

Inferring the Surface Energy Distribution of Low Dimensional Materials



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Dedication

To my Mam and Granny,

Declaration

I declare that this thesis has not been submitted as an exercise for a degree at this or any other university and it is entirely my own work.

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Ivan Caffrey

Abstract

Two dimensional nanomaterials exhibit novel and superlative properties, as such; the last decade has seen huge research interest in 2D nanomaterials. To fully exploit these properties it is essential to have an accurate description of them. One such property is the surface energy of a material. It directly influences the interaction the material has with its environment. Since 2D nanomaterials are by definition dominated by their surface, the surface energy is an exceptionally important property. An example of this is the liquid phase exfoliation of 2D nanomaterials which relies on matching the surface energy of the solvent and the material. Despite its importance it remains poorly understood, often quoted as single value. What is needed is a complete description of a material's surface energy, one that takes into account the heterogeneity of a material.

This thesis establishes an approach that can be used to infer the surface energy distribution and assign surface energies to the different aspects of a material, in the case of layered materials these are the edges, basal plane and the defects in the basal plane. This work takes advantage of the ability of Finite-Dilution Inverse Gas Chromatography to measure surface energy over a wide range of surface coverages. This allows it to probe the high and low surface energy sites of the material. This data is plotted in what is known as a surface energy profile. The first section of this work focussed on examining the relationship between the surface energy distribution and the surface energy profile.

The profiles are fitted to a stretched exponential function in order to quantitatively describe them and objectively study alterations in their shape resulting from changes to the surface energy distribution. From the fits it was possible to extract the following descriptive parameters; surface energy at zero coverage ($\gamma_{d,\varphi=0}$), surface energy at full coverage ($\gamma_{d,\varphi=1}$), and the decay constant (φ_0). To systematically study the dependence of these parameters on the surface energy distribution this work employs a method developed by Smith et al. to simulate the surface energy profile produced by a given surface energy distribution.

Starting with the simplest distributions consisting of only a single Gaussian curve two important relations were discovered. First, the surface energy at full coverage was found to equal the mean value of the distribution. Second, the difference between $\gamma_{d,\varphi=0}$

and $\gamma_{d,\varphi=1}$ was found to depend mainly on the standard deviation of the Gaussian curve. The complexity of distributions was increased by introducing a second and third Gaussian curve. Simulating the profiles for a huge array of distributions it was found that most distributions do not produce profiles of the exponential-like shape seen experimentally. Fortunately three types of distributions were identified as being able to produce exponential-like profiles. It is demonstrated that using the behaviour of the $\gamma_{d,\varphi=0}$ and $\gamma_{d,\varphi=1}$ it is possible to identify the type of distribution, infer the surface energy distribution and assign surface energies to each aspect of a material. The method was applied to molybdenum disulphide (MoS_2) and boron nitride. All aspects of MoS_2 were found to have a mean surface energy of $\sim 40 \text{ mJ/m}^2$. While the defects of MoS_2 have a low mean surface energy, they cover a wide range of energies up to 100 mJ/m^2 . On the other hand the edges were found to have a narrow range of energies and behave as low energy sites. Modelling the flake as rhombuses, two simple models were developed relating the specific surface area and the decay constant, φ_0 , to the mean flake length. The results from these models support the conclusions regarding the surface energy of the defects and the edges. The results also indicate that the defect density of MoS_2 is dependent on flake length; this is supported by an example from the literature.

A slightly different conclusion is drawn regarding boron nitride. In this case, the edges are found to have a mean value of $\sim 70 \text{ mJ/m}^2$ and cover a wide range of surface energy. The defects and basal plane sites are found to be indistinguishable; both have a surface energy with a mean value of $\sim 40 \text{ mJ/m}^2$ and a narrow range of energies.

It is hoped that this work demonstrates the utility of the method described and that it will be applied to materials outside of the field of nanoscience. Another potential avenue for further research could be the use of lasers to induce defects in the basal plane of 2D materials and study the change in surface energy.

Publications

[1] A. Ferguson, I. Caffrey, C. Backes, J. N. Coleman and S. D. Bergin. Differentiating Defect and Basal Plane Contributions to the Surface Energy of Graphite Using Inverse Gas Chromatography. *Chemistry of Materials*. 28 (17), 6355-6366, 2016.

“The reasonable man adapts himself to the world: the unreasonable one persists in trying to adapt the world to himself. Therefore all progress depends on the unreasonable man.”

– **George Bernard Shaw, Man and Superman**

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Of course, top of the list, Dr. Shane Bergin. Thanks for going out on a limb and hiring me four years ago. He was always a great source of encouragement and advice during my first three years. Next, I would like to thank Professor Coleman for all the help during my final year, especially for the kind admonishments when a presentation or my writing was completely opaque to anyone but myself; without him there isn't the faintest chance I would have finished with a coherent body of work.

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Chapter 1

Introduction

1.1 Motivation

Throughout its history, from the Stone Age to the modern day the creation or discovery of new materials has been central to the progress of mankind. A new wave of materials known as nanomaterials, are revolutionising science and technology. They exhibit properties such as conductivity and strength many times greater than observed in conventional materials. They are having impacts in battery technology, solar cells, transistors, and composites. Crucial to the development of new nanomaterials and their applications is the ability to study and measure their properties. One such property is the surface energy, it is important for composites and material processing. This thesis set out to devise an approach for its measurement and analysis. It demonstrates this method for two distinct 2D layered materials. It should be possible to apply this method to other classes of materials.

1.2 Thesis Outline

Chapter 2 – Materials and Background:

This chapter provides an introduction to the two materials used in this work; molybdenum disulphide (MoS_2) and boron nitride. It first discusses their history and properties before moving on to possible applications. It then outlines top down and bottom up fabrication methods for nanomaterials along with examples specific to each material. Finally, the chapter finishes with a discussion on surface energy and several methods of measuring it.

Chapter 3 – Methods:

The topic of chapter 3 is the methods used during the course of this work. It begins by introducing the techniques used to characterise the samples. Special consideration is given to IGC as it is the source of most of the measurements in this work. It explores the theory of IGC, as well as the practical considerations when conducting experiments. It then outlines SEM and centrifugation as a technique for changing the mean flake length of samples. The chapter closes by detailing the procedure to simulate the surface energy profile of a given surface energy distribution.

Chapter 4 – Simulations:

Using the procedure outlined in chapter 3 to simulate surface energy profiles. A systematic study of the relationship between the distributions and the profiles is undertaken. It explores how specific changes to the shape of the distribution affect the surface energy profile. To aid in this analysis the profiles are fitted to a stretched exponential function. Several useful relations are found between the fitting parameters and the distribution. These relations enabled the development of a method to infer the surface energy distribution of a material from surface energy measurements.

Chapter 5 – Molybdenum Disulphide:

The method developed in chapter 4 is put to the test by determining the surface energy distribution of MoS₂. IGC is used to measure the surface energy profiles of samples of MoS₂ with different mean flake lengths. Surface energies are assigned to the different types of surface sites (Edges, Basal plane and defects). Several simple models relating the flake length to surface area and the shape of the profiles are developed that allow us to corroborate the conclusions drawn from the surface energy data. It is shown that the edges sites behave as low surface energy sites and that the defects are the source of the high surface energy measured at low surface coverages.

Chapter 6 – Boron Nitride:

To demonstrate the generalisability of the method from chapter 4, it is applied to a second material. Boron nitride has a structure and chemistry distinct to that of MoS₂. We show that the behaviour of the surface energy is different to that observed with MoS₂. We are still able to successfully determine the surface energy distribution of

boron nitride and assign surface energies to the edge, defects and basal planes sites. Again we are able to corroborate the results from the surface energy data with simple models relating surface area and profile shape to mean flake length.

Chapter 7 – Conclusions and Future Work:

The thesis ends with a chapter summarising the results from the previous chapters and outlines possible avenues for future research.

Chapter 2

Materials and Background

2.1 Introduction

Throughout history the mastery of materials has heralded a new age and increased the living standards of humans. Every new material brings with it a set of properties which, through our imagination, can be put to use in new applications. When a material is broken down to ever smaller sizes, beyond a certain point the properties of the material undergo a significant change. This occurs when one of the dimensions of the material is small enough to restrict the motion of the electrons contained within. This change in behaviour provides a massive opportunity to create and engineer a myriad of nanomaterials. These can be exploited in applications ranging from integrated circuits to energy generation and biomarker detection.[1][2][3] Graphene has long been the public face of nanoscience, with a long list of superlatives attached to its name. [4] As such, it has received a huge amount of research attention. There are, however, some applications for which it is unsuitable, for example, field-effect transistors require a bandgap. This is absent in graphene and means it cannot be used to fabricate post-silicon FETs. [5] Fortunately, there exists a multitude of other layered crystals which can be divided into families such as the transition metal dichalcogenides (TMDs) and transition metal oxides (TMOs), as well as graphene analogues like boron nitride.

Similar to graphene these materials are 2-dimensional layered crystals with weak interlayer bonding and strong in-plane bonding. [6] When thinned to monolayers, some, such as molybdenum disulphide (MoS_2) have direct bandgaps making them ideal candidates for FETs and optoelectronic devices. [7] They have also been shown to catalyse the hydrogen evolution reaction at edge sulphur sites. [8]–[10]

The first part of this chapter will introduce the two materials studied in this work; molybdenum disulphide (MoS_2) and boron nitride (BN). There will also be a discussion on some of their applications; energy storage[11] and gas sensing[12]. After that, several methods of top down and bottom-up fabrication will be outlined for each.

Crucial to developing applications using these materials; is a knowledge of how they will interact with their environment. This interaction is in large part mediated by its surface energy. The final section of this chapter will describe surface energy, its importance in applications and a discussion on several measurement techniques.

2.2 Transition Metal Dichalcogenides

Exfoliated TMDs were first studied in the 1960s [13], but have since seen renewed attention following the isolation of graphene and the introduction of novel production methods of monolayers such as liquid phase exfoliation (discussed in a later section).[14] Transition Metal Dichalcogenides are a family of inorganic layered crystals with around forty members sharing a common crystal structure but a diverse array of properties.[13] Taking electrical conductivity as an example, TMDs have been shown to be insulating (HfS_2), semiconducting (MoS_2 and WS_2) through to metallic (NbSe_2 and VSe_2). [15] This variety stems from the large number of possible configurations of transition metal and chalcogen (S, Se or Te). They each have the stoichiometric form MX_2 , where M and X is the metal and the chalcogen respectively. When viewed from the side the metal atom is sandwiched between the chalcogenides in creating a layer in the form X-M-X. These layers are then stacked together, each with a thickness of 6-7 angstrom [16]. The stacking sequence of the layers give rise to different forms of TMDs; trigonal prismatic, hexagonal or rhombohedral.[17] For example, the sequence AbA BaB (where the capital and lowercase are the chalcogenide and metal respectively) is that of the “2H – hexagonal phase”.[13] A diagram of this is shown in figure 2.2. The atoms within a layer are bound by strong covalent bonds, but the interlayer bonding is due to Van der Waals interactions and is therefore much weaker. This disparity in bonding strength has been exploited in dry lubrication because of the low amount of friction between layers.[18] It’s also what allows the crystal to be exfoliated into monolayers.[6] The subsequent sections will summarise the novel

properties of monolayer TMDs as well as how they can enhance existing technologies and provide opportunities for novel applications. Examples include flexible optoelectronic devices and energy storage devices. For the potential of nanostructured TMDs to be realised it is crucial that production methods are cost-effective and able to produce consistent monolayers with uniform properties. The final section is an outline of the new synthesis and fabrication techniques being employed. These include chemical vapour deposition (CVD) and chemical/mechanical exfoliation.

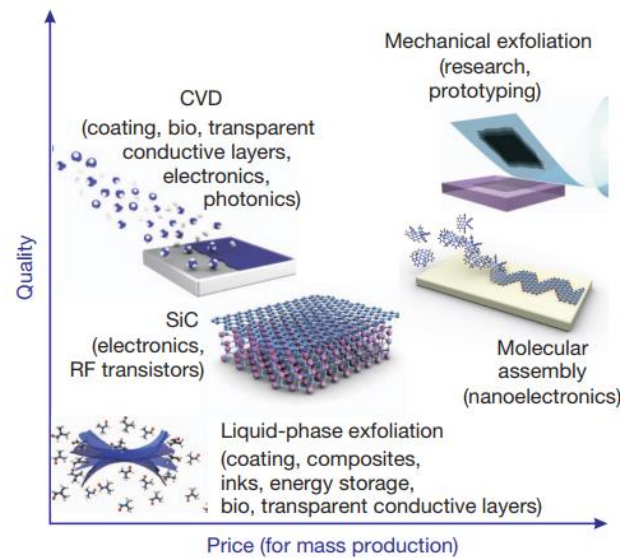


Figure 2.1. Plot of the quality of the nanosheets produced versus the price of the method. The ideal method lies in the top left of the diagram. However, there still remains a trade-off between cost and quality and there is still much research to be done in improving the scalability of production methods. [19]

2.2.1 Properties and Applications

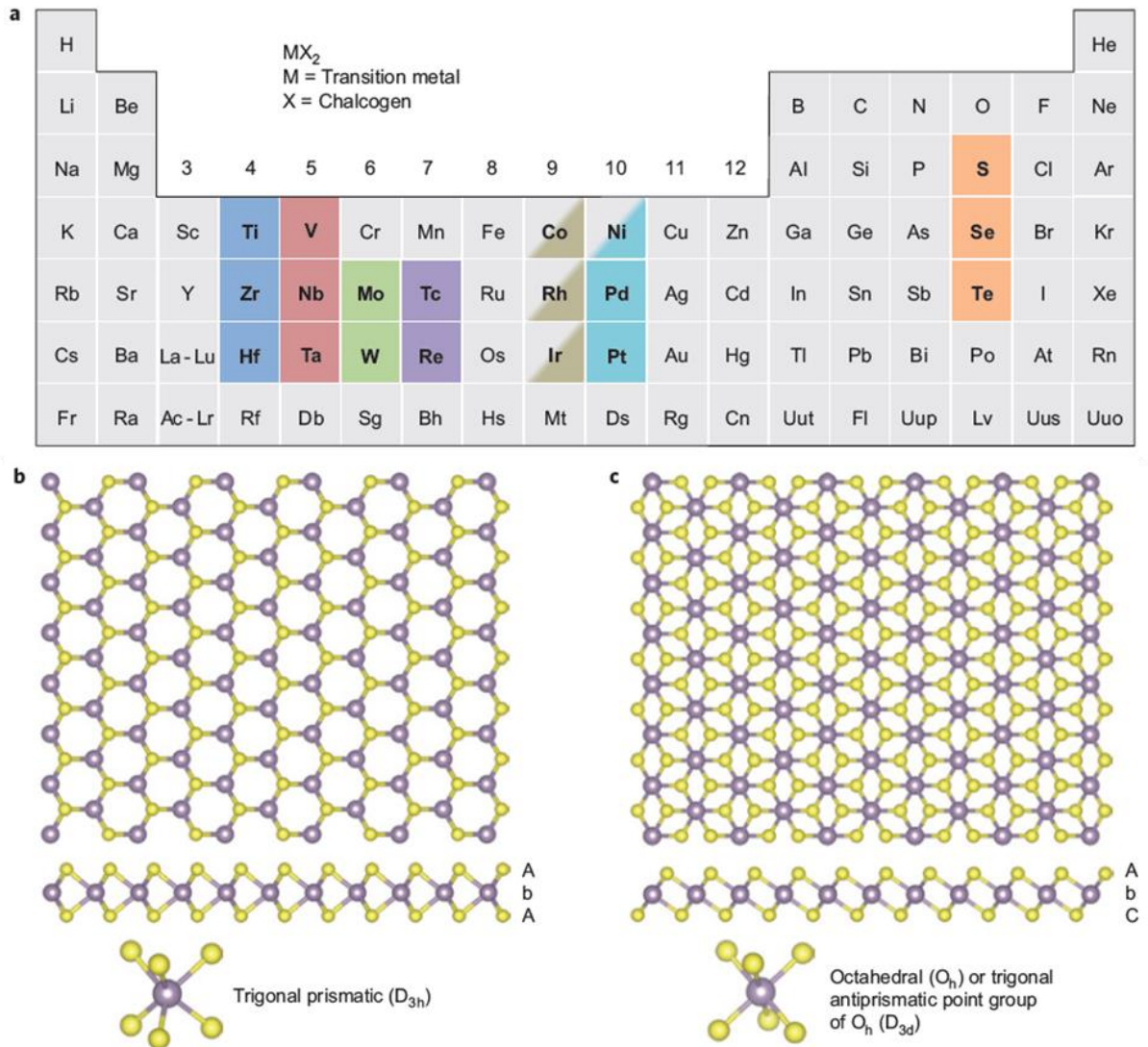


Figure 2.2. (a) A periodic table; highlighted are the transition metals and chalcogenides most commonly found to form TMDs. Diagrams of the top and side view of TMD structure in (b) trigonal prismatic [1T] and (c) octahedral [2H] forms. [17]

Monolayers of TMDs have properties not seen in their bulk counterparts.[20], [21] This happens because as one dimension is reduced the electrons and holes become confined in that direction. The confinement leads to quantised levels known as sub-bands. This

change in the density of states causes changes in electric and optoelectronic properties such as absorption and fluorescence.[22]

In TMDs, one consequence of the quantum confinement is a downward shift of the valence band and an upward shift of the conduction band.[23] For example, in MoS₂, as the layer number is decreased the bandgap changes from an indirect bandgap of 1.3 eV to a direct bandgap of 1.8 eV, one outcome of this is the photoluminescence of MoS₂. [24] That the bandgap is a function of the layer number allows for a tunable direct band gap. This ability to tune its direct bandgap between 1.2 and 1.9 eV makes MoS₂ suitable for optoelectronic applications in the visible range.[24] When a photon with an energy greater than the bandgap strikes the surface an exciton (electron-hole pair) is created, under an electric field this generates a photocurrent allowing the detection of light.[25] Photodetectors fabricated from single, double (1.83, 1.65 eV) and triple (1.35 eV) layers of MoS₂ have been shown to detect green and red light.[7] TMDs have also been used to harvest light as nanocrystals and as part of a Schottky junction.[26], [27] Another commercially important application, LEDs, can make use of TMDs emission of light in response to a current. Excitons can recombine to emit photons. Monolayer LEDs of WSe₂ have been demonstrated with an emission efficiency of 0.2%.[28] The solution processability of MoS₂ coupled with its flexibility make it an enticing prospect for use in the fabrication of solution processed OLEDs.[29]

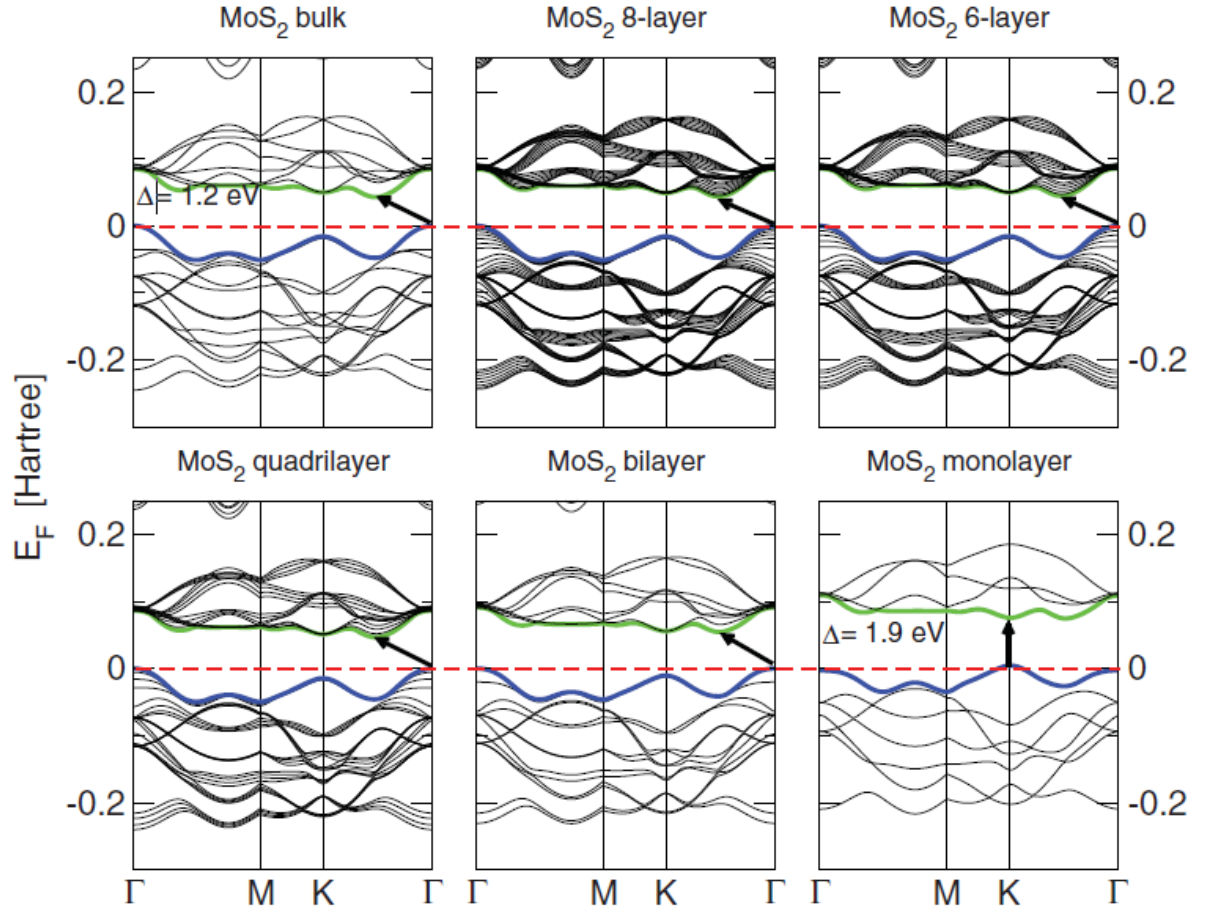


Figure 2.3. Calculated using DFT the diagram shows the evolution of the density of states in MoS₂ as the numbers of layers is brought from that of bulk MoS₂ to monolayer. The Fermi-level is shown by a dashed red line. The valence and conduction bands are marked by a blue and green line respectively. [22]

TMDs show promise as materials for electronics. Short channel effects are absent in 2-dimensional materials.[30][31] Graphene, despite having amazing properties such as high mobility[32], lacks a bandgap which limits its suitability for certain electronic applications; in particular FETs. This is where other TMDs such as MoS₂ can fill (or even provide) the gap. As mentioned a monolayer of MoS₂ has a direct bandgap of 1.9 eV. It also has a large On/Off ratios (10^7) and low off state conductance. These properties make it an excellent candidate for low-power electronic applications.[33][34]

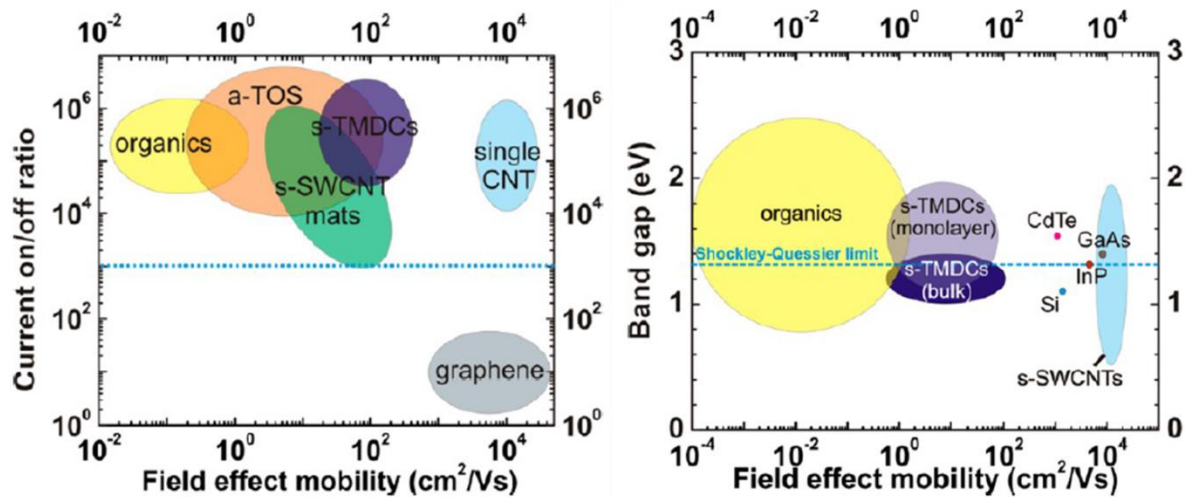


Figure 2.4. (a) Plot of On/Off ratios and mobility for a selection of types of novel materials. TMDs occupy the top left corner with advantageous properties for microelectronics. Graphene is shown near the bottom with poor On/Off ratios. (b) Plot showing the Band gap of a similar grouping of experimental materials. Again, TMDs occupy a favourable position on the plot indicating their suitability as a semiconductor. [35]

Quantum confinement is not the only effect of reducing the number layers in a TMD crystal. The surface to volume ratio converges to unity thus making them extremely sensitive to their environment. This makes them ideal candidates for gas sensors as their electrical and optoelectronic properties can be altered significantly upon analyte adsorption.[36][37] It has been previously shown that graphene oxide based TFTs can be used to detect gases.[38] This has led others to experiment with fabricating TFTs using MoS_2 . [39][40] Zeng et al were able to create a sensor capable of detecting NO gas at concentrations as low as 190 ppt.[41][12]

The surface chemistry also becomes increasingly important as the layer number decreases. At the edge there are low coordination step-edges, kinks and corners which play a larger role than in the bulk material. The unsatisfied bonds cause the edges to have metallic edge states, which DFT studies have shown to be the active sites in catalysis.[42][43][44][45] Bulk TMDs have shown poor HER performance. However through nanostructuring and increasing the density of active sites they have been shown to be a viable candidates for catalysing the hydrogen evolution reaction.[8][9][10] This

has been shown to depend largely on the edge sites due to their unsatisfied bonds and increased surface energy.[43][46] Hydrogen evolution could play a large role in providing an alternative energy source in the future due to its high energy density.

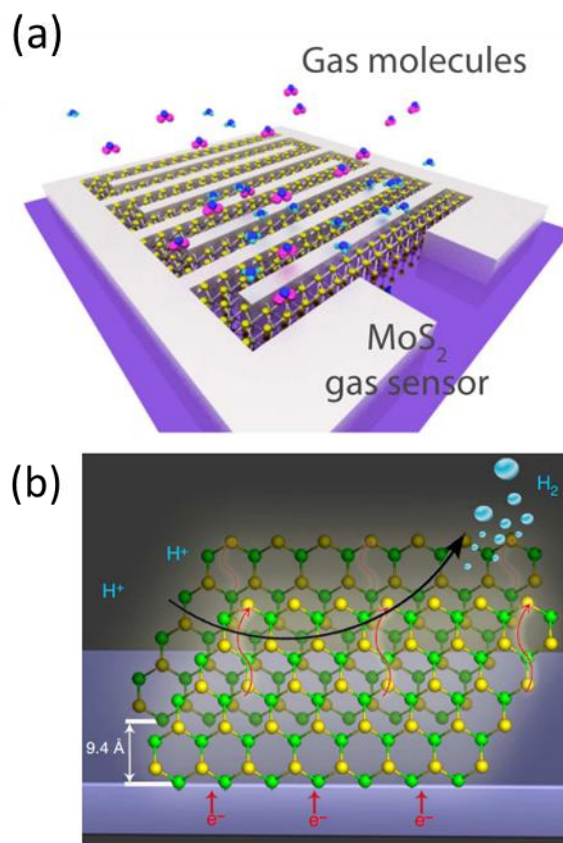


Figure 2.5. (a) 3-Dimensional schematic of a gas sensor fabricated using a monolayer of MoS₂. (b) Schematic representation of the edge-terminated MoS₂ on glassy carbon electrode for HER. Green and yellow spheres represent Mo and S atoms respectively. [40][10]

Lithium ion batteries are a widespread power storage device and typically use graphite as the cathode, however it has a low charge capacity (372 mAh/g).[47] MoS₂ has been shown to have a much higher charge capacity of 800 mAh/g.[11] Monolayer TMDs have also been suggested as a material for the anode as they do not suffer the structural instability of their bulk form since the loosely stacked nanosheets are more able to withstand structural changes and stress gradients caused by intercalating lithium during charging. This increases their cycling capacity. By virtue of their increased surface area

the charge capacity of nanomaterials is larger than their bulk equivalents. Composites of MoS₂ and graphene display a charge capacity of ~1,100 mAh/g as well as good cycling stability.[48][49] This could pave the way to batteries with greater energy densities than before.

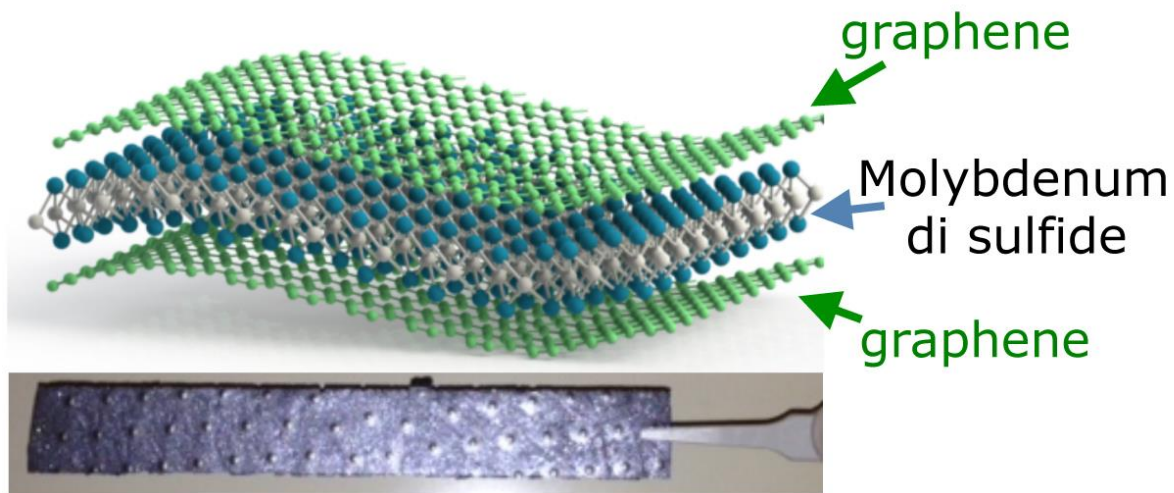


Figure 2.6. Shown on top is a schematic of a heterostructure of graphene and MoS₂ to be used as an anode. The image below is a free-standing graphene-MoS₂ paper electrode. [50]

2.2.2 Fabrication

In order to capitalise on the properties of 2-dimensional TMDs it is necessary to devise fabrication techniques capable of producing high quality ultra-thin crystals and at sufficient scale to be commercially viable. Since both TMDs and graphene are layered crystals and there is some overlap in production techniques (CVD, mechanical exfoliation etc.) the difference in chemistry also needs to be taken into consideration. Each production method has its own advantages and disadvantages. Techniques can be broken into two branches; bottom-up and top-down. In general, top-down approaches produce larger quantities of lower quality material and bottom-up approaches yield high quality samples but are difficult to scale. This trade-off can be overcome by selecting the appropriate method for the required application. Slower methods such as CVD can

be used for high precision use-cases in circuitry or electronics. Whereas, applications with a reduced quality requirement, for example, large area displays, can make use of large scale and low cost methods e.g. liquid phase exfoliation.

2.2.2.1 Bottom Up

Precision applications require a high degree of reproducibility and uniformity. For applications like integrated circuits it's essential for the method to be compatible with current semiconductor industry techniques, simplifying the adoption of these new materials. Chemical vapour deposition (CVD) is one such method and has been demonstrated for MoS_2 and WS_2 . A few approaches have been proposed, each strategy consists of applying a high temperature to sources of the metal and the chalcogenide.

Lee et al described a method using vaporised MoO_3 and S powders that were then deposited onto a nearby substrate of SiO_2 . [51] The result is mono or few layer TMDs with crystalline domains of ~ 100 micron. A second method requires the substrate to be dip-coated in ammonium thiomolybdates $[(\text{NH}_4)_2\text{MoS}_4]$ and annealed at 500°C to produce sheets of MoS_2 . [51], [52]

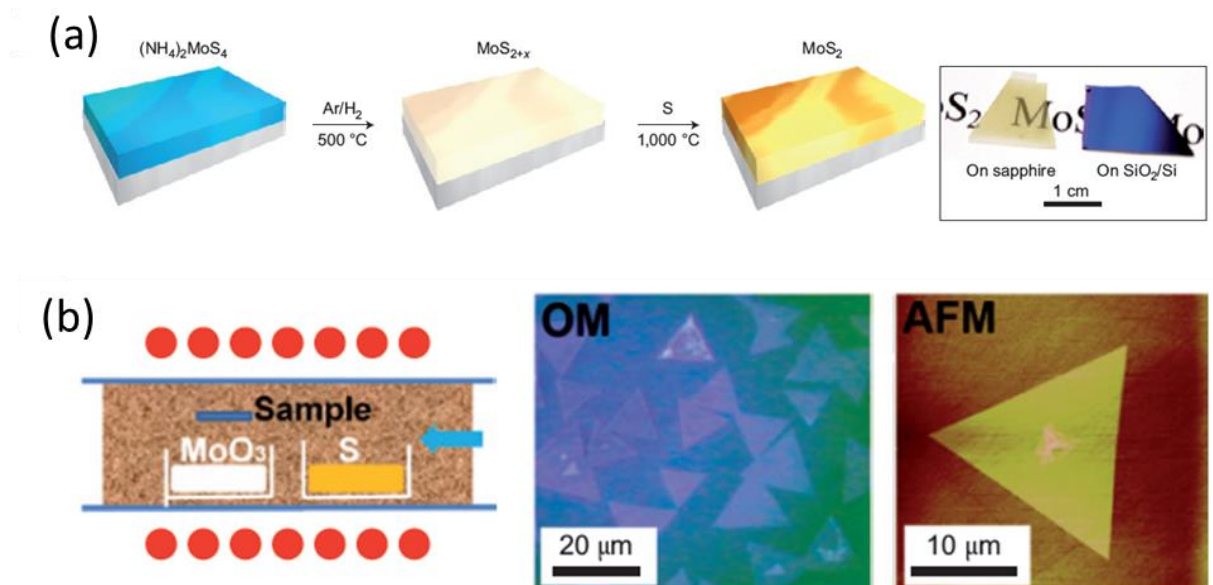


Figure 2.7. (a) Schematic of the two step thermolysis method of producing layers of MoS_2 . On the left is an example of the films obtained on a sapphire and a silica substrate. (b) Alternative method using the gas phase reaction of MoO_3 and S powders. Examples of flakes grown using this method are shown to the left. OM is an optical micrograph and AFM is an image taken using atomic force microscopy. [51]

Given the increased complexity of the stoichiometry, the boundaries between these domains are more complicated than those seen in graphene. These can be tilt boundaries or mirror twins where the positions of Mo and S atoms are switched. Depending on their identity and concentration, defects can affect the electronic and photonic properties of the material. This can be seen in conductivity and photoluminescence measurements.[53][54][55][56] Work is ongoing to improve the resulting films and extend these methods to other TMDs using tungstic acid and thiourea or selenourea.[57]

2.2.2.2 Top Down

Mechanical Exfoliation

The simplest method for producing monolayers of a layered crystal is micromechanical cleavage using adhesive tape. This method was first developed by Frindt et al. [58]. It is based on peeling apart successive layers before achieving single layer sheets. It has since been successfully applied to TMDs and other layered crystals such as BN to produce monolayers.[59][60] While this method produces high quality sheets suitable for academic research and fundamental characterisation, it is not scalable and does not allow control over lateral size and layer number.[34], [61] For this reason it is not suitable for large scale production.

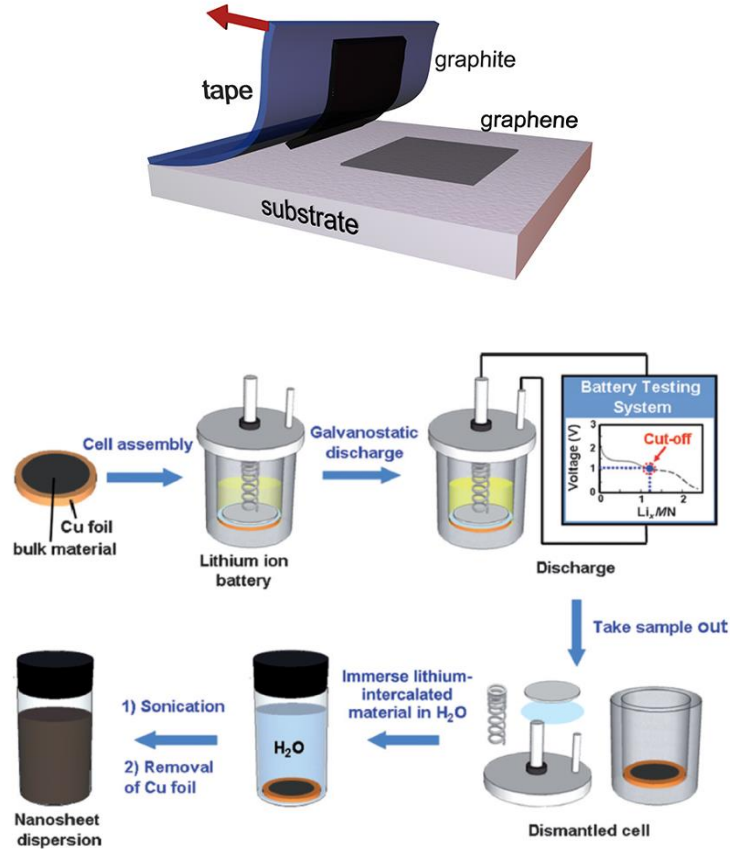


Figure 2.8. On the left is diagram of the scotch tape method, whereby layers are successively peeled away from a bulk flake to eventually obtain a monolayer sample. To the right is a schematic of the electrochemical lithium intercalation process to produce 2D nanosheets from the layered bulk material ($MN=BN$, metal selenides, or metal tellurides in Li_xMN). [62][63]

Chemical Exfoliation

Lithium can be used to intercalate between the crystal layers. This is done by submerging the TMD sample in hexane with dissolved n-butyllithium or other lithium containing compound for 48 hours.[64] Once the lithium has had time to intercalate the sample is exposed to water which then reacts with the lithium producing H_2 gas, forcing apart the layers. There are drawbacks to this technique. Including lithium's reactivity with water, requiring that the process take place in a dry environment, the formation of a complex, $Li_x MoS_2$, this alters the structure of the layer from the semiconducting

trigonal prismatic (2H) to the metallic octahedral (1T) phase, evidenced by the quenching of the photoluminescence. This phase change can be reversed by annealing at 300 °C. The long duration of the method (days) and the need to carefully avoid the formation of LiS_2 . [65]

More recently, a method using a lithium foil anode as part of an electrochemical cell has been reported by Zeng et al. This method allows a greater degree of control of the lithiation process. It also takes several hours compared to the days of the previous method. [63]

Liquid Phase Exfoliation

The impetus behind this work and studying the surface energy of 2D nanomaterials stems from this method of production. Solubility theory and how it applies to liquid phase exfoliation will be covered in greater depth later in this chapter. An appropriate solvent is chosen based on solubility theory to obtain a thermodynamically stable dispersion and lower the energetic cost of exfoliation. [66][67] The material is submerged in this solvent; the TMDs are then subjected to either sonication or shear mixing to delaminate the layers from one another. This method obtains large quantities of nanosheets and because they are in solution they can then be easily used in the creation of composites, thin films, in inkjet printing and spraycoating. [68], [69] In applications where solvent toxicity poses a difficulty the dispersion can be created in an aqueous surfactant solution. Unfortunately, while this method produces large amounts of nanosheets, the resultant dispersion is polydisperse with only a small amount of monolayers. This can be remedied using centrifugation which through the use of trapping steps and density gradients it is possible to size select the nanosheets. [67], [70]

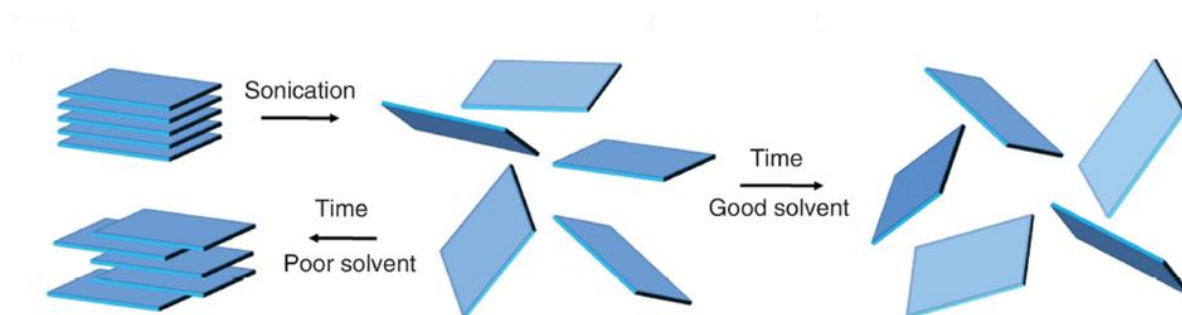


Figure 2.9. Representation of the process of liquid phase exfoliation. On the left hand side sonic energy is added to disperse the nanosheets. It then shows the successful stable dispersion with the use of a “good solvent” or the re-aggregation of the sheets with the use of a “bad solvent”. [71]

2.3 Boron Nitride

Just as with TMDs, the discovery the single layer graphene has led to renewed interest in Boron Nitride (BN). It has three distinct allotropes; wurtzite (w-BN), cubic (c-BN) and hexagonal (h-BN). Each has an equal number of boron and nitrogen. Cubic BN is structured like diamond and one of the hardest known materials.[72] Hexagonal BN has a structure similar to that of graphene. It is lamellar, with layers of hexagonally arranged boron and nitrogen bound strongly together within the plane by sp^2 hybridised orbitals.[73] Interaction between the layers is mediated by weak Van der Waals forces.[74] The weak interlayer bonding makes the bulk form soft and suitable for dry lubrication, and it is commonly used in cosmetics.[75][76] As h-BN has a layered 2-dimensional structure it is the form of interest to this work and from here on is referred to as BN.

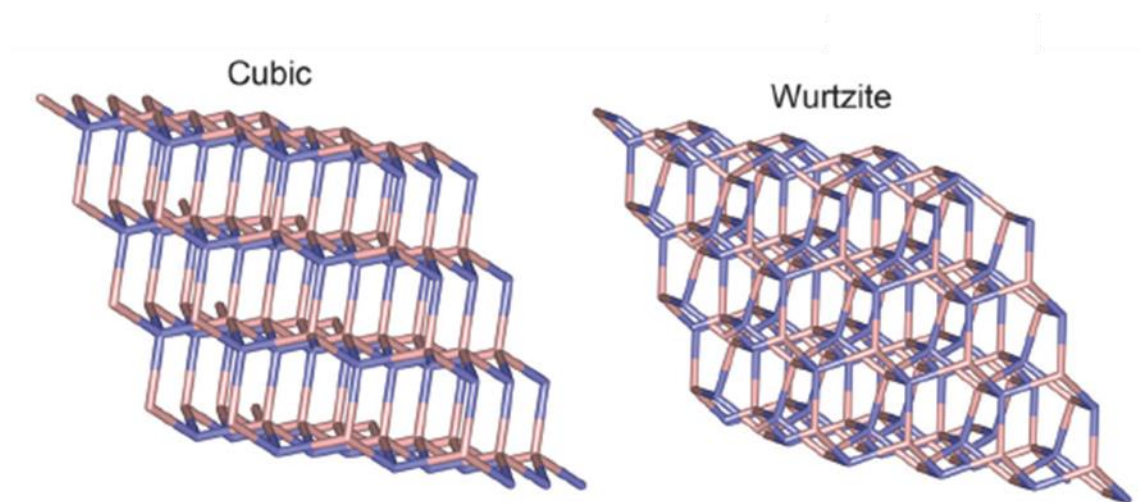


Figure 2.10. Models of the cubic and wurtzite structures of boron nitride. [77]

As the layers are stacked they alternate, with a boron atom sitting above and below a nitrogen atom. This is because of the difference in electronegativities between the two species inducing a dipole and adding an ionic component to the interlayer bonding.[74] This extra interaction results in stronger bonding between the layers than seen in graphene.[78] It can also cause lip-lip interactions at the edges between layers.[79], [80] This can create bridges between layers facilitating growth of BN nanotubes but hindering some other properties.

Due to the localisation of the electron cloud around the nitrogen a large band gap opens causing it to be electrically insulating and have a white appearance.[81][82]

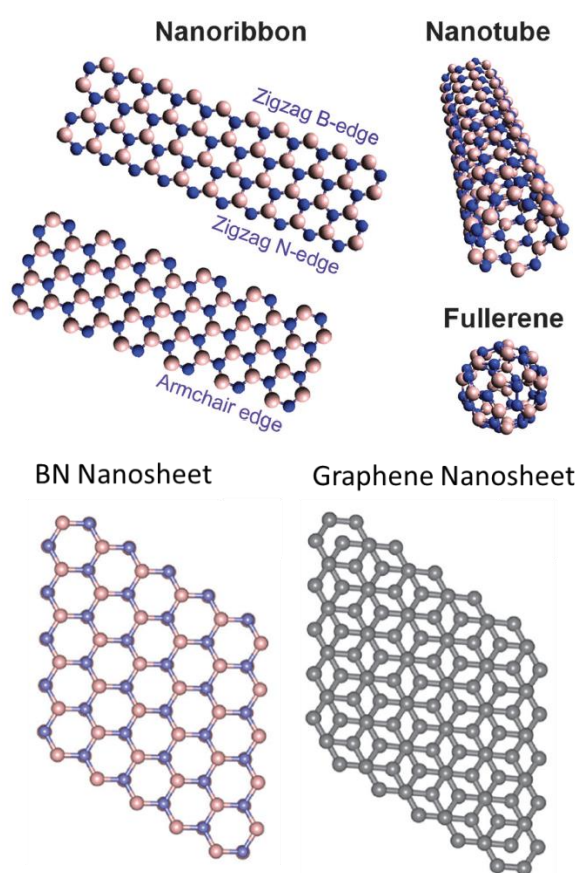


Figure 2.11. Left: Diagrams of 2D, 1D and 0D boron nitride nanostructures. Edges of the flat nanostructures can be either zig-zag or armchair. Right: Comparison of stacks of boron nitride sheets to graphene sheets. [77]

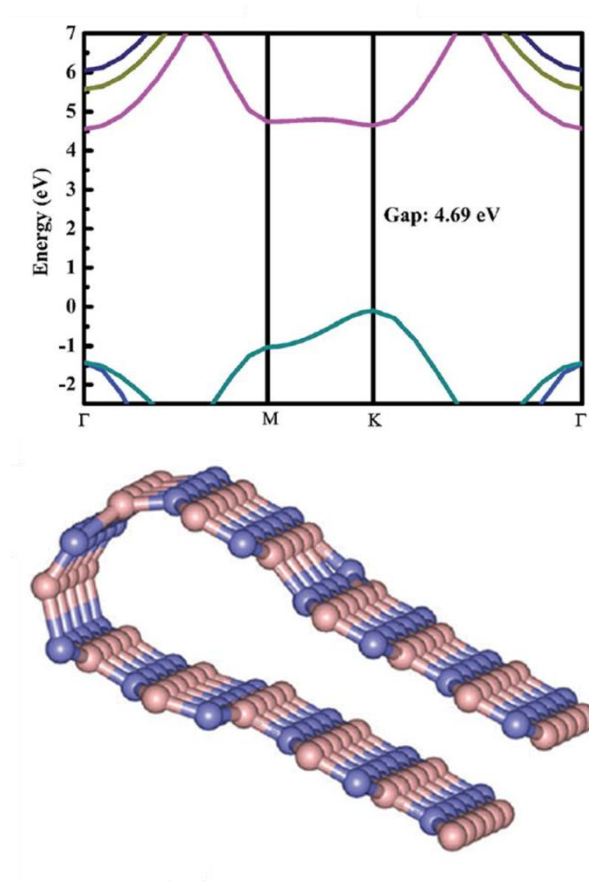


Figure 2.12. Band structure of hexagonal boron nitride. Cross-sectional view of the bridges formed across two monolayers resulting in what is essentially a folded monolayer.[82][77]

2.3.1 Properties and Applications

2D h-BN possesses an array of useful properties; high thermal conductivity, low electrical conductivity, high mechanical strength, low density and it is chemically inert. This collection of properties allows it to be used in a wide variety of applications; high temperature crucibles, protective coating, an ultraviolet source, dielectric layers and even in cosmetics.[76][83][84][85]

One promising application of h-BN as a dielectric layer is as a part of heterostructures with graphene.[86][87][88] As an atomically thin insulator it can be used as a barrier between conductive components in microelectronics. Tri-layer heterostructures of BN-C-BN have been shown to have exceptionally high charge mobility ($\sim 500,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).[89] FETs with this composition have been shown to have on/off ratios of $>10^4$,

overcoming the issue of graphenes lack of a bandgap.[90] The smooth surface of h-BN helps improve device quality and performance.[91] When placed on a substrate of h-BN, FETs made from WS₂ and black phosphorus have improved mobilities (214 and 1350 cm² V⁻¹ s⁻¹) and on/off ratios (10⁷ and 10⁵).[92][93] In the case of black phosphorus, h-BN prevents corrosion from ambient moisture which rapidly degrades the structure and electronic properties.[94]

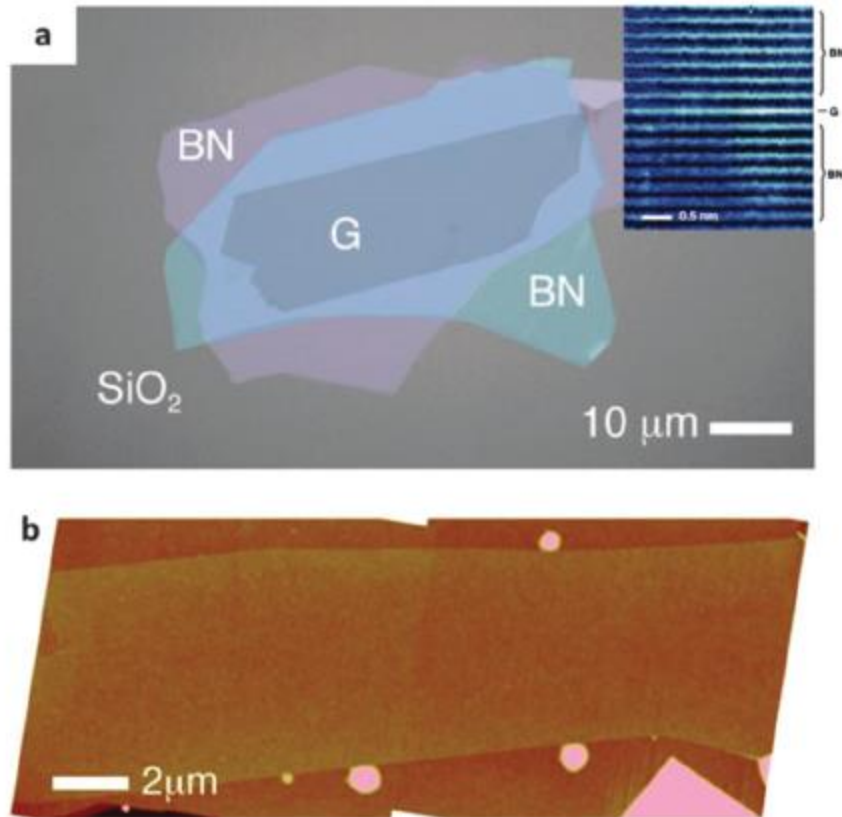


Figure 2.13. (a) Optical image of a heterostructure of boron nitride encapsulating a monolayer of graphene. Inset is a cross-section ADF-STEM image of the device. (b) AFM image showing that it is free of wrinkles and bubbles. [95]

The electronic properties of boron nitride nanostructures can be altered through a variety of means. Theoretical studies have shown that the bandgap of a boron nitride nanoribbon depends on its width and edge type. Zigzag edged nanoribbons have an indirect bandgap that decreases with as width increases and armchair edged nanoribbons have a direct bandgap. It is also possible for the band gap to be altered

with doping, strain engineering or an external electric field, further adding to the versatility of h-BN for microelectronics.[96][97][98]

The high strength and stiffness of h-BN make it an interesting candidate for polymer composite reinforcement. The stiffness of a single layer of h-BN has been calculated to be 267 Nm^{-1} .[99] Its mechanical properties have been studied using an atomic force microscope to carry out nanoindentation measurements. Nanosheets of h-BN were suspended above holes in a Si wafer. A diamond tip was used to press on the sample. The nanosheets were found to have an elastic modulus in the range of $220 - 510 \text{ Nm}^{-1}$.[81] It was also observed that increasing defect density degraded the mechanical properties of the nanosheets.

Due to their low density and mechanical toughness boron nitride nanostructures have been used to make reinforced composites. PMMA films had their elastic moduli and strength increased by 22% and 11% respectively with only a 0.3 wt% of boron nitride.[100] In this case the surface energy is crucial to ensuring adequate binding between the polymer and the boron nitride.

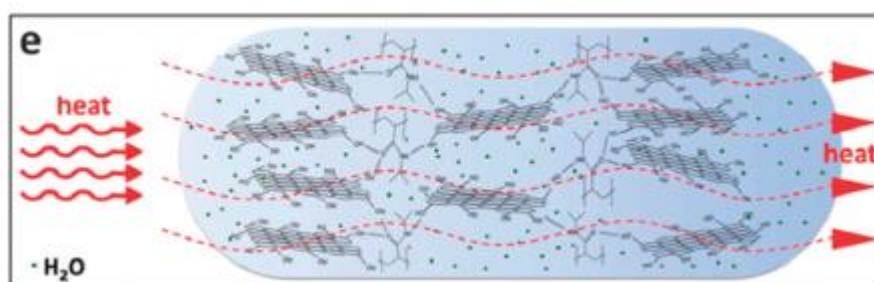


Figure 2.14. Illustration of the enhanced heat transfer in PNIPAM/OH-BNNS hydrogel, which has resulted from the excellent integration between the OH-BNNS and the cross-linked PNIPAM. [101]

Its high thermal conductivity can also be exploited when added as a filler to polymers. The thermal conductivity of h-BN along its plane is $600 \text{ W m}^{-1} \text{ K}^{-1}$.[102][103] Compared to mechanical reinforcement a much higher volume fraction of filler required. This is in order to build thermally conductive network of h-BN. Zhu et al reported a 50/50 by mass composite film of h-BN and cellulose with a thermal conductivity of $145.7 \text{ W m}^{-1} \text{ K}^{-1}$, 4000 times greater than that of cellulose alone.[104]

While boron nitride nanosheets do not absorb in the visible region of the electromagnetic spectrum, they show a strong absorption in the UV at ~215 nm. They also show a strong cathodoluminescence in the same region. This makes it ideal for compact UV laser devices used in optical storage, sterilisation and photocatalysis.[105]

h-BN can be formed into porous structures which have extremely high specific surface area. This can be achieved either with or without a template. There are a wide selection of templates that can be used; zeolites, activated carbon and graphene aerogels.[106][107][108] A non-templated method was reported by Weng et al. using boric acid-dicyandiamide as a precursor yielding a nanostructure with a specific surface area of $1900 \text{ m}^2 \text{ g}^{-1}$.

This high porosity can be exploited in applications ranging from H_2 storage and removing pollutants from water. Doped h-BN nanostructures have been shown to have uptake capacities of 1.07 %wt at 77 K and 1 bar.[109] Theoretical studies have that cage-like structures may hold up to 12 %wt of H_2 . [110] It has been reported that a wide range of pollutants in water can adsorb to the surface of porous h-BN structures; oil, organic solvents and dyes.[111][112][113] What's more is that the h-BN can be restored to its original condition with little loss in adsorption capacity. This would be an invaluable environmental application.

Finally, toxicity of carbon based nanomaterials has been a major barrier to biological applications.[114] Fortunately, h-BN has much lower cytotoxicity and better biocompatibility and has been shown to be suitable for drug delivery.[115] Weng et al were able to load the drug doxorubicin to OH-BN, exhibiting much higher potency than the free drug.[116]

2.3.2 Fabrication

Like carbon, h-BN has been synthesised not only as sheets but also 1D nanotubes and 0D fullerenes.[117][118][119][120][121] Commercially, h-BN is sold in its bulk form, with a lateral size usually in the microns and made from stacks of a few hundred sheets. Ordinarily boron nitride is synthesised but it has been recently discovered occurring in nature.[122] It was first synthesised by Balmain in 1842 using boric acid and potassium cyanide.[123] Since many more fabrication methods have been developed. As before

when discussing TMDs the fabrication methods are broken into Top-Down and Bottom-Up. There is significant overlap with the methods discussed previously; this is to be expected given the similarities in bulk structure of these layered materials. Nevertheless, there are chemical differences which affect the fabrication so it is prudent to present an overview.

2.3.2.1 Top Down

Mechanical Exfoliation

At the edges of a h-BN crystal the ionic nature of the interlayer bonding can cause “lip-lip” interactions where the two layers form a chemical bond becoming a continuous folded layer.[79] This lowers the energy of the system by decreasing the number of dangling bonds.[124] This stabilises the structure as a whole and impedes the exfoliation through now famous “scotch-tape” method used first for isolating monolayer graphene. A second approach is the use of shear forces, this has been used to successfully exfoliate boron nitride, TMDs and graphite. Shear forces can be applied either with a ball mill or shear mixer. In a ball mill the shear forces can be tailored by changing ball mass, speed of milling and milling agents can be added to reduce impacts, milling contamination and prevent agglomeration due to its similar surface energy. For example benzyl benzoate was used by Li et al. to obtain h-BN nanosheets.[125] Coleman et al have applied their shear mixing technique to h-BN and were able achieve high concentrations of a number of 2D materials.[126], [127] Shear mixing is done using an industrial mixer, it has a stator and rotor which are kept a small fixed distance apart. They are placed into a vessel containing an appropriate solvent and some of the material to be exfoliated. As the rotor spins within the stator a shear force is generated. This shear force slides the sheets of the bulk h-BN or other layered crystal past one another producing exfoliated nanosheets.

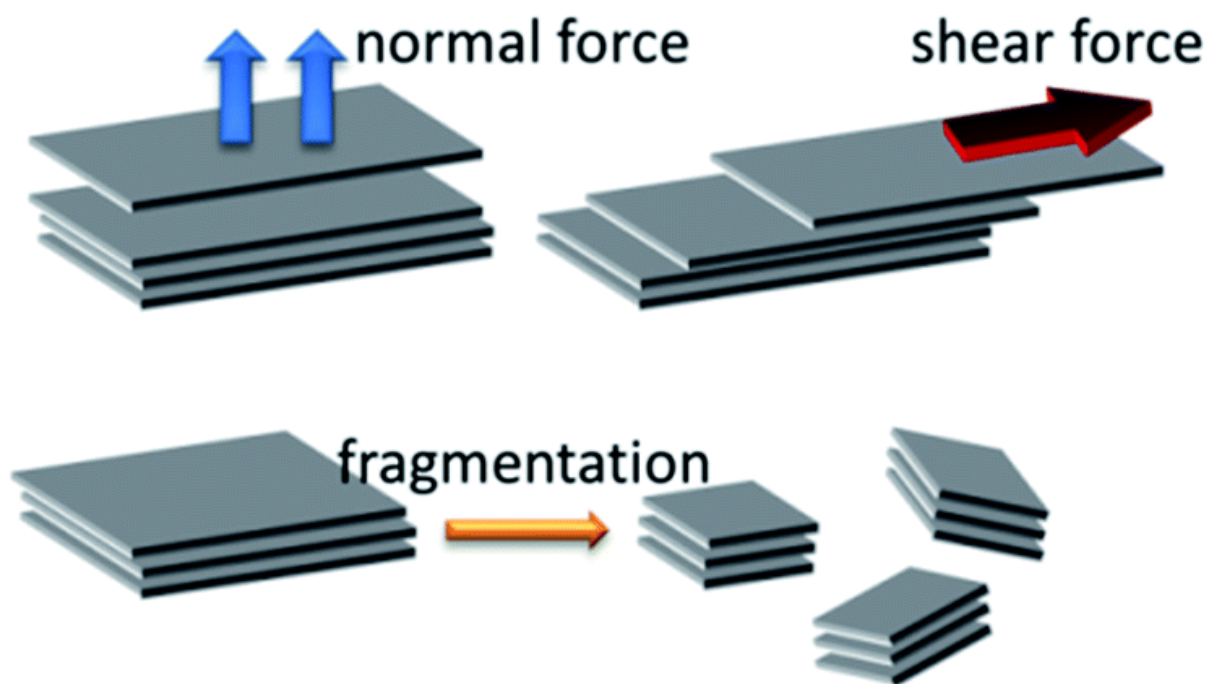


Figure 2.15. Top: Illustration of the normal forces resultant in the scotch tape method and the shear forces resulting from either ball-milling or shear mixing. Bottom: Illustration of the fragmentation that can occur during ultrasonication. [128]

Chemical Exfoliation

As mentioned earlier, h-BN has a polar component to it. This property can be exploited when choosing a solvent to promote exfoliation. DMF, a polar solvent has strong interactions between the solvent molecules and the h-BN surface. Both DMF and chloroform have been shown to disperse nanosheets in solution.[100]

It is possible to functionalise h-BN in order to make it soluble in water.[129] This is important in the biological applications mentioned earlier because the body is an aqueous environment. This can be done with amine molecules with long hydrophilic chains. Since amines are Lewis bases they attach to the electron poor boron atoms.

2.3.2.2 Bottom Up

CVD

Chemical Vapour Deposition has been used to synthesise boron nitride since the 60's.[130][131] The process was based on the reaction between ammonia (NH_3) and boron trichloride (BCl_3) at a temperature of $\sim 1800^\circ\text{C}$. Since then many other recipes for the deposition of boron nitride films have been published, with most using a variation of borazine (borazine, borazane, trichloroborazine etc.). The first monolayer of h-BN was grown in 1990 using the decomposition of borazine on transition metals.[132] Borazine is an analogue of benzene where the carbon atoms are replaced with alternating boron and nitrogen atoms. These types of molecules are ideal because of their low toxicity and 1:1 ratio of boron to nitrogen. Boron nitride films can be deposited onto either silicon or metallic substrates at temperatures ranging from 600 to 1000°C . [133][76][134]

2.4 Solubility Theory

As mentioned previously, liquid phase exfoliation (LPE) is made possible through the choice of a suitable solvent. This section will go into greater detail about the physics behind how a solvent can create a stable dispersion of nanomaterial.

Nearly a decade ago it was shown that carbon nanotubes could be exfoliated in N-methylpyrrolidone.[66], [135] It was posited that because of the similarity between carbon nanotubes and graphene that the same technique could exfoliate graphene sheets. Since then LPE has been shown to exfoliate a wide array of layered materials such as TMDs and TMOs.[126] Not only does the appropriate choice of solvent enable exfoliation but it also inhibits re-aggregation and maintains a stable dispersion of nanosheets in solution. This happens because of the strong interaction between the nanosheet surface and solvent minimises the energetic penalty of exfoliation.[136] Solution thermodynamics can be used as a framework to explain the miscibility of nanomaterials with some solvents and help find suitable solvents for a given material.

2.4.1 Solution Thermodynamics

The quantity that governs whether a mixture of two components is thermodynamically stable is the free energy of mixing (ΔG_{mix}). It represents the difference in energy between the two components when they are separate and when they are mixed. It can be expressed as:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad (2.1)$$

Where ΔH_{mix} is the enthalpy change of mixing and ΔS_{mix} is the change in entropy after mixing. Mixing is favourable when ΔG_{mix} is negative. In cases when the two components being mixed are small molecules the entropy change is large and causes the ΔG_{mix} to be negative.[137] In the cases of comparatively large rigid nanosheets or nanotubes the entropic term is quite small and may not be sufficient to overcome the enthalpy of mixing.[66][67] The focus must then turn to minimising the enthalpic term. It can be thought of as the energetic “cost” of separating the nanosheets to infinity and subtracting the energy to disperse them in a solvent. Hernandez et al. [67] showed that the energetic cost of exfoliating nanosheets per unit volume could be expressed as:

$$\frac{\Delta H_{\text{mix}}}{V_{\text{mix}}} \approx \frac{2}{T_{\text{flake}}} (\delta_{\text{flake}} - \delta_{\text{solvent}})^2 \phi \quad (2.2)$$

Where V_{mix} is the mixture volume, T_{flake} is the thickness of the dispersed flakes, δ_{solvent} and δ_{flake} is the square root of the surface energy of solvent, γ_i and the flake respectively, $\delta_i = \sqrt{\gamma_i}$ and ϕ is the volume fraction of the dispersed nanosheets. This expression shows that to minimise ΔH_{mix} it is necessary to minimise the difference between the surface energy of the solvent and of the solute.

To get a more intuitive sense of why it is important to match the surface energy of the solvent to that of the nanosheets we can imagine nanosheets suspended in an unsuitable solvent. If the solvent has a surface energy much higher than that of the nanosheets the solvent molecules will have a preference to interact with each other than the nanosheets. This is in order to minimise the energetic cost associated with having weaker interactions between its neighbours. This process causes the nanosheets to re-aggregate and fall out of solution.

This is related to the process that occurs when the surface of a liquid minimises its surface area. In a droplet on a surface, the molecules are more attracted to one another than the substrate, this causes the droplet to minimise the number of molecules at its interface. This means there is a free energy cost to creating more interfacial or surface area. This quantity is labelled the surface energy. As the surface energy of the substrate is increased above that of the liquid, the molecules will favour interacting with the substrate and spread out across the surface in a process known as wetting.

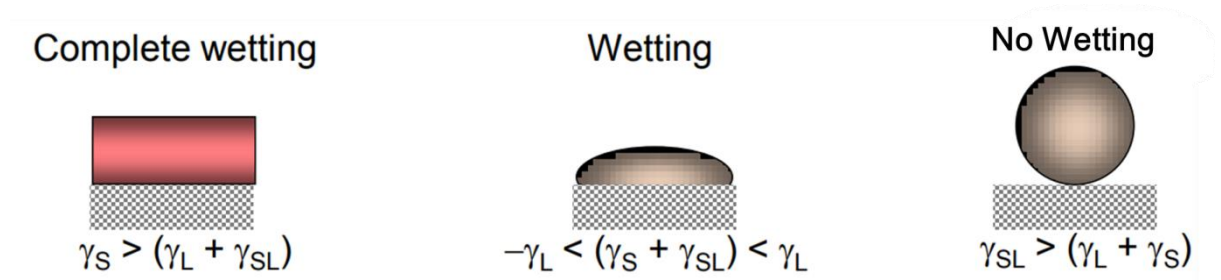


Figure 2.16. Diagram showing how the surface energy of the substrate and liquid affect the wetting of a surface.

The surface energy of liquids is not a commonly known material parameter, it can however be estimated from a simple relationship with surface energy, E , and surface entropy, S .

$$\gamma = E_{surface}^{solvent} - TS_{surface}^{solvent} \quad (2.3)$$

The surface tension, γ , of a liquid is readily available for most solvents. The entropic term has a universal value of $0.1 \text{ mJ m}^{-2} \text{ K}^{-1}$, thus at room temperature the entropic term can be approximated at $\sim 30 \text{ mJ m}^{-1}$. [66]

2.5 Surface Energy

The previous section discussed surface energy with little explanation or description. To address this, the following presents an overview of the theory and causes of surface energy. The final section compares three different methods to measure surface energy.

Atoms at the surface of a material are not bonded to the maximum number of nearest neighbours possible. This causes the atoms at the surface to feel a net inward force; this is in contrast to bulk atoms which feel no net force in any direction. In liquids we see this manifested as bubbles and droplets minimising their surface area and thereby their surface energy. Unsatisfied bonds cause the exterior atoms to occupy a higher energy state than those within the bulk structure. This additional energy, expressed in units of (J/m^2) is known as the surface energy of a material. In a related manner the surface energy can also be thought of the energy required to form a new surface of this material.

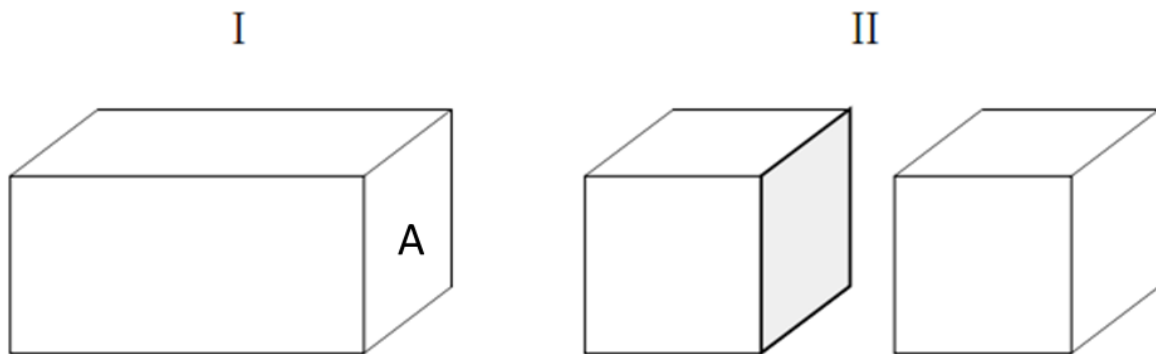


Figure 2.17. Diagram showing two states (I and II). On the left is a block with cross-sectional area A and a Gibbs free energy of ΔG_I , on the right is the same block cut in two but now with a different Gibbs free energy, ΔG_{II} . The difference in the free energies of these two states is related to the surface energy of the block.

Shown in figure 2.17 is a single block on the left with a free energy of G_I on the right is the same block cut in two with a new higher free energy of G_{II} . The difference between the free energies of these two systems is due to the newly broken, unsatisfied bonds. The surface energy is the difference in free energy between the two states divided by the newly formed area, $2A$.

$$\Delta G = G_{II} - G_I = 2A\gamma \quad (2.4)$$

Surface energy has contributions from two types of intermolecular interactions; the dispersive and specific interactions. The dispersive component is due van der Waals forces caused by London dispersive interactions; it is present in all molecules and atoms.[138] The specific surface energy is due to the Debye induced dipole force, Keesom permanent dipole force and hydrogen bonding.[138] Specific interactions only occur when the system contains a polar molecule. The relative strength of these interactions varies between materials. In the case of TMDs the specific component is quite weak and can be neglected.

The electron density at a point in the electron cloud around a molecule is continually fluctuating. This spontaneous uneven distribution results in a temporary dipole, this dipole can then induce a complementary dipole in a neighbouring molecule. The two molecules then feel an attractive force toward one another. This force can be described by the Lennard-Jones potential.

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2.5)$$

With V as the Lennard-Jones potential, ϵ is the potential well-depth and is a measure of strength of attraction, σ is known as the van der Waals radius and is the distance at which the potential is zero and r is the distance between the particles. The Lennard-Jones potential combines the attractive van der Waals force with the (much shorter range) repulsive force caused by overlapping electron clouds and the Pauli exclusion principle.

When the two particles are at infinity the potential is zero, as they move closer the potential becomes negative and their separation decreases until they fall into the

potential well and become bound. They reach an equilibrium distance, $r_{\min}$, at the bottom of the well. If their separation reduces they will be repelled and fall back toward $r_{\min}$. The strength of the van der Waals interaction felt by a molecule is dependent on its molecular weight and the polarizability of its constituent atoms. This can be seen by comparing the elution times of a large molecule (decane) to that of a smaller molecule (hexane) which can be many times shorter.

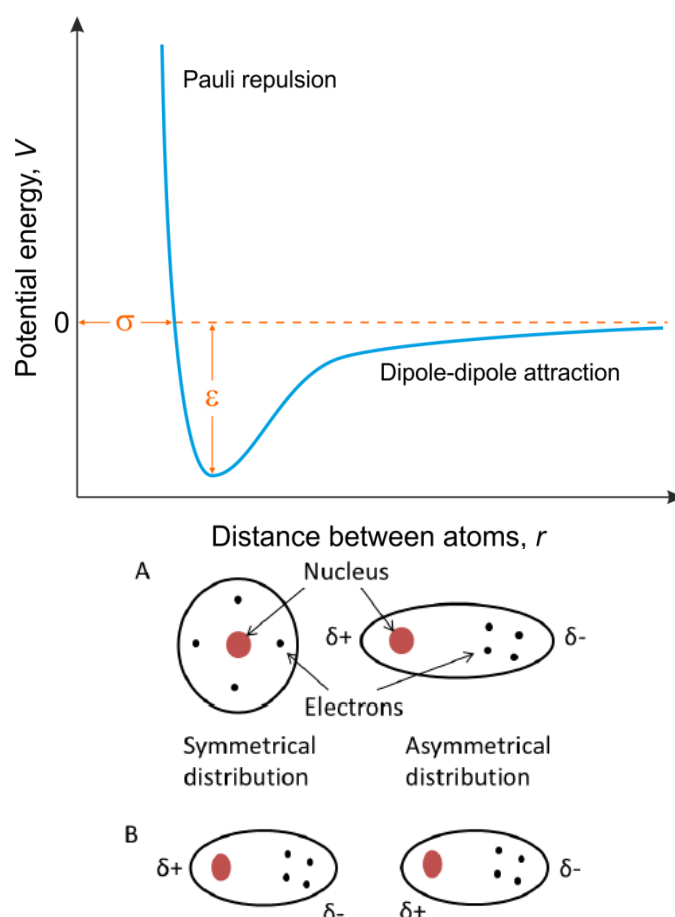


Figure 2.18. Plot of the Lennard-Jones describing the potential felt between to particles due to van der Waals forces. At relatively large distances (5 nm), there is no attractive force between the two particles. As the particles approach one another the potential slopes downward resulting in an attraction. If they get closer than $r_{\min}$ a repulsive force due to the Pauli exclusion principle begins to dominate pushing the particles back toward $r_{\min}$. (A) Two non-polar molecules, the electron distribution around a molecule can spontaneously become asymmetric leading to a small polar moment. (B) This temporary dipole can lead to an induced polarisation in a nearby molecule. This will cause the two to become attracted to one another.

The specific contribution to surface energy is caused predominantly by dipole interactions, either permanent or induced along with hydrogen bonding. A dipole is a molecule that has an uneven electron density, with one part of the molecule having a slight positive charge, the other a slight negative charge. It can be a permanent dipole, in this case it is caused by a difference in electronegativity between the atoms of the molecule. An example of this is sulphur dioxide where the oxygen atoms, having a higher electronegativity, pull on the electrons more strongly than the sulphur. Thus the oxygen atoms are shrouded in a greater electron density causing them to have a slight negative charge.

A polar molecule, by distorting its electron cloud, can induce a complementary dipole in another, neighbouring molecule. This sets up an attractive force between the two particles. This is known as the Debye force.

The final component of the specific interaction is hydrogen bonding. It is very similar to the permanent dipole. It occurs when hydrogen is bonded to another atom with a much higher electronegativity causing an imbalance in the distribution of the electron density. Water is the most obvious example of this, the oxygen atom has a high electronegativity and is able to pull the shared electrons from the two hydrogen atoms. The oxygen now is surrounded by greater electron density, whereas the hydrogen atoms are comparatively bare. This hydrogen bonding is the main reason behind water high boiling point and specific heat capacity.

So far this section has spoken about the surface energy of a material as though it can be described as a single value. For the majority of materials this is not the case. All materials have defects of one type or another. In the case of layered materials, such as the TMDs studied in this work there will also be edge sites. These defects and edge sites can behave differently to the rest of the surface. This may be due to fewer satisfied bonds (as is the case for edges) or it may be that there are dopant atoms or stress along a grain boundary. All these can cause the surface energy to differ from that of a pristine sample. A full description of the heterogeneity of a material's surface and its surface energy is essential for a full understanding of a material's behaviour.

2.5.1 Measurement Techniques

The surface energy of a material dictates how it interacts with its environment, as such a full understanding of a materials surface energy is important for many applications; from gas sensing[139], to adhesion[140] and composites[141]. The following section discusses how the surface energy of a material might be measured. It describes three methods in particular; Contact Angle, Atomic Force Microscopy and Inverse Gas Chromatography. In each case the advantages and disadvantages are considered.

Contact Angle

Probably the most widespread and simplest technique to measure surface energy is contact angle. A droplet of a solvent is syringed onto the sample surface, an image is taken and the angle the droplet makes with the surface is measured. This is repeated several times to ensure an accurate measurement. This process is replicated for several solvents of different surface energies. The angle droplet makes with the surface is given by Young's equation:

$$\gamma_{lv}\cos\theta_Y = \gamma_{sv} - \gamma_{sl} \quad (2.6)$$

Where θ is the contact angle, γ_{sv} , γ_{sl} and γ_{lv} are the solid-vapour, solid-liquid and liquid-vapour interface surface tensions respectively.

The contact angle and the surface energies of the solvents can be used to calculate the surface energy of the material. There are a few methods to do this each giving similar results; Fowkes[142], Neumann[143][144] and Owen-Wendt[145].

While contact angle is relatively inexpensive and straightforward it has significant downsides. A contact angle can only be measured on a flat surface; this makes it impossible to measure the surface energy of powders, fibres or rough surfaces. This made it unsuitable for the materials used in this work. Another major drawback is that it can only measure the average surface energy of a sample. This is because the droplet will interact with all sites simultaneously. As mentioned earlier, a material is heterogeneous, so this method disregards important information about the highest

energy sites of a surface. This is a significant shortcoming as these sites play an outsized role in applications like catalysis.

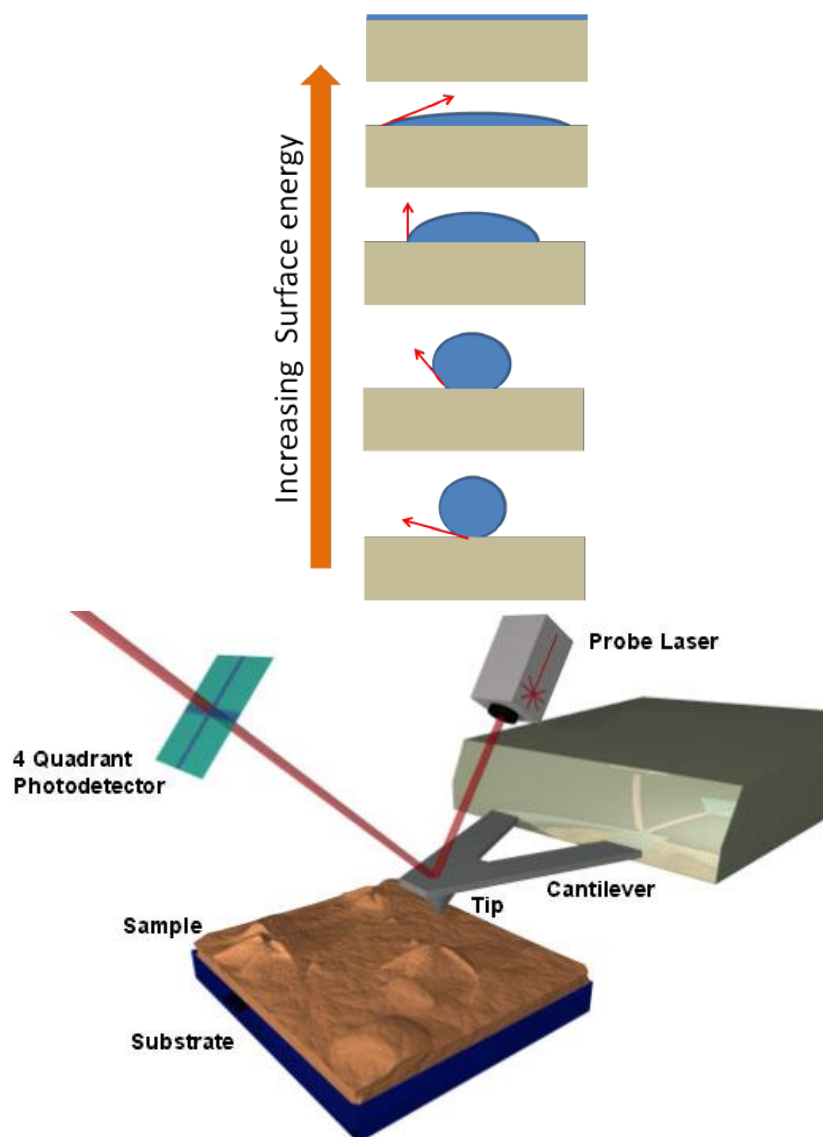


Figure 2.19. *Left: A representation of the changing contact angle of a droplet as the surface energy of the substrate is increased. Right: A diagram of the AFM setup for measuring the surface energy of a sample.*

AFM

Although AFM is mostly known for imaging because of the fact that it interacts mechanically with the sample there are many inventive ways to characterise a sample; thermal, electric or adhesion. It can even be used to measure the surface energy.[146][147] By bringing the tip down onto the surface, pulling it back and then measuring the deflection of the cantilever, the force required to free the tip from the surface can be calculated. This force can then be related to the thermodynamic force of adhesion, which in turn is related to the surface energy. Unfortunately this only gives information on that single point; to overcome this and generate statistically significant values, many measurements must be made. While it is possible to measure the heterogeneity of surface energy with repeated measurements this is a very time consuming and costly process. Another downside is that as with contact angle it also suffers from an inability to measure powders and fibres. These shortcomings rule out AFM as a suitable method for this work. To overcome them we turned to Inverse Gas Chromatography which is outlined in the next section.

IGC

Inverse gas chromatography is similar to standard analytic chromatography. In standard chromatography there is a known standard material (stationary phase) through which the unknown substance is carried by the mobile phase. Chromatography is able to separate the components of a mixture based on the time taken to elute. The time to elute depends on the degree to which the individual components interact with the stationary phase.

Inverse Gas Chromatography also makes use of the time to elute. However, in the case of IGC, the roles of the stationary and mobile phases are switched. In IGC the stationary phase is the material being studied and the mobile phase is the known standard.

A sample is placed inside a silanised glass column which is then inserted into the instrument. A series of specified volumes of standard (e.g. alkane) vapour are injected into the column. These are passed through the sample by an inert gas (helium,

nitrogen). As the vapour molecules pass through the sample they adsorb and desorb with the surface of the sample. The rate of adsorption and desorption is related to the surface energy of the probe and the sample. The time taken for the vapour to elute is related to the rate of adsorption/desorption. Therefore the elution time can be related to the surface energy of the sample. The following chapter delves into greater detail about the instrument and the theory behind calculating the surface energy.

There are two advantages to this technique which make it ideally suited to this work. The first is the method's versatility, unlike AFM and Contact Angle, IGC can be used on powders and fibres, porous and non-porous materials and rough surfaces.[148][149][150] The second is that the new generation of IGC instruments can measure surface energy at a wide range of surface coverages. The volumes of the injected probe molecules are precisely known and the cross-sectional surface area of each molecule is approximately known, from this the total surface coverage of the sample can be estimated. This means that it is possible to measure the surface energy at low coverages and interact with only the highest energy sites, then as the coverage is increased, the probe molecules will begin to interact with the lower energy sites as well.[151] As expected the surface energy measured at greater coverages matches well with values found using contact angle.[151]

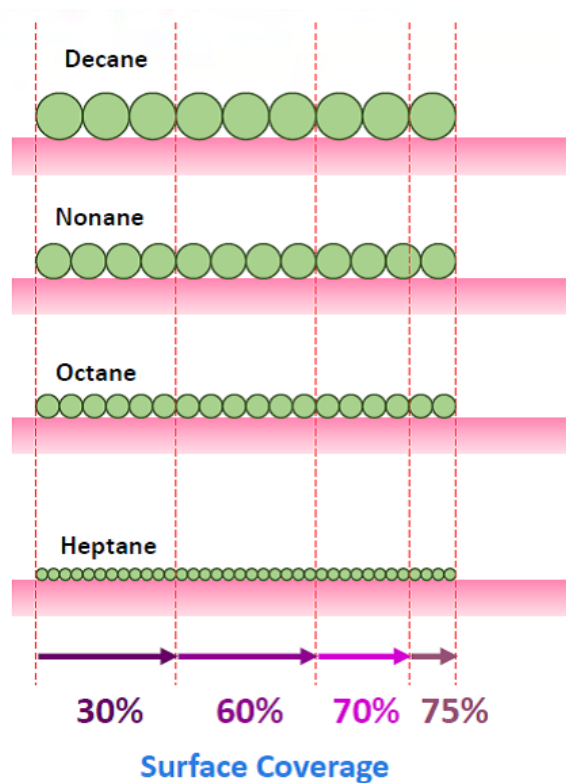


Figure 2.20. By knowing the surface area of the sample and the cross-sectional area of the alkanes it is possible to calculate the volume required for a specific surface coverage. This is illustrated here as varying numbers of spheres for each alkane. The larger alkanes require fewer moles to reach the same surface coverage as shorter alkanes. [152]

Chapter 3

Methods

3.1 Introduction

The work done in this thesis in deconvolving the contributions of edges and defects to a materials surface energy relies on a set of microscopic and characterisation techniques. Inverse Gas Chromatography was used to measure the surface energy profile and specific surface area of each sample. The theory and background of this technique is explained in detail. Samples of different flake lengths were produced using centrifugation assisted sedimentation. Microscopy was required to image these samples and obtain an accurate measure of their flake lengths. This enabled the investigation of the relationship between surface energy and flake length. As such, sedimentation theory and scanning electron microscopy are introduced. Finally, there will be a detailed discussion of the computational model used to create a theoretical framework for the analysis of the surface energy data.

3.2 Surface Energy

How a material interacts with its environment and other materials is heavily dependent on its surface energy. As such, knowledge of a materials surface energy is crucial to a multitude of industrial applications. These include pharmaceuticals where surface energy affects behaviours such as flowability and mixing, or determining adhesion in composites. Or even, as in our case, a material's stability in a solvent dispersion. [153][154][140], [141]

The aim then is to develop a method to determine an accurate description of a materials surface energy. Previous attempts have included contact angle measurements, however

this method samples 100% of the sites simultaneously and can only give the average surface energy value, omitting any information on the material's heterogeneity.

An alternative method is atomic force microscopy (AFM). This suffers from practical difficulties in probing the surface a sufficient number of times to minimise errors and construct a credible model of the surface, as well as accounting for tip size and shape. There are also theoretical difficulties in interpreting the data, with numerous models of tip-surface interactions. [146], [147]

Clearly there is a need for a method that can not only provide information on a surface's heterogeneity, but that is also time effective and easy to interpret.

3.3 Inverse Gas Chromatography

The vast majority of the experimental work in this thesis was carried out using Inverse Gas Chromatography (IGC). It was used to measure both the surface energy and specific surface area (S_{BET}) of the materials being studied. IGC was first demonstrated in 1941 by Martin and Synge to measure the partition coefficients between two liquids. [155] Since then it has found a wide range of use cases, providing information on many physicochemical properties; BET surface area, work of cohesion, glass transition temperature, acid-base properties and surface energy.[156][157][158][159][160] This versatility has made it an attractive technique for researchers in many fields including; polymer fillers, biscuits and pharmaceuticals.[148][161][162] In standard Chromatography a known stationary phase is used to separate and identify the components of either a gaseous or liquid mixture. Whereas with IGC known probe molecules in vapour form are used to measure the properties of a solid sample. This difference is illustrated in the figure 3.1 below.

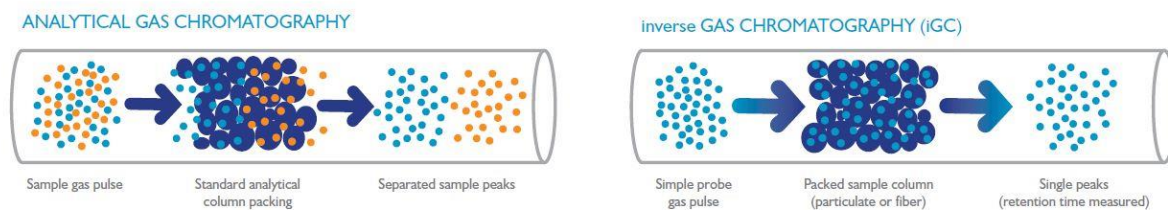


Figure 3.1. Diagram illustrating the differences between standard (left) and inverse gas chromatography (right). Standard GC studies the substance carried by the mobile phase. IGC studies the stationary phase. [163]

As the probe molecules are eluted they are detected and recorded as a chromatogram, examples of which are shown in figure 3.2. There are numerous types of detectors available, each with their own advantages and disadvantages. We will briefly outline the two most common detectors for IGC. The thermal conductivity detector (TCD) relies on the difference in thermal conductivities between the probe molecule and the carrier gas. This means that it is able to detect almost any analyte. Its main drawback is that it is less sensitive than other types of detector. Fortunately, the Flame Ionisation Detector (FID) is extremely sensitive to hydrocarbons, which is ideal for this work and hence was the detector of choice. It works by burning the analyte in a hydrogen flame. The resulting ions are detected as a change in the current between two electrodes. While it is very sensitive to hydrocarbons it lacks the universality of the TCD.[162]

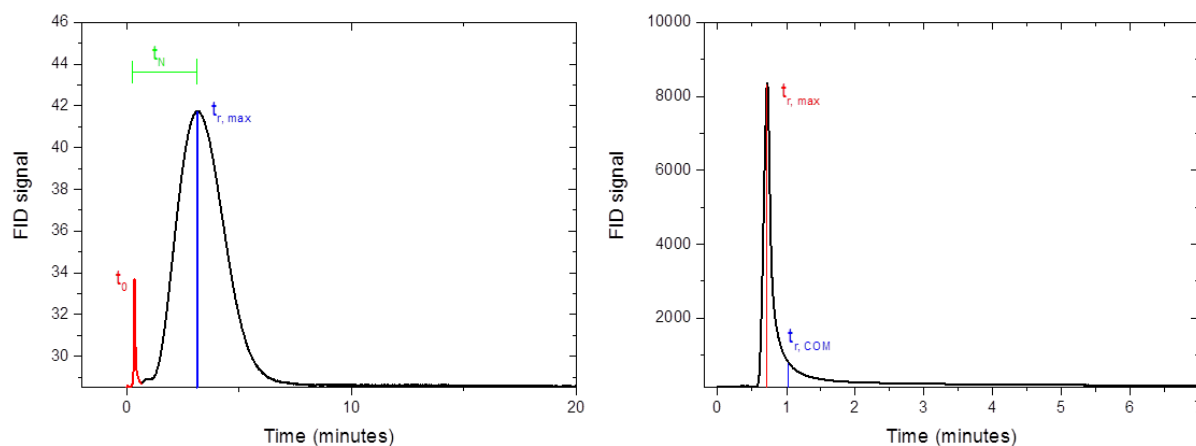


Figure 3.2. *Illustrative elution chromatograms. Shown in A and B are example chromatograms from low (infinite dilution) and high (finite dilution) coverage injections respectively. The dead-time (t_0) is subtracted from the retention time (t_r) to find the net retention time (t_n). Note the symmetric shape of the low coverage chromatogram as well as the skewed shape of the high coverage chromatogram. This asymmetry results in the need to use peak centre of mass (COM) as a measure of the retention time.*

The time taken for a probe to elute, known as the retention time, is affected by the rate of adsorption to and desorption from the sample surface. This time is therefore determined by a materials surface energy, allowing us to calculate it. IGC experiments can be conducted as either infinite dilution (ID-IGC) or finite dilution (FD-IGC). Infinite Dilution injects only miniscule volumes of probe molecule. Henry's Law is obeyed so the adsorption isotherm is linear and the chromatograms are symmetric and Gaussian, this is depicted in figure 3.2. The advantage is that we can be certain that there are no probe-probe interactions. Unfortunately this technique is limited when it comes to studying energetically heterogeneous materials as it can only probe the higher energy sites. FD-IGC involves the injection of larger volumes of probe molecules. This causes the probe molecules to interact with sites of a lower surface energy. It has been previously used to determine the heterogeneity of a material [164]. The instrument used for this thesis (Surface Energy Analyzer) can perform both types of measurement; allowing us to translate the dependence of surface energy on coverage to the energetic heterogeneity of the surface.

3.3.1 Theory

All surface energy results in this thesis stem from the measurement of the retention time, t_r . At infinite dilution, the chromatograms are Gaussian and t_r can be taken as the time at the maximum signal from the FID. Unfortunately, the chromatograms resulting from injections at finite dilutions are skewed (figure 3.2), leading to a dilemma. The two ways of measuring t_r , are peak max and peak COM (centre of mass). As with infinite dilution injections, peak max takes the time at which the signal from the FID reaches its maximum. The second method is to take the centre of mass (COM) of the chromatogram as the retention time, t_r . Peak max and Peak COM can differ from one another by a large margin. Fortunately, the difference is rarely that stark. Also, what is important in these measurements is not the absolute value of the retention time but how it varies with the length of the probe alkane. Thus even if the values of peak max and peak COM are quite different once they vary with probe size in the same manner we should obtain a similar result. Peak COM is calculated from the following.

$$t_{r,COM} = t, \quad \text{when } \frac{\sum(I_{FID}t)}{\sum I_{FID}} = 0.5 \quad (3.1)$$

One way they can differ not only in absolute value but in how they vary is due to “fronting”. This artefact is due to column overloading and the interactions between probe molecules. It is discussed more thoroughly by Caldwell et al and Zenkevich et al. [165], [166] It causes both peak max and COM to shift to longer times but affects peak max more. This is demonstrated in figure 3.3. To minimise the effects this might have on measurements we took all times using peak COM.

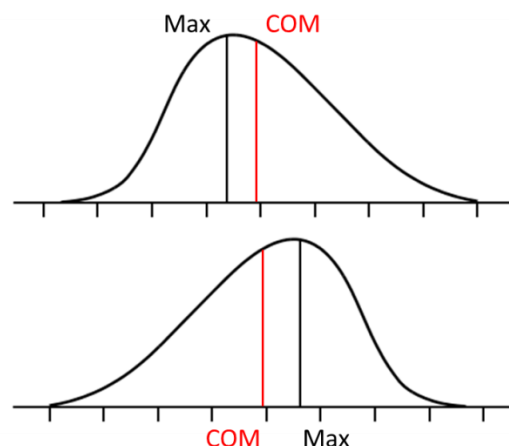


Figure 3.3. Diagram showing two chromatograms. The lower chromatogram is displaying the artefact known as “fronting”. Note the larger shift of retention time as measured by peak max compared to peak COM. Adapted from Zenkevich et al. [166]

To account for the finite time, known as the dead-time (t_0) that even a non-interacting probe takes to pass through the sample, the measured retention time needs to be converted to the net retention time (t_n). The dead-time is measured as the time taken for an injection of methane to pass through the sample column, this time is subtracted from the gross retention time ($t_n = t_r - t_0$). Using the net retention time means that the time is a reflection of interactions between probe and sample, and not of the mass or path lengths of a sample.

The net retention time is converted to the specific net retention volume, V_g ; this is the amount of gas that was required to push the injection of probe molecule through the sample column. It is calculated with the following formula. Dividing by temperature and the sample mass eliminates their effects on the result.[167]

$$V_g = \frac{j}{m}(t_r - t_0)F \frac{273.15}{T} \quad (3.2)$$

where m is the mass of the sample, F is the flow-rate of the carrier gas, T is the temperature and j is the James-Martin correction factor which corrects for the

compressibility of the gas and variation of packing density in the column. It is given by the formula below

$$j = \frac{3}{2} \left[\frac{(p_{in}/p_{out})^2 - 1}{(p_{in}/p_{out})^3 - 1} \right] \quad (3.3)$$

where p_{out} is atmospheric pressure and $p_{in} = p_{drop} + p_{out}$, p_{drop} is the pressure drop across the column. [168][167]

3.3.2 Dispersive Surface Energy

The dispersive surface energy of a solid is due to Van der Waals forces caused by the random variation of the electron cloud. The two methods for calculating the dispersive surface energy are the Schultz-Lavielle (more commonly known as Schultz) and Dorris-Gray methods. Both calculate the surface energy (γ_d) from the dependence of the retention volume on the length of the alkane. Alkanes are assumed to have only dispersive interactions; this is because the electrons are spread evenly across the entire molecule as there are no strongly electronegative atoms.

3.3.2.1 Schultz

The free energy of adsorption and desorption (ΔG) can be related to the net retention volume V_g through the following expression [167], [169]

$$\Delta G_{de} = -\Delta G_{ad} = -RT \ln V_g + C \quad (3.4)$$

where R is the gas constant, T is the temperature and C is a constant that depends on the reference state.[170] ΔG can be related to the work of adhesion (W_{adh}) by

$$\Delta G = N_A a W_{adh} \quad (3.5)$$

where N_A is Avogadro's number, a is the cross sectional area of the probe molecule.

The work of adhesion (W_{adh}) is then related to the dispersive surface of the sample through the Fowkes eqn. [171]

$$W_{adh} = 2\sqrt{\gamma_s^d \gamma_L^d} \quad (3.6)$$

where γ_s^d is the dispersive surface energy of the solid and γ_L^d is the dispersive surface energy of the liquid (probe molecule).

By combining the previous three expressions we can obtain a relation between V_g and γ_s^d .

$$RT \ln V_g = 2N_A a \sqrt{\gamma_s^d \gamma_L^d} + C \quad (3.7)$$

For a series of n-alkanes the above expression is linear when plotted as $RT \ln V_g$ against $a \cdot \sqrt{\gamma_L^d}$. From the slope of the line we can obtain γ_s^d

$$\gamma_s^d = \left(\frac{\text{slope}}{2N_A} \right)^2 \quad (3.8)$$

An example of this plot is shown in figure 3.4 below.

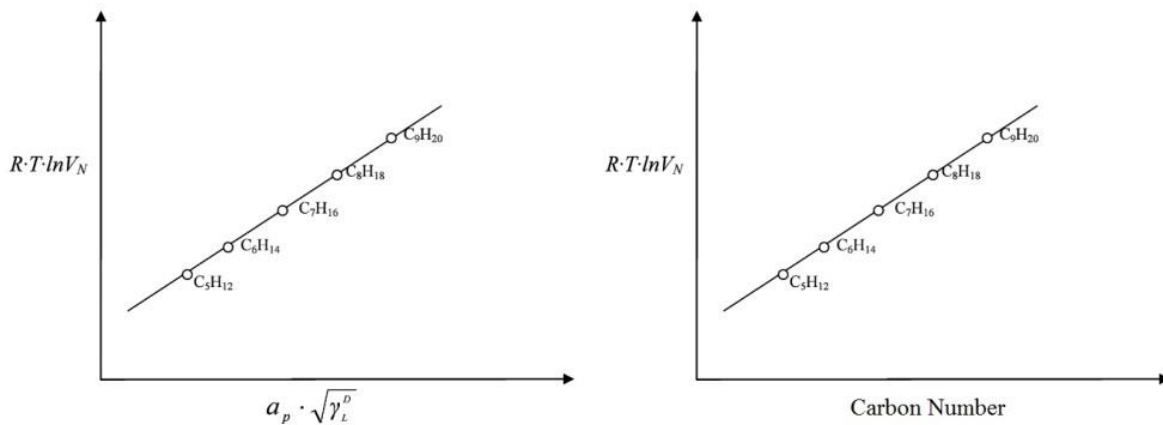


Figure 3.4. Shown in both plots is an example alkane line from pentane to nonane. On the left is an example of the Schultz method. γ_s^d is calculated from the slope and equation (8). On the right is an example of the Dorris-Gray method. The alkane line is

plotted against the carbon number. In this case γ_s^d is calculated from the slope and equation (8).

Adapted from Voelkel et al. [172].

3.3.2.2 Dorris-Gray

A second method to measure the surface energy was outlined by Dorris and Gray.[173] It calculates γ_s^d by considering the free energy of adsorption between the sample and a methylene group (ΔG_{CH2}). Considering ΔG_{CH2} as the difference in free energy between an alkane with n carbon atoms and a second alkane with an additional carbon atom.

$$\Delta G_{CH2} = \Delta G_{n+1} - \Delta G_n \quad (3.9)$$

This can be re-expressed in terms of the increase in retention volume for each additional carbon atom.

$$\Delta G_{CH2} = -RT \ln \left(\frac{V_{g,n+1}}{V_{g,n}} \right) \quad (3.10)$$

where n is the carbon number of the alkane probe. Similar to the Schultz method above in equations (3.5) and (3.6)

$$\Delta G_{CH2} = -N_A a_{CH2} W_{CH2} \quad (3.11)$$

$$W_{CH2} = 2 \sqrt{\gamma_s^d \gamma_{CH2}^d} \quad (3.12)$$

$$-\Delta G_{CH2} = 2N_A a_{CH2} \sqrt{\gamma_s^d \gamma_{CH2}^d} \quad (3.13)$$

where γ_{CH2}^d is calculated from the following[169]:

$$\gamma_{CH_2}^d = 35.6 - 0.058(293.15 - T) \quad (3.14)$$

By combining the equations (10 – 13) above we arrive at the final expression for γ_s^d .

$$\gamma_s^d = \frac{1}{4\gamma_{CH_2}^d} \left[\frac{RT \ln(V_{g,n+1}/V_{g,n})}{N_A a_{CH_2}} \right]^2 \quad (3.15)$$

Both methods have been reported to give very similar results [174], [175][176]. Shi et al.[177] derived an expression for the ratio of the calculated surface energies resulting from each method. They also found that the ratio will always be greater than 1, meaning the Dorris-Gray method will return larger values.

$$\frac{\gamma_{S,Dorris\ Gray}^d}{\gamma_{S,Schultz}^d} = \frac{(a_{n+1} * \sqrt{\gamma_{n+1}} - a_n * \sqrt{\gamma_n})^2}{\gamma_{CH_2} * a_{CH_2}^2} \quad (3.16)$$

This process of measuring the surface energy is repeated for many surface coverages; usually in the range of 0.5 % and 40 %. The measured values are then plotted against surface coverage resulting in what is commonly called a surface energy profile, examples are shown below in figure 3.5. Note the different shapes of the profiles; this is due to the individual distribution of surface energies of each material. Chapter 4 will discuss the parameters suitable for adequately describing the behaviour and shape of a profile. As well as how these parameters can be used to determine the surface energy distribution of a material.

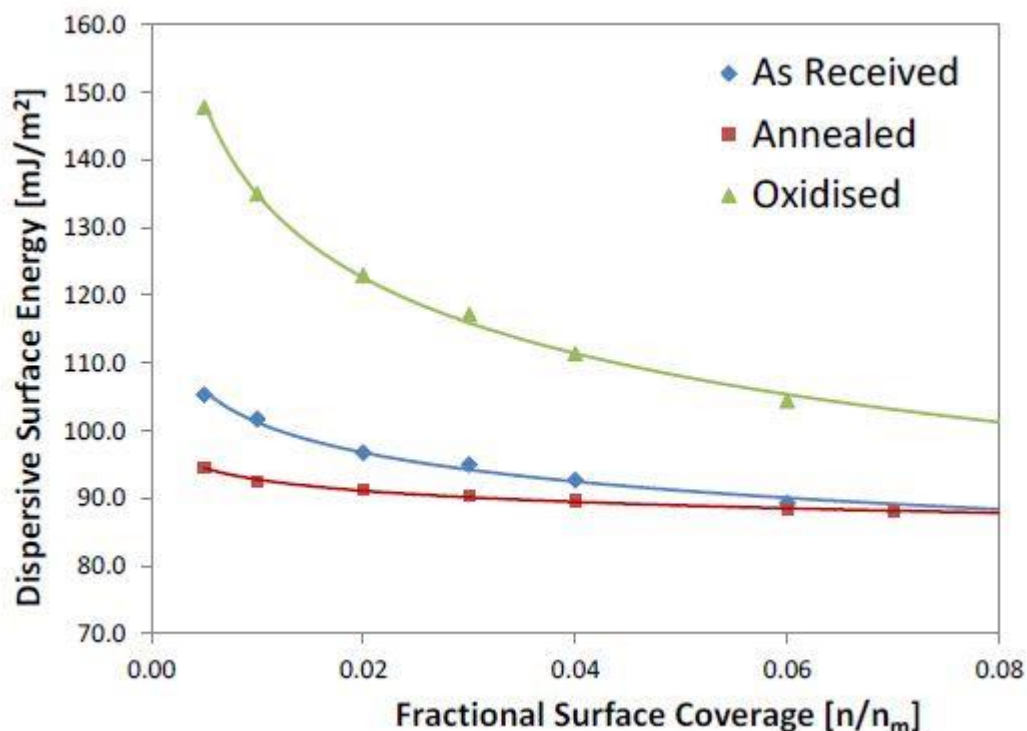


Figure 3.5. Plot of three sample surface energy profiles demonstrating how the shape of the profile can change depending on the underlying surface energy distribution. [178]

3.3.3 Specific Surface Energy

The total surface energy is a combination of dispersive and specific interactions. The specific component of surface energy is considered to be any interaction that is caused by the effect of a polar molecule on intermolecular interactions, e.g. hydrogen bonding, polar or acid-base [169].

The specific surface energy (γ_{sp}) can be measured by using probes that have a specific component e.g. any polar molecule. By carefully choosing a selection of probes it is possible to distinguish between the polar and hydrogen bonding [176]. Polar probes still have a dispersive component and so care must be taken when trying to discriminate between the specific and dispersive components of a sample. When the polar probe datum is plotted on the alkane plot it will sit above the alkane line as illustrated in figure 3.6. The additional adsorption energy is assigned to the specific component (ΔG_{sp}).

$$\Delta G_{sp} = RT \ln V_{g,sp} - RT \ln V_{g,ref} \quad (3.17)$$

$V_{g,ref}$ is the retention volume of the hypothetical alkane with the same cross-sectional area and surface energy of the chosen polar probe molecule.

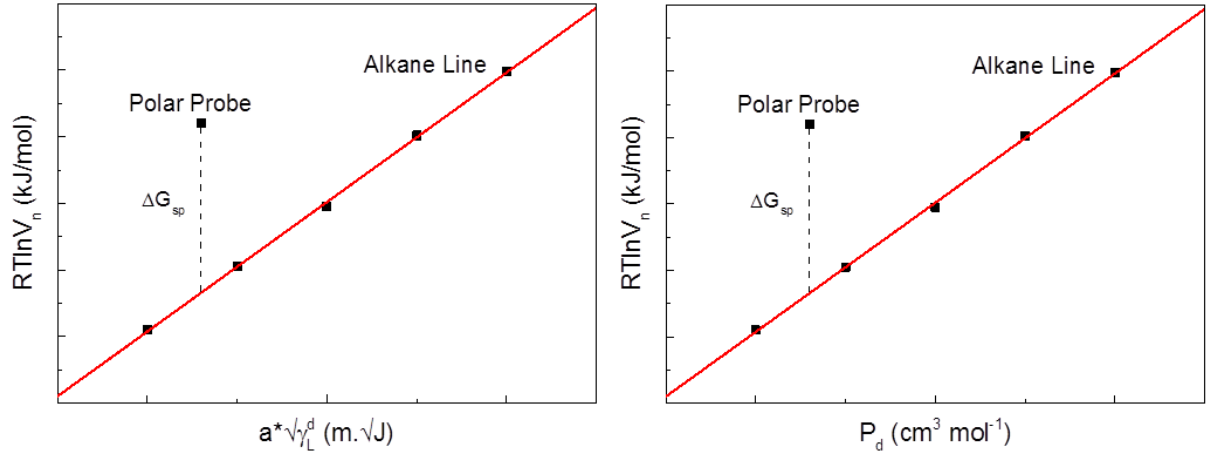


Figure 3.6. Plots of the Schultz (left) and Dorris-Gray/Polarisation (right) methods for calculating the specific component of the surface energy ΔG_{sp} .

The Dorris-Gray method is more involved as specific probes cannot be plotted on the same ordinate (carbon number). The x-axis can be changed using the polarisation method which replaces the carbon number with the molar deformation polarisation of the probes (P_D , cm³ mol⁻¹) [179], [180].

$$RT \ln V_g + C = C' * P_{DP} * P_{DS} \quad (3.18)$$

where P_{DP} and P_{DS} are deformation polarisations of the probe and sample respectively. The deformation polarisation is an intrinsic property of a material and can be calculated using the equation below [179], [181].

$$P_D = \frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho} \quad (3.19)$$

where n , M , and ρ are respectively, the refractive index, molar mass and density of the probe molecule. The same principle can then be applied as with the Schultz method where the additional adsorption energy is assigned to the specific component.

The free energy of adsorption (J/mol) is not the same as surface energy (mJ/m²). The value of ΔG_{sp} needs to be converted to surface energy. One method for this is the Van Oss method, ΔG_{sp} is divided into two components: Lewis acid (electron acceptor), γ_s^+ and Lewis base (electron donor), γ_s^- . By injecting monopolar acid and base probes it is possible to calculate these components of γ_{sp} [182].

$$-\Delta G = 2N_A a \left(\sqrt{\gamma_s^+ \gamma_L^-} + \sqrt{\gamma_s^- \gamma_L^+} \right) \quad (3.20)$$

3.3.4 Specific Surface Area

Surface coverage is calculated using the specific surface area; since this work relies heavily on the surface energy profile of sample it is essential to measure this material property. It is done by injecting increasing amounts of a single probe species, producing an adsorption isotherm [183][184]. Octane is usually the probe of choice as it strikes the right balance between retention times and sensitivity to surface roughness [183]. Other alkanes could be used and will give different values; smaller alkanes will give higher values of S_{BET} because their smaller size allows them to more completely cover a samples uneven surface [149].

An adsorption isotherm shows the amount of analyte adsorbed (n) as a function of either the partial pressure (p) or the relative pressure (p_{rel}). The relative pressure can be found from the partial pressure of the probe within the column and the saturation vapour pressure of the probe at temperature T . A typical isotherm from this work is shown in figure 3.7 below.

$$p_{rel} = p/p_{sat} \quad (3.21)$$

The saturation pressure of the probe is calculated using the modified Antoine equation.

$$p_{sat} = \exp \left[C_1 + \frac{C_2}{T} + C_3 \ln(T) + C_4 T^{C_5} \right] \quad (3.22)$$

where C_1 , C_2 , C_3 , C_4 and C_5 are the Antoine coefficients. The amount adsorbed, (n) is calculated from V_g with the following:

$$n = \frac{1}{RT} \int_0^p V_g dp \quad (3.23)$$

where p is the partial pressure calculated from the chromatogram using

$$p = \frac{n_i R H_{peak} 273.15}{F A_{peak}} \quad (3.24)$$

where n_i is the number of moles of probe injected into the column, H_{peak} is the FID signal at the peak of the chromatogram, F is the flow rate of the carrier gas and A_{peak} is the area of the chromatogram.

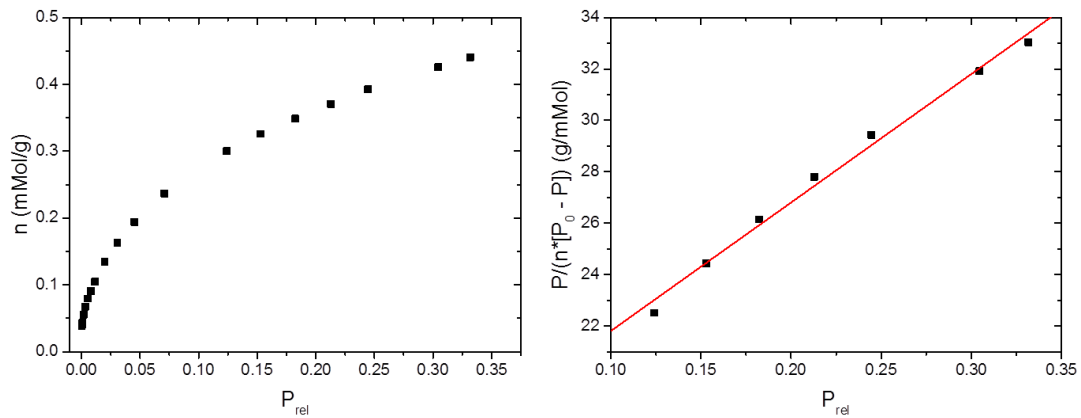


Figure 3.7. The plot on the left is a representative adsorption isotherm. It shows the amount of probe molecule adsorbed to the sample surface (n) as a function of the relative pressure (P_{rel}). The plot on the right is the linear portion of the isotherm. Fitting it to the BET equation it is possible to calculate the monolayer capacity of the sample.

The Brunauer-Emmett-Teller equation is applied to the isotherm data from which we can calculate the monolayer capacity [185].

$$\frac{p}{n[p_{sat} - p]} = \frac{C - 1}{n_m C} \frac{p}{p_{sat}} + \frac{1}{n_m C} \quad (3.25)$$

C is the sorption constant related to the enthalpy of adsorption between the probe and the sample. The monolayer capacity can be calculated by plotting $\frac{p}{n[p_{sat} - p]}$ against p_{rel} and fitting a straight line to the linear region of the isotherm, the BET range is considered to be $(0.05 < p_{rel} < 0.35)$ as shown in figure 3.7 above. To be confident in the accuracy of the S_{BET} result the fit must be above $R^2 = 0.995$. The monolayer capacity can then be found from the slope and the intercept

$$n_m = \frac{1}{slope + intercept} \quad (3.26)$$

which is then related to S_{BET} through:

$$S_{BET} = N_A a n_m \quad (3.27)$$

where N_A is Avogadro's number and a is the cross-sectional area of the probe molecule.

3.3.5 Equipment

Measurements of the specific surface area and surface energy profiles of each sample were conducted using the Surface Energy Analyzer (SEA) from Surface Measurement Systems, UK. It is the latest generation of IGC instruments and can precisely control the volume of injected probe thus allowing the accurate measurement of surface energy at a wide range of surface coverages.

It houses 12 solvent reservoirs, 6 on either side of the column oven. Each containing either a dispersive or specific solvent. Below is a schematic of the instrument along with a schematic of the Flame Ionisation Detector. The injection manifold is what allows the instrument to precisely control the amount injected. The carrier gas Helium pushes the injected probe molecules through the silanised glass sample column. Once they elute they are detected using a FID (Flame Ionising Detector). While other detectors are available, as discussed earlier this chapter, the FID was most suited for the purpose of this work. It is able to measure the current created by the ions produced during the combustion of hydrocarbons in a hydrogen flame with a high degree of sensitivity.

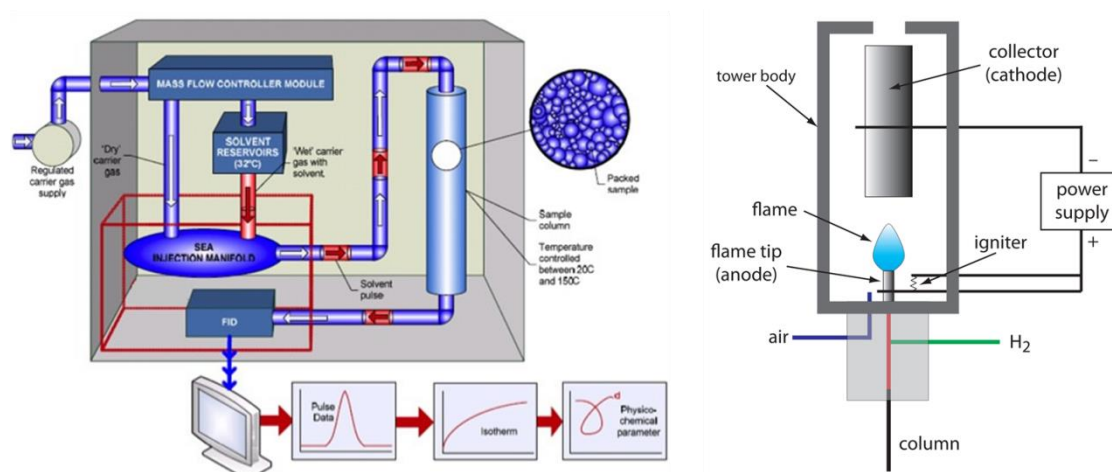


Figure 3.8. On the left is a schematic of an IGC instrument. On the right is a schematic of the flame ionisation detector (FID).

3.4 SEM

Optical microscopes run into fundamental limitations when trying to resolve dimensions on the nanoscale. The resolving power of optical microscopes is limited by the wavelength of light. The finest resolution achievable is half the wavelength of the light used to image a sample.[186] Beyond ultra-violet wavelengths the light becomes

more difficult to control and focus the light. This makes it impractical to image below a certain feature size with optical microscopes.[187] To overcome this shortcoming of optical microscopes electron microscopes were developed in the 1930's. They are based on the wave property of particles. This was first theorised by Louis de Broglie in 1924 and verified experimentally in 1931. Just as with photons of light the wavelength of electrons decreases with increasing energy. There are several types of electron microscopes. The most common are scanning electron microscopes and transmission electron microscopes. There are also now microscopes using ions of helium or gallium that can be used for milling as well as imaging samples.

The images in this thesis were taken using a scanning electron microscope (SEM). This was to measure the mean flake dimensions of the samples. It is widely used as a method for imaging conductive or insulating samples.

A beam of electrons is generated through thermionic emission; the beam is then accelerated toward the specimen. The accelerating voltage can be between 2 and 10 keV. The beam is focussed with electromagnetic lenses on to the specimen and rastered across it. The specimen must be kept in a vacuum on the order of less than 10^{-6} mbar. This prevents the beam from being scattered by molecules in the sample chamber before reaching the specimen. The beam interacts with the specimen and produces a signal which is converted to an image.

The signal comes from the interaction of the primary electrons (those emitted by the SEM) and the sample. The interaction is caused by a variety scattering processes. These take place within a tear shaped volume illustrated in figure 3.9. The size of this interaction volume depends on the atomic density and topography as well as the energy of the incident electron beam. Of interest in this work are the secondary electrons generated through inelastic scattering. The energy lost to the impacted atom can lead to one of the outermost electrons being dislodged. These secondary electrons typically have low energies in the region of 3 – 5 keV. Due to their low energy only those emitted close to the surface (2-5 nm) can escape, making them sensitive only to the surface.

Another set of electrons that are often of interest are the backscattered electrons, which are scattered elastically resulting in them having much higher energies and larger escape depths. Another property of these electrons is that the number of them elastically

scattered increases with atomic number. Thus high Z-number atoms show up as bright spots on images allowing for elemental analysis. These secondary and backscattered electrons are depicted in the schematic shown in figure 3.9(B).

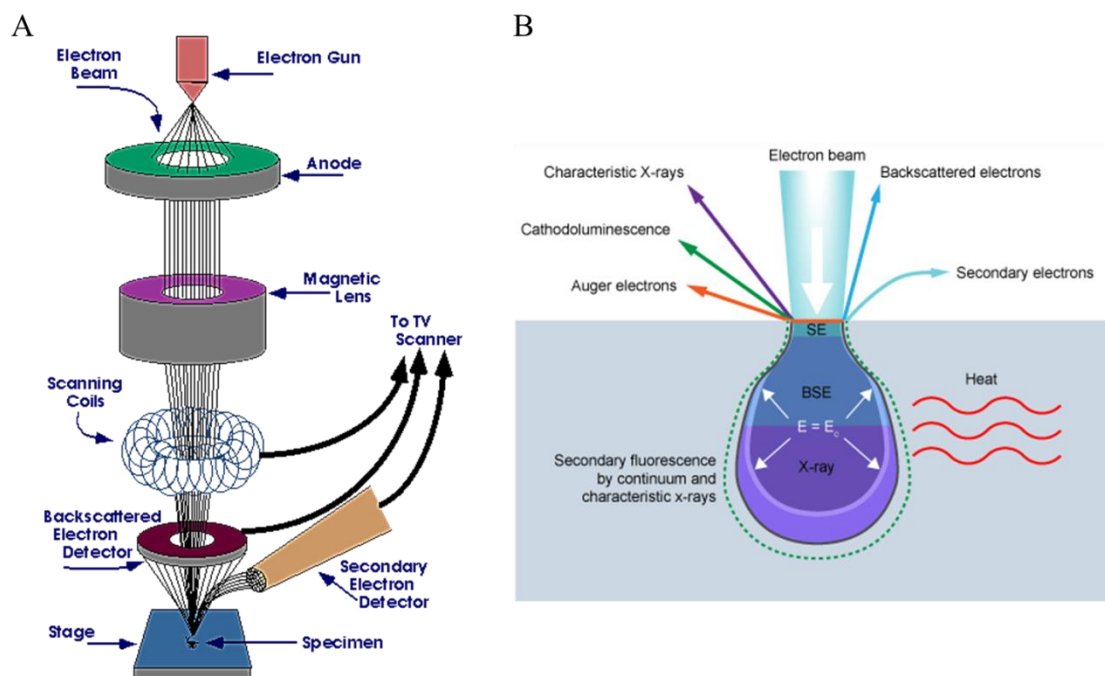


Figure 3.9. Illustration of the internals of an SEM column; showing the electron gun, the lenses and detectors. The second illustration is of the tear-shaped interaction volume of the incident electrons.

All images in this work were taken using the secondary electrons. It is important to note that on insulating samples charge can build up and cause bright spots, reducing image quality. As the samples in this work are insulating they were sputtered with a 10 nm layer of Au/Pd to avoid this. This layer is thin enough so as not to impede the analysis being undertaken. SEM images were acquired using a Zeiss Ultra Plus SEM with a LaB6 source and an accelerating voltage of 5 keV.

3.4.1 Statistical SEM Analysis

To measure the average flake length of a sample this work employs a technique used previously in this group that statistically quantifies a samples mean length and

width.[136] When a sample has been produced using the centrifugation method outlined in the following section, it is oven-dried and applied to SEM stubs with carbon tabs. As the samples were insulating they were sputtered with a roughly 10 nm layer of Gold-Palladium to prevent charge building up.

The statistical analysis is carried out by randomly selecting locations to image at varying magnifications. This is necessary to achieve a representative sampling of the distribution of flake sizes present in the sample. After the images are collected analysis software is used to generate the statistics. This consists of drawing a line along the longest axis of a flake (denoted “length”) and another line perpendicular to the first (denoted “width”). This is repeated over 200 times to minimise any errors that may occur during measurement. The result is a lognormal distribution of flake lengths; these are shown in the following chapters 5 and 6. Determining the average flake size is crucial to this work as it allows us to extract important material parameters from the IGC data.

3.5 Size Selection through Centrifugation

This work rests on studying how the surface energy profiles are affected by the mean length of the sample changing. By measuring the surface energy profile of samples with different mean flake length it is possible to separate the contribution of edge and basal plane sites. For geometric reasons, as the length is changed the ratio of edge to basal sites is changed.

Rather than purchasing material from several suppliers we decided to alter the length ourselves. This was to avoid any difference in the composition of the samples that might arise from the location of the mine, mining processes or purification techniques. It also means that we were able to study a wider range of lengths than is available commercially.

The first technique we trialled was ball-milling. This was deemed unsuitable due to concerns about the possible introduction of additional defects into the basal plane [188]. It was also very time consuming and labour intensive. We then turned to centrifugation,

a technique that has been used extensively in the group for exfoliated material and producing samples with narrow distributions.[189]

When suspended in a liquid, flakes will feel a force of gravity pulling them to the bottom causing them to sediment out. The rate at which flakes sediment out of solution is dependent on flake size. We can exploit this difference in sedimentation rate to produce samples consisting of differently sized flakes. This process can be quite slow but it is possible to speed it up using centrifugation. This process is simple, quick (on the order of minutes for this work) and produces consistent results.

To better understand the processes involved in sedimentation the following is a discussion of the theoretical model. In an unstable dispersion a particle will fall out of solution in a short period of time due to the force of gravity (F_g). A particle will also feel a buoyant force (F_B) and a force due to viscous drag (F_D) as it passes through the liquid. This is depicted in figure 3.10.

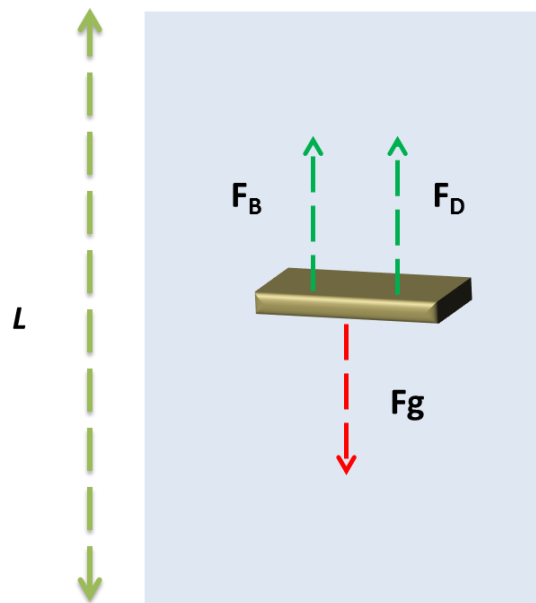


Figure 3.10. Force diagram of particle in suspension. The buoyancy and drag forces are shown in opposition to the gravitational force.

The force of gravity on a particle is given by the following:

$$F_g = m \cdot g \quad (3.28)$$

where m is the particle mass and g is the acceleration due to gravity. As it challenging to know the mass of the particles used in this work; equation (3.29) is re-expressed in more suitable parameters yielding:

$$F_g = \frac{4}{3} \pi r^3 \rho_f g \quad (3.29)$$

Approximating the particle as sphere, r is the radius of the particle, ρ_f is the particle density. The buoyancy force can be expressed similarly. It is defined as the weight of the fluid displaced by the particle.

$$F_B = \frac{4}{3} \pi r^3 \rho_s g \quad (3.30)$$

In this case the density ρ_s is the density of the fluid. Drag force experienced by a particle moving through a fluid can be modelled with Stokes' Law:

$$F_D = 6\pi r \eta v \quad (3.31)$$

where η is the viscosity of the fluid and v is the velocity of the particle. The net force experienced by the particle can be found by combining the above expressions:

$$\frac{4}{3} \pi r^3 (\rho_{ns} - \rho_s) g = 6\pi r \eta v_t \quad (3.32)$$

From this we can see that if a particle has a greater density than the surrounding fluid it will feel a net downward force and accelerate towards the bottom of the vial. As it accelerates the drag force will increase until it matches the net gravitational force. The velocity at which this occurs is the terminal velocity v_t .

$$\frac{2r^2 (\rho_{ns} - \rho_s) g}{9\eta} = v_t \quad (3.33)$$

This velocity governs the rate of sedimentation of a particle, where sedimentation time T_{sed} is given by:

$$T_{sed} = \frac{9l\eta}{2r^2(\rho_{ns} - \rho_s)g} \quad (3.34)$$

where l is the length the vial. The above derivation applies to particles assumed to be spherical. While the drag force is shape dependent this method can be used as an approximation to flakes in solution. [189] The ability of centrifugation to separate flakes of different sizes arises because of the dependence of terminal velocity on particle size. The acceleration due to gravity, g , can be replaced with the centripetal force. This force is related to the radius of the centrifuge and the rotational speed.

$$a = \omega^2 r = (2\pi N)^2 r \quad (3.35)$$

where ω is the angular velocity of the centrifuge, r is its radius and N is the number of revolutions per second. The acceleration is more commonly quoted in terms of g and called the relative centrifugal force (*RCF*)

$$RCF = \frac{(2\pi N)^2 r}{g} \quad (3.36)$$

By fixing the angular velocity and increasing the duration of centrifugation, smaller and smaller flakes sediment out, thus decreasing the mean length of the flakes remaining in the supernatant. This was confirmed using statistical SEM analysis mentioned previously.

A stock dispersion of the raw unexfoliated powder was made by adding 1 gram of material to 200 mL of deionised water. This was shaken by hand to mix the two phases together. The mixture was split between 4 50 mL centrifuge tubes. All samples were subjected to 500 rpm for a duration of 5 seconds to 8 minutes depending on the material and the desired final flake length. The supernatant was carefully transferred to a flask to avoid disturbing the sediment. The collected supernatant was then centrifuged at a much higher (5000 rpm) speed for 10 minutes. This was to separate the flakes from the

deionised water. The sediment was collected and placed in a glass vial and oven-dried under vacuum at 80 °C for 24 hrs.

3.6 Simulations

Every material surface is heterogeneous; there will always be defects and edges. These sites will have a different behaviour and surface energy to the rest of the surface, the basal plane. Of interest in this work is how the surface energies of these sites differ from that of the basal plane sites. The relative fraction of each site and its surface energy can be described by a surface energy distribution, an example of which is shown below in figure 3.11.

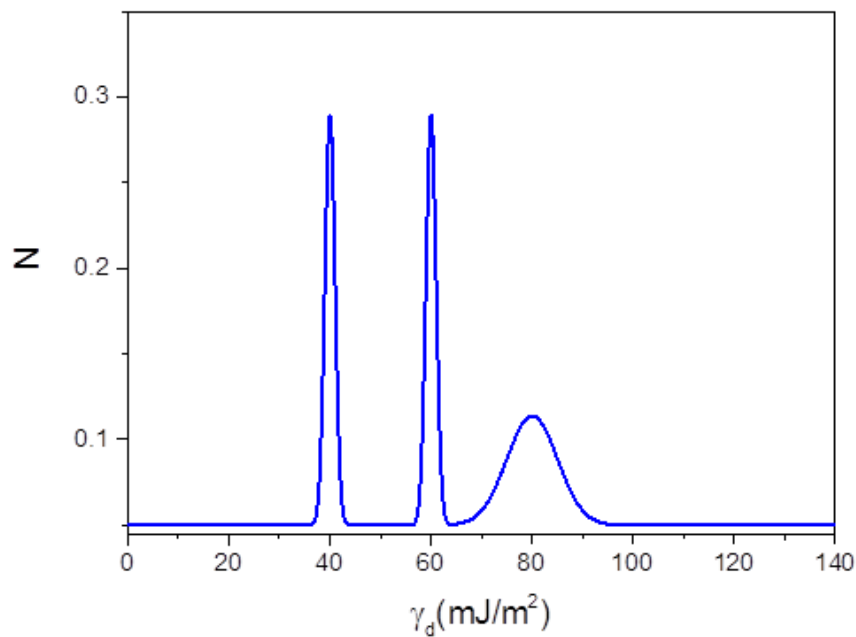


Figure 3.11. Plot depicting an example surface energy distribution. The distribution consists of three Gaussian curves. With mean values of 40, 60 and 80 mJ/m². The highest energy curve has a larger standard deviation ($\sigma = 10$ mJ/m²) than the other two.

The shape of a surface energy profile depends on the surface energy distribution of the sample. It therefore stands to reason that it is possible to glean some information about

the underlying distribution from the profile. By generating the surface energy profiles for many different surface energy distributions it is possible to determine several general rules of how different aspects of a surface energy distribution are translated to a surface energy profile. Chapter 4 will discuss the findings in detail. Chapters 5 and 6 will apply the model to two layered crystals.

The following is an explanation of how a surface energy profile can be generated from a surface energy distribution and was first described by Smith et al. [190] In practice a surface energy profile is built up by injecting successively greater volumes of probe molecules starting at infinite dilution. Starting at the beginning of this process and imagining a single probe passing through the sample, the probe will adsorb to and desorb from many different sites. The total time to elute through the sample is split between sites of different energies.

The fraction of the elution time spent on a site with a certain surface energy can be thought of as equivalent to the probability of adsorption. For example if a probe has a 50% chance of adsorbing onto a site with a surface energy γ_s^d , then half of the elution time will be spent adsorbed to sites of surface energy γ_s^d . The probability of adsorption to each site is governed by both the population and energy of that site.

The adsorption probability due to surface energy can be found by using the Boltzmann distribution to estimate the relative occupancy of each site

$$\frac{N_i}{N} = \frac{e^{-(E_i/k_b T)}}{\sum_i e^{-(E_i/k_b T)}} \quad (3.37)$$

where N_i is the number of particles in state i , N is the total number of particles, E_i is the energy of site i , k_b is the Boltzmann constant and T is temperature. The energy E_i is the Gibbs free energy of adsorption which is given by:

$$\Delta G_A = -2a_m \sqrt{\gamma_s^d \gamma_l^d} \quad (3.38)$$

where γ_s^d is the surface energy of the site in question, γ_l^d is the surface energy of the probe, and a_m is the cross-sectional area of the alkane molecule. This relative occupancy is equivalent to the probability of adsorption to a site of energy E_i .

The adsorption probability due to the population of a site is simply the population fraction of that site. In this work the surface energy distribution was constructed from multiple Gaussian distributions each representing either the basal plane or edge sites. These are described by the equation shown below.

$$f(\gamma_s^d) = \frac{1}{\sigma\sqrt{2\pi}} e^{(-1/2)[(\gamma_s^d - \mu)/\sigma]^2} \quad (3.39)$$

These two contributions to adsorption probability can be combined through multiplication and normalisation to arrive at the overall probability of a probe molecule adsorbing to a site.

$$P_i = \frac{N_i}{N} * f_i \quad (3.40)$$

The surface energy felt by the very first probe is the energy of each site weighted according to the adsorption probability from above.

$$measured \gamma = \sum_i^n P_i * E_i \quad (3.41)$$

This first probe has modified the population distribution by occupying some of the sites, this filling needs to be taken into account by subtracting the filled sites from the starting distribution. This modified distribution is used to calculate the population fractions of sites. The second probe “sees” this new distribution and feels a new surface energy. This process is repeated until the entire distribution is filled.

It is important to note that each probe, depending on its surface energy, will have a different relative affinity to the available energy states. Probe molecules with a higher surface energy, such as Decane, are more likely to inhabit higher energy sites compared with a probe with a lower surface energy such as Hexane. This is illustrated in the

figure 3.12 below. This means that the surface energy experienced by each probe will differ resulting in different surface energy profiles as shown in figure 3.12.

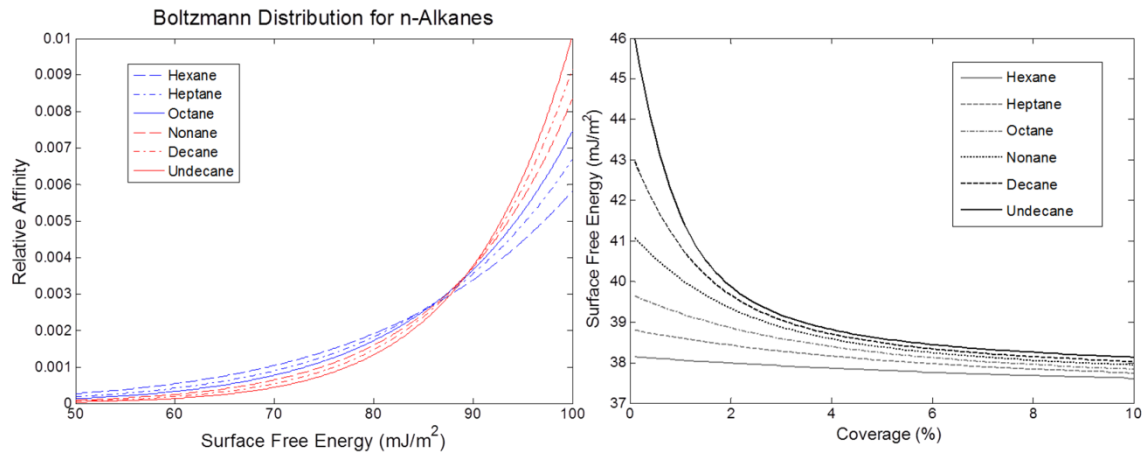


Figure 3.12. The left-hand side plot shows, for a range of alkanes, the relative affinity of an alkane to sites of increasing energy. The plot on the right shows the effect the difference in relative affinities has on the surface energy profiles of each alkane. The longer, higher energy alkanes experience a higher surface energy due to their greater affinity to high energy sites. Adapted from Smith et al. [190]

To resolve this issue and find the “true” surface energy it is necessary to repeat the simulation with several probes and record the energy “experienced” by each. This “experienced” energy is then used to calculate the surface energy in the same way as with a typical IGC experiment.

It has been shown in a previous section that the Gibbs free energy of adsorption can be expressed in terms of the net retention volume:

$$\Delta G_A = -RT \ln V_g - K \quad (3.42)$$

It can also be expressed as a function of the surface energies

$$\Delta G_A = -2N_a a_m \sqrt{\gamma_s^d \gamma_L^d} \quad (3.43)$$

By combining the two equations we can relate the “experienced” energy γ_{Si}^d to an “experienced” retention volume V_{ni} .

$$RT \ln V_{gi} + K = 2N_a a_m \sqrt{\gamma_{Si}^d \gamma_L^d} \quad (3.44)$$

Either the Dorris-Gray or the Schultz method can be applied to this retention volume in the standard manner to calculate the true surface energy profile. In the work presented here we used the Dorris-Gray method to maintain consistency with the experimental work.

A script was written in Python to undertake all the calculations required to generate the profiles. It should be noted that choosing a suitable increment for surface coverage is critical. The increment should be small enough so as to accurately represent the true profile but not so small that it would cause the simulation to run for excessive amounts of time. We found that below a coverage increment of 0.1% there was no further change in the profiles being generated.

Chapter 4

Simulations

4.1 Introduction

Previous chapters have discussed alternative techniques to measure a material's surface energy. The disadvantages for each technique were outlined; providing either only an average value of the surface energy (contact angle) or the surface energy of just the highest energy sites (ID-IGC). What is required is a full description of the surface energy of a material. Knowledge of the surface energy distribution allows better prediction of material behaviour in processing wetting, composites, blends, coating, etc. [191],[148],[192],[193] High energy sites may have an outsized effect on behaviour and it may be critical to know not just the surface energy but also the relative population of those sites. While Finite-Dilution IGC (FD-IGC) was proposed in an earlier chapter as a technique with which to overcome the limitations of other techniques, this thesis has yet to discuss how it is possible to derive the surface energy distribution of material.

The FD-IGC measures surface energy at various surface coverages. The measured values of surface energy are then plotted against surface coverage resulting in what is known as a surface energy profile. The measured values of surface energy will depend on the surface energies present in the sample and so the shape of this plot will depend on the distribution of surface energies. It should therefore be possible to infer the surface energy distribution of a sample from its surface energy profile.

A method to simulate a surface energy profile from a specified surface energy distribution has been published by Smith et al [194],[195]. They then use this method to repeatedly generate surface energy profiles until a match for the experimental profile is found. The quality of fit is judged using the squared error (χ^2). The surface energy distribution that generated that profile is then deemed to be the distribution of the material being studied. One drawback of this is that it may lead to cases where a local

rather than a global minimum is found or even due to experimental error the global minimum does not correspond to the actual distribution of surface energies. We propose a method that solves this problem and allows us to ascribe surface energies to the basal plane, defects in the basal plane and edge defects.

Briefly, a surface energy profile is measured for the same material at different particle sizes. By changing the particle size of the material, the relative fractions of edges and basal plane sites change. The relative fractions of the surface energies associated with these sites are then also altered. This change in the overall surface energy distribution is reflected in the surface energy profile. The profiles are all fitted to a stretched exponential function (equation 4.1) and the three characteristic, fitting parameters ($\gamma_{\phi=1}$, $\gamma_{\phi=0}$ and ϕ_0) are extracted and used to study the dependence of profile shape on the surface energy distribution.

$$\gamma_d(\phi) = \gamma_{d,\phi=1} + (\gamma_{d,\phi=0} - \gamma_{d,\phi=1})e^{-\left(\frac{\phi}{\phi_0}\right)^j} \quad (4.1)$$

The variable, j , controls the stretching ($k < 0$) or compression ($k > 0$) and ϕ is the surface coverage. These parameters will be explained in more detail in a later section. Using the Smith method we were able to simulate distributions and their resultant surface energy profiles. This allowed us to systematically study how these parameters depend on the distribution of surface energies. General relationships between these parameters and the underlying surface energy distribution are then applied to experimental data in order to glean information about a material's surface energy distribution. Eventually, we show how these parameters can be used as a unique identifier for a surface energy distribution.

The method to generate surface energy profiles from surface energy distributions has been discussed in detail in chapter 3 and will be briefly recapped below. The probability of a probe occupying a particular energy state is a function of the surface energy of the probe and of the site. This probability is given by equation (4.2)

$$\frac{N_i}{N} = \frac{e^{-\left(\left(-2a_m\sqrt{\gamma_L^d\gamma_i^d}\right)/k_BT\right)}}{\sum_i e^{-\left(\left(-2a_m\sqrt{\gamma_L^d\gamma_i^d}\right)/k_BT\right)}} \quad (4.2)$$

where a_m is the cross-sectional area of the probe molecule, γ_L^d is the dispersive surface free energy of the probe and γ_i^d is the dispersive surface free energy of the site i . The probability of a probe occupying a site with a particular surface energy also depends on the number of those sites available. The number of sites as a function of surface energy is approximated a Gaussian distribution as described by equation (4.3).

$$f(\gamma_S^d) = \frac{1}{\sigma\sqrt{2\pi}} e^{(-1/2)[(\gamma_S^d - \mu)/\sigma]^2} \quad (4.3)$$

Where γ_S^d is the surface energy, μ is the centre of the curve and σ is the standard deviation. These two contributions to the likelihood of a probe adsorbing to a site are multiplied together and the resulting probability distribution is normalised so that it sums to 1. The energy “experienced” by the probe molecule can be calculated from the probability of adsorption and the surface energy of a site. This calculation was explained in chapter 3. After a site has been filled, the probability distribution needs to be altered accordingly. This new distribution is what the next probe “experiences”. The entire process is repeated until all the sites have been filled and a full surface energy profile has been constructed.

Solvent-solvent interactions have been ignored. At infinite dilution, there are too few probe molecules to have any appreciable effect. At higher coverages, these interactions can still be neglected as even the lowest energy sites of the materials being studied will dominate the solvent-solvent interactions. We have simulated what effect solvent-solvent interactions have on the generated surface energy profiles and found the difference was found to be minimal. A fidelity of 0.1% surface coverage was chosen since a value any coarser gave nonsensical profiles, any value finer than this gave the same profile but took longer to compute.

4.2 Characterisation of Profiles

4.2.1 Surface Energy Distributions with a Single Gaussian

To begin, we will look at distributions that are described with a single Gaussian curve as described by equation (4.3), with a centre of μ and standard deviation of σ . We

simulated the surface energy profile for many different values and combinations of μ and σ . Shown in figure 4.1(A) are three example distributions and their resultant surface energy profiles figure 4.1(B). The centre μ is kept constant at 60 mJ/m^2 while the standard deviation, σ , takes the values 5, 10, 15 mJ/m^2 . Similar to the experimental profiles, these simulated profiles always decrease monotonically. However, experimental surface energy profiles seen in the literature and our own experiments have an exponential-like decay with coverage but a surface energy profile generated from a single Gaussian distribution is convex-like in shape [180], [196], [197]. Clearly, the single Gaussian distribution is too simplistic to model the heterogeneity present in most materials. Despite this, there are still some important lessons to take from this simple system which will be useful when analysing more complex systems.

As mentioned, this work will utilise the three characteristic parameters ($\gamma_{d,\phi=1}$, $\gamma_{d,\phi=0}$ and ϕ_0) to gain some basic understanding of the relationship between the underlying distribution of surface energies and the shape of the surface energy profile.

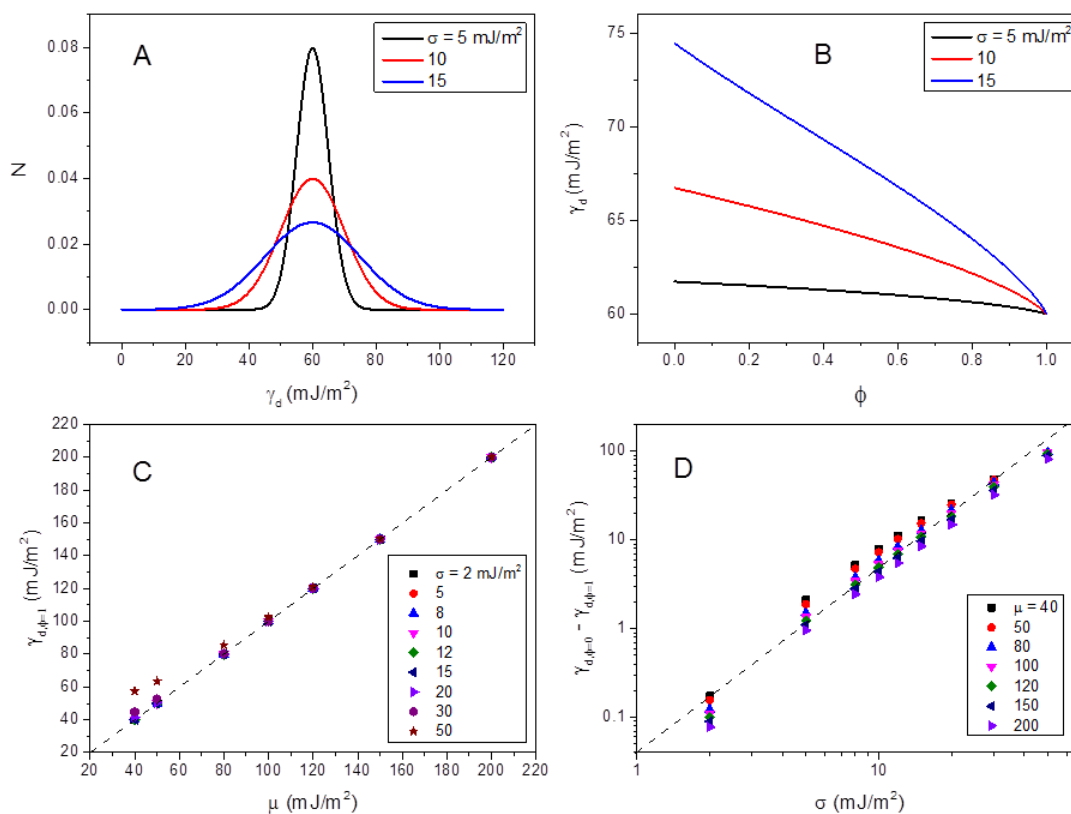


Figure 4.1. Examining the effect of the parameters of a surface energy distribution comprised of a single Gaussian curve. (A) Sample distributions each consisting of a single Gaussian function. The centre of each is fixed at 60 mJ/m^2 , while the standard deviation is varied. (B) Simulated surface energy profiles corresponding to distributions shown in (A). (C) The simulated surface energies at full coverage ($\phi = 1$) for a variety of distributions are plotted against the centres of those distributions. Each symbol represents a different standard deviation. (D) Difference between the simulated surface energies at zero ($\phi = 0$) and full coverage plotted against the standard deviation of the distribution. Each symbol represents a different centre.

The first of these is the surface energy at full coverage, $\gamma_{d,\phi=1}$. From the plots shown in figure 4.1(B) it is clear that, regardless of σ , $\gamma_{d,\phi=1}$ has a value equal to that of the centre, μ , in this case 60 mJ/m^2 . In figure 4.1(C), the $\gamma_{d,\phi=1}$ is plotted against μ , demonstrating that this relationship holds for all values of μ and σ . This is because the $\gamma_{d,\phi=1}$ represents the mean value of the distribution. This conclusion becomes useful when analysing more complex systems and will be discussed again in later sections.

The second parameter is the surface energy at zero coverage, $\gamma_{d,\phi=0}$. This clearly has a dependence on the standard deviation. What we found was that the difference between the zero and full coverage surface energies ($\gamma_{d,\phi=0} - \gamma_{d,\phi=1}$) is strongly dependent on the standard deviation, σ , of the curve, scaling approximately as

$$\gamma_{d,\phi=0} - \gamma_{d,\phi=1} \approx 0.3 \times \sigma^{1.7} \quad (4.4)$$

This relationship is shown in figure 4.1(D). It also depends more weakly on the distribution centre with the approximation holding well between 40 and 200 mJ/m² with deviations of no more than 25%. This second conclusion will also be put to use when analysing more complex systems. This relationship reflects the fact that sites with the highest energy fill first, allowing us to make two simple observations: the value of $\gamma_{d,\phi=0}$ represents the contribution to the surface energy of those sites with the highest energy and that $\gamma_{d,\phi=1}$ is a measure of the mean surface energy of the system.

4.2.2 Surface Energy Distributions with two Gaussian curves

It is not all that surprising that a system consisting of a single Gaussian curve cannot perfectly replicate the surface energy profiles seen experimentally. We hypothesised that the surface energy distributions can rarely, if ever be described by a single Gaussian. It is more likely that real materials have more complex distributions consisting of multiple Gaussians each representing a separate aspect of the surface. If we wish to understand how the profile shape depends on the underlying distribution we must move toward these more complex distributions.

To this end, we carried out a range of simulations with two normalised Gaussians, representing the populations N_1 and N_2 such that the total population of binding sites is given by $N_T = N_1 + N_2$, where $f_1 = N_1/N_T$ is the fraction of lower energy sites. Here, the subscripts “1” and “2” correspond to “Low Energy” and “High Energy” such that $\mu_1 < \mu_2$. More properly, surface energy is negative but is usually quoted as a positive number. So, to clarify, when this text discusses energies that are “higher” or “high” it is referring to energies that are larger in absolute terms than those energies which are “lower” or “low”.

For a distribution comprised of two Gaussian curves, the number of parameters increases from 2 to 5 ($\mu_1, \mu_2, \sigma_1, \sigma_2, f_2$) as such the parameter space is much larger. To simplify things, we first wanