{aligned}$$

Furthermore, we can rearrange these equations to give an expression for the spin echo time  $t$ . Trivially, this is

$$t = \frac{\gamma \hbar}{m \langle v_1 \rangle^3} B_{eff1} I_1.$$

Similarly, we can also see that

$$\frac{B_{eff1} I_1}{B_{eff2} I_2} = \frac{\langle v_1 \rangle^3}{\langle v_2 \rangle^3}.$$

The so-called spin echo time has an elegant interpretation. This will be explored in a later section.

## Quantum Form

The final two equations above are the most significant from the same section, and are what should be learned. There is more that we can infer; the particles are on very small scales, and so exhibit quantum effects - which we can easily describe. Recalling that the de Broglie wavelength  $\lambda$  of a non-relativistic particle is given by:

$$\lambda = \frac{h}{mv},$$

where  $h$  is Planck's constant, it is possible to form an elegant expression for the spin phase  $\phi$ . Additionally recalling that this spin phase can be written as:

$$\phi = \frac{1}{v_1} \gamma B_{eff1} I_1 + \frac{1}{v_2} \gamma B_{eff2} I_2,$$

we will use the de Broglie wavelengths of the incident and scattered beams to write the spin phase as a linear expression in terms of the de Broglie wavelengths. Defining the constant  $\kappa_j$  as:

$$\kappa_j = \frac{1}{2\pi h} \gamma m B_{effj} I_j,$$

the spin phase becomes

$$\phi = 2\pi \kappa_1 \lambda_1 + 2\pi \kappa_2 \lambda_2.$$

This is a very important conclusion! It allows us to see that the spin phase of a particle, once it reaches the analyser, is a linear combination of an experimentally controllable parameter  $\kappa$ , and the de Broglie wavelengths of the beams.

## INTERPRETATION OF SPIN ECHO TIME

This section aims to draw together some of the theory presented so far. The general spin state along  $x$  is:

$$|+\rangle_x = \frac{1}{\sqrt{2}}(|+\rangle_z + |-\rangle_z),$$

where the symbols have their usual meanings. When the beam enters the precession fields, the two spin components separate. Assigning them times  $t_+$  and  $t_-$  as the time taken to move through the field, the time difference for them taken to get to the sample is:

$$t = t_+ - t_-,$$

where  $t$  is the spin echo time.

## THE 2D WAVELENGTH INTENSITY MATRIX

### Aside

Before we proceed, it is best that we reflect on the implications of the maths above. We have an expression that describes the spin phase of a beam of atoms. What can we do with this maths? It does not tell us anything about our detector - we have effectively tracked the beam between the polarising and analysing filters. This also does not contain the source of the atoms! A discussion of this is not needed to understand the apparatus. The objective of this section is to discuss the formalism for the signal received.

### Count Rates and Polarisation

The formalism we use to provide a signal arises from one simple statement: that the probability of transmitting a helium atom through the analyser is proportional to the projection of the spin of the helium atom on the analysing filter. From this, we can conclude that the count rate is proportional to the expectation value of the projection of the spin on the analysing filter. How do we quantify this? We first need to introduce two new quantities: defining  $\rho(\phi)$  as the probability density of states and  $T(\phi)$  as the probability of detecting a particle with phase  $\phi$ , it is evident that the probability  $\delta P$  of finding a phase between  $\phi$  and  $\phi + \delta\phi$  is

$$\delta P = \rho(\phi)T(\phi)\delta\phi.$$

Then it is reasonable to suggest that the measured quantity, known as the “polarisation”  $P_X$ , which is proportional to the count rate, can be written in the form

$$P_X \propto \sum \cos \phi \rho(\phi)T(\phi)\delta\phi.$$

Taking the limit of small  $\delta\phi$ , this sum becomes an integral over the spin phase. We are left with:

$$P_X \propto \int_{\phi_{\min}}^{\phi_{\max}} \cos \phi \rho(\phi) T(\phi) d\phi + C,$$

where  $C$  is a constant, corresponding to the count rate due to unpolarised atoms incident on the analyser. The subscript  $X$  represents measuring along the  $X$ -axis.

### Complex Polarisation

We define a phase shifted version of the polarisation as  $P_Y$ . This takes the form

$$P_Y \propto \int_{\phi_{\min}}^{\phi_{\max}} \sin \phi \rho(\phi) T(\phi) d\phi + C.$$

What can we do with this? We define the complex polarisation as  $P$ , where:

$$\begin{aligned} P &= P_X + iP_Y; \\ &\propto \int_{\phi_{\min}}^{\phi_{\max}} e^{i\phi} \rho(\phi) T(\phi) d\phi + C, \end{aligned}$$

which is a Fourier transform. This immediately invokes the numerous pieces of intuition involved in Fourier algebra.

### Wavelength Form

Integrating with respect to the phase is not particularly easy to do. It makes more sense to integrate with respect to the variables we already know - the de Broglie wavelengths of the incident and scattered beams. Recalling that we can write the spin phase as:

$$\phi = 2\pi\kappa_1\lambda_1 + 2\pi\kappa_2\lambda_2,$$

it is obvious that the differential  $d\phi$  can be written as:

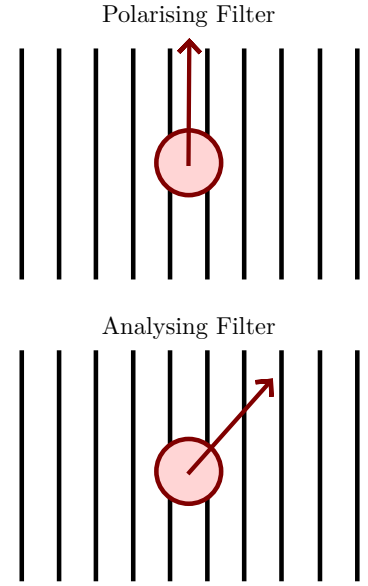
$$d\phi = 2\pi\kappa_1 d\lambda_1 + 2\pi\kappa_2 d\lambda_2,$$

assuming the two constants  $\kappa$  are held constant. Thus the complex polarisation  $P$  is the rather nasty line integral

$$P \propto \int e^{i\phi} \rho(\phi) T(\phi) (2\pi\kappa_1 d\lambda_1 + 2\pi\kappa_2 d\lambda_2) + C.$$

What do we do with this to make it useful? Green's theorem in the plane suggests that this is alternatively expressed as:

$$P(\kappa_1, \kappa_2) \propto \iint I(\lambda_1, \lambda_2) \exp(2\pi i\kappa_1\lambda_1 + 2\pi i\kappa_2\lambda_2) d\lambda_1 d\lambda_2 + C,$$



**Figure 3** | The two filters. The spin is projected onto the analysing filter, to give the likelihood of being transmitted.

over all possible de Broglie wavelengths  $\lambda_1$  and  $\lambda_2$ . The amalgamation of terms arising from Green's theorem have been absorbed into the function  $I(\lambda_1, \lambda_2)$ . We define this function as the wavelength intensity matrix. This can be interpreted as the relative probability of detecting an atom, at a given scattering geometry, which had a wavelength of  $\lambda_1$  before scattering and a wavelength  $\lambda_2$  after scattering. Read through this interpretation again! It is a very useful one. In addition, comparing the form of this equation to that in terms of  $\phi$  supports the interpretation of the wavelength intensity matrix as a probability. Convince yourself of this.

Furthermore, there is an additional comment to make. This equation represents a Fourier transform. Thus we can see that it is possible to write:

$$P(\kappa_1, \kappa_2) \propto \mathcal{F}[I(\lambda_1, \lambda_2)] + C,$$

where  $\mathcal{F}$  represents a two-dimensional Fourier transform. The interpretation of this is rich; we can see that the polarisation “picks out” the intensities of the frequencies making up the wavelength intensity matrix  $I(\lambda_1, \lambda_2)$  - the arguments have been written explicitly as  $\kappa_1$  and  $\kappa_2$  to reflect this FT relation.

To conclude, we note that the measured quantity is the real part of the complex polarisation. Thus:

$$P_X(\kappa_1, \kappa_2) \propto \mathcal{R}(\mathcal{F}[I(\lambda_1, \lambda_2)] + C),$$

where  $\mathcal{R}$  denotes the real part of a complex number.

## Application

How do we use the wavelength intensity matrix to analyse the system? It is reasonable to write the wavelength intensity matrix  $I(\lambda_1, \lambda_2)$  as the product of two different probability functions. This is:

$$I(\lambda_1, \lambda_2) \propto \rho(\lambda_1)S(\lambda_1 \rightarrow \lambda_2),$$

where:

1.  $\rho(\lambda_1)$  is the wavelength density function. This has been discussed before.
2.  $S(\lambda_1 \rightarrow \lambda_2)$  is the probability that when a particle of de Broglie wavelength  $\lambda_1$  is incident on a surface, it is scattered to a de Broglie wavelength  $\lambda_2$ .

The reader should note that the equation above denotes proportionality, but not equality. This reflects that the wavelength intensity matrix may not be normalised.

The new form of the wavelength intensity matrix will be explored with the two examples, which lead on from each other. In our first

case, an elastic scattering event occurs; this implies the de Broglie wavelength does not change, and so  $\lambda_1$  and  $\lambda_2$  are the same number. Thus  $S(\lambda_1 \rightarrow \lambda_2)$  is a Dirac delta function for elastic scattering. In the case of inelastic scattering, the de Broglie wavelength will change upon scattering -  $S(\lambda_1 \rightarrow \lambda_2)$  is no longer a Dirac delta function.

## THE TILTED PROJECTION THEOREM

An ideal experiment would measure a very thorough selection of values of  $\kappa_1$  and  $\kappa_2$ , which allows the entire polarisation matrix to be inverse Fourier transformed. However, this is not very easy in practice! It would require a tremendous number of data points to be taken: this is not appropriate, due to time constraints. How can the issue of the vast number of data points be avoided? The so-called “Fourier projection theorem” is called. The behaviour of this is very similar to the convolution theorem; try to look for the similarities as it is introduced.

### General Case

Take two matrices,  $F(x, y)$  and  $G(k_x, k_y)$ . They are related by a Fourier transform, following the usual convention between  $x, y, k_x$  and  $k_y$ . Let  $L$  be an axis that passes through a set of points in the matrix  $G(k_x, k_y)$ ; denote these points  $G(L)$ . The next part is a little more confusing - read it carefully. The Fourier transform of  $G(L)$  is  $P(L')$ . The projection theorem states that  $|P(L')|$  is identical to the projection of  $F(x, y)$  onto an axis, parallel to  $L$ , in the  $xy$  plane.

### Measuring Polarisation Along an Axis

This section contains a description of the process that allows measurements to be taken in a sufficiently fast time scale to be viable. First, we must comment on the currents through the coils. Recalling that the currents through the first and second coils are  $I_1$  and  $I_2$ , we may wish to know the “magnitude” of their combination. Defining the “current vector magnitude”  $|I|$  as:

$$|I| = \sqrt{I_1^2 + I_2^2},$$

we can follow a very simple procedure to project the values along an axis. How do we do this? Slowly increasing  $|I|$  from zero to a maximum value is a natural, and intuitive, thing to do. However, do not interpret this in too deep a detail yet - it is essentially meaningless at this stage.

Recall the constant  $\kappa_j$  was defined by:

$$\kappa_j = \frac{1}{2\pi\hbar} \gamma m B_{\text{eff}} I_j,$$

and that the spin phase  $\phi$  was given by

$$\phi = 2\pi\kappa_1\lambda_1 + 2\pi\kappa_2\lambda_2.$$

It should be clear that each constant  $\kappa_j$  is proportional to the corresponding current  $I_j$ . This is important! How do we ensure that all of our data points lie on the desired axis  $L$ ? First note that  $L$  is an axis defined through the wavelength intensity matrix  $I(\lambda_1, \lambda_2)$ . In general, this means that the slope can be expressed as the derivative of one wavelength  $\lambda_2$  with respect to the other  $\lambda_1$ . Defining the angle of the axis  $L$  to the horizontal axis  $\lambda_1$  as  $\alpha$ , we can see that

$$\frac{d\lambda_2}{d\lambda_1} = -\tan \alpha.$$

What can we do with this? Noting the proportionality between  $\kappa_j$  and  $I_j$  (and that  $\kappa_j$  is the reciprocal variable of  $\lambda_j$ ), this expression can be rewritten as:

$$\tan \alpha = \frac{I_1}{I_2},$$

implying that the ratio of the currents  $I_1$  and  $I_2$  must be kept constant in order to measure along an axis. Thus, to state clearly, to measure along a fixed axis, scan the current vector magnitude from 0 to a fixed maximum, while keeping the ratio of  $I_1$  to  $I_2$  constant.

## SUMMARY

This chapter discusses the origin, and basic use, of the physics behind the helium spin echo machine.

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# THE RDF

## INTRODUCTION

The radial distribution function (RDF) is a mathematical function that provides information about the distribution of particles in a system. One of the properties that makes the RDF especially useful in simulations is its range, covering microscopic to macroscopic levels. On small scales, it can be used to describe the microscopic order of a system. At long ranges, it provides insight into the macroscopic properties of the system. In addition, the sharpness of peaks in the RDF indicates the thermal activity of the particles in the system. In this chapter we will first explore the intuition behind the RDF that makes it powerful, then we will introduce a mathematical description that stems from statistical mechanics. The tutorial related to this chapter includes more detail instruction on the usage of RDF in a simulation setting.

## INTUITION

What is the radial distribution function? What does it do, and how can it be calculated? These are among the questions that will be answered in this section. We will first use an example for a 1D system, illustrating why a radial distribution function is useful. We will then generalise this to two dimensions, which provides an effective model for surfaces of solids.

### An Example

Suppose there ten students in a queue of 20 metres. We could say that the number density of students along the queue is 0.5 students per unit length - but this is not an accurate representation of the distribution of students. If the beginning of the queue is marked as  $l = 0$  and the end as  $l = 20$ , there is no way to know whether there are students standing between *e.g.*  $5 \leq l \leq 7$ , despite the expected number of students to be found is 1. The issue with this model is obvious - not only are the students spatially discrete and not a continuous distribution;

but they could move around, talking to other people, and changing the distribution. The number of students in the interval  $5 \leq l \leq 7$  could change drastically over time. Particles are similar to students in this scenario - they are (as far as we are concerned) discrete; they shuffle around, transferring momentum and energy. Knowing that the average number of particles in the space  $\rho_0$  is

$$\rho_0 = \frac{\text{Number of particles}}{\text{Volume occupied}}$$

does not tell us much about how the particles are distributed. Hence we construct a *radial distribution function* (RDF)  $g$  that tells us how "likely" it is to find a student/particle distance  $r$  away from the origin. This is similar to the wavefunction from quantum mechanics.

### General Treatment

The radial density function is a spatial correlation function, meaning it describes how the location of a fixed particle affects the distribution of the other particles. The RDF can be written in vector or scalar form, dependent on how important the angular distribution is. If the RDF is written in terms of a position vector (*i.e.* when  $g$  is written as  $g(\mathbf{r})$ ), then the function  $g$  preserves the information about the angular structure of the substance we are studying. On the other hand, writing the radial distribution as  $g(r)$  averages out the distribution in the angular direction; this would be suitable for isotropic materials, and when the angular direction is not a significant factor for the system.

The newly modified version of the spatially-dependent density function  $\rho(r)$  now contains information about the local density. This can be written as:

$$\rho(r) = \rho_0 g(r),$$

which is a more accurate representation of the distribution of particles.  $\rho(r)$  is the number density of particles that you are expected to find at distance  $r$  away from the origin. It can be described as the "local" distribution, as opposed to the scaling factor  $\rho_0$ , which represents the "global" property.

How do we find the radial distribution function, for a given system? Consider a region of space, where the origin coincides with the centre of an atom. Are there any general comments we can make? As should be evident from the figure in the margin, there cannot be any atoms centred any closer to the origin than two times the atomic radius! Note that this assumes the atoms cannot overlap. Thus  $g(r)$  is always 0 inside two atomic radii. Furthermore, we expect a peak at twice the atomic radius, since this is the most closely packed distance from the origin. As the radius  $r$  approaches infinity, the density distribution is

dominated by the macroscopic properties of the solid. Therefore, the atomic number density  $\rho$  approaches the bulk density  $\rho_0$ .

What does this mean? Consider the following example. Picture a body of water, first at atomic scale, and then at a macroscopic scale. The way water molecules are packed within the vicinity of each other becomes less important as the macroscopic property (bulk density) takes over and all we see is a pool of water. In addition, the function appears to be a continuous and smooth distribution. Why is this? The thermal vibration of the particles causes them to move through small displacements about an equilibrium. When averaged over many particles, this makes the atomic positions less well-defined.

### Derivation

To calculate the RDF quantitatively in a simulation, there is a very simple procedure to follow. Consider a circular shell, at a distance  $r$  from the origin. This shell is positioned in two dimensions. The area enclosed between this shell and an additional shell with radius  $r + \delta r$  is  $2\pi r \delta r$ , equivalently written as  $\delta A$ .

The number of atoms  $\delta n(r)$ , enclosed in a small region  $\delta A$  is given by the definition of the atomic density function. This can be written as

$$\delta n(r) = \rho(r) \delta A.$$

Thus by the definition of the radial distribution function as the ratio of the local density to the bulk density, we can see that  $\delta n(r)$  can be written as:

$$\delta n(r) = \delta A \rho_0 g(r),$$

which, at the limit, becomes

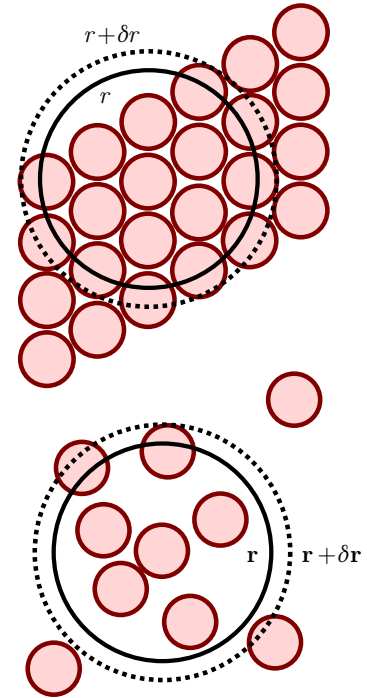
$$\frac{dn(r)}{dr} = 2\pi r g(r) \rho_0.$$

While running a simulation, we will be able to calculate the radial distribution function using this expression. This can be easily generalised to three dimensions. It is important to note that, in a three dimensional space, the radial distribution function only accounts for the radial direction. This reduces the distribution to an isotropic object.

### SUMMARY

The radial distribution function (RDF)  $g$  satisfies

$$\frac{d}{dr} n(r) = 2\pi \rho_0 r g(r).$$



**Figure 1** | A comic for the construction of the radial distribution function (RDF) for close-packed planes (top), and a disordered selection of particles (bottom).

$g(r)$  approaches 1 as the radius  $r$  becomes infinitely large, and is 0 when  $0 \leq r \leq 2\alpha$ , where  $\alpha$  is the atom/particle radius. The continuous span of the distribution is caused by the thermal vibration of particles. The radial distribution function  $g(r)$  describes local density, which quantitatively can be expressed as

$$\rho(r) = \rho_0 g(r).$$

## REFERENCES

1. D. Chandler *Introduction to Modern Statistical Mechanics*. Oxford University Press (1987).

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# CONCLUSION

## SUMMARY

- The **Fourier transform** is used to pick out the intensities of the terms of the reciprocal representation of a function. This process is important to both maths and physics.
- **Convolution** is used to find the overlap between functions. This is very closely linked to Fourier transform, due to some properties of the convolution. This is used frequently in maths and physics.
- **Lattices** are a mathematical construct, which when combined with a motif, describe the positions of atoms in a perfect crystal. The lattice is a periodic array of points, throughout all of space.
- **Verlet integration** is used to compute numerical solutions to differential equations. This is a particularly useful algorithm when applied to surface physics.
- **Langevins** are the equations of motion that dictate the motion of an adsorbate on a surface.
- The process of **scattering** occurs when a particle is incident on a solid.
- The **intermediate scattering function** is a detectable quantity in spin-echo experiments, such as the  $^3\text{HeSE}$  apparatus at Cambridge. The **dynamic structure factor** is an observable in time-of-flight experiments.
- **Helium-3 spin echo spectroscopy** can be used to investigate processes on picosecond time scales on surfaces.
- The **radial distribution function** can be used to model the number density of particles.

## NEXT STEPS

With the knowledge in this handbook, the reader should have enough knowledge to approach all of the general assignments given out. The program leaders will have given out a recommended reading list. It is our recommendation that the reader either begins to read through some of these papers, or to visit more handouts produced by the authors of this handbook.

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# APPENDICES

## LIST OF ACRONYMS

- EELS: Electron Energy Loss Spectroscopy
- FFT: Fast Fourier Transform
- FT: Fourier Transform
- FWHM: Full Width at Half Maximum
- HAS: Helium Atom Scattering
- <sup>3</sup>HeSE: Helium-3 Spin Echo
- IRAS: Infrared Adsorption Spectroscopy
- ISF: Intermediate Scattering Function
- LEED: Low Energy Electron Diffraction
- MD: Molecular Dynamics
- NSE: Neutron Spin Echo
- PEEM: Photoemission Electron Microscopy
- QDCS: Quantum Differential Cross Section
- QE: Quasi-Elastic
- QHAS: Quasi-Elastic Helium Atom Scattering
- QNS/QENS: Quasi-Elastic Neutron Scattering
- STM: Scanning Tunneling Microscope/y
- TDS: Thermal Decomposition Spectroscopy
- TEAS: Thermal Energy Atom Scattering
- TOF: Time of Flight

## VARIANCE OF THE STOCHASTIC FORCE

We wish to solve the Langevin equation:

$$m_i \ddot{\mathbf{r}}_i = -\eta m \dot{\mathbf{r}}_i + \boldsymbol{\xi}(t),$$

where all symbols are defined in the main body of the text. The components of the stochastic force  $\boldsymbol{\xi}$  have the properties that

$$\begin{aligned}\langle \xi_i(t) \rangle &= 0; \\ \langle \xi_i(t_1) \xi_j(t_2) \rangle &= 2m\eta k_B T_s \delta_{ij} \delta(t_2 - t_1).\end{aligned}$$



This equation has the analytical solution:

$$\dot{x}_i(t + \delta t) = \dot{x}_i(t) e^{-\eta \delta t} + \frac{1}{m} \int_t^{t+\delta t} e^{-\eta(t+\delta t-s)} \xi_x(s) ds,$$

where  $s$  is a dummy time variable, and  $x_i$  is the  $x$  coordinate of particle  $i$ . How do we interpret this solution? Consider the equation

$$\ddot{x}(t) = -\eta \dot{x}(t).$$

Solving this equation at a time  $t + \delta t$  suggests:

$$\dot{x}(t + \delta t) = A e^{-\eta t - \eta \delta t},$$

where  $A$  is a constant. Thus we absorb the constant with the expression

$$\dot{x}(t + \delta t) = \dot{x}(t) e^{-\eta \delta t}.$$

This represents the classical loss of velocity of the particle due to friction! Thus the first term in the analytical solution represents a loss of energy. The second term is more complicated. In order to restore the lost energy, the stochastic force acts to add energy to the particle. Why is there an exponential in this integral? When there is a “kick” from the stochastic force, occurring at time  $s$ , imparting an impulse to the particle, the energy it contains decays until the end of the time interval  $(t + \delta t)$ .

Taking the expectation value of both sides, it is evident that the expectation value of the integral is 0. This is because the expectation value of the velocity at any time is 0.

We wish to analyse the impulse term from the stochastic force in greater detail. Squaring the integral, and taking the expectation value, we obtain the equation:

$$\left\langle \left( \frac{1}{m^2} \int_t^{t+\delta t} e^{-\eta(t+\delta t-s)} \xi_x(s) ds \right)^2 \right\rangle = \frac{1}{m^2} \int_t^{t+\delta t} e^{-\eta(t+\delta t-s)} \int_t^{t+\delta t} e^{-\eta(t+\delta t-s')} \langle \xi_x(s) \xi_x(s') \rangle ds' ds,$$

where  $\delta t$  is a very small increment in time, and  $s'$  is a second dummy variable. For space, we denote the expectation value of the integral as  $I_{rms}^2(\delta t)/m^2$  (as it is the mean square impulse per unit mass). Then, integrating through the formula for the stochastic force suggests

$$\begin{aligned} \frac{I_{rms}^2(\delta t)}{m^2} &= \frac{1}{m^2} \int_t^{t+\delta t} e^{-\eta(t+\delta t-s)} \int_t^{t+\delta t} e^{-\eta(t+\delta t-s')} 2m\eta k_B T_s \delta(s-s') ds' ds; \\ &= \frac{2\eta T_s k_B}{m} \int_t^{t+\delta t} e^{-2\eta(t+\delta t-s)} ds. \end{aligned}$$

Following through with the integral:

$$\begin{aligned} \frac{I_{rms}^2(\delta t)}{m^2} &= \frac{T_s k_B}{m} e^{-2\eta(t+\delta t)} [e^{-2\eta(t+\delta t)} - e^{2\eta t}]; \\ &= \frac{k_B T_s}{m} (1 - e^{-2\eta \delta t}), \end{aligned}$$

which is the mean square change in velocity imparted by the stochastic force in a small time  $\delta t$ . The variance is the mean square impulse minus the square of the mean impulse. Thus the standard deviation in the impulse imparted is:

$$\sigma = \sqrt{k_B T_s m (1 - e^{-2\eta \delta t})},$$

which in the small time limit yields

$$\sigma = \sqrt{2k_B T_s m \eta \delta t}.$$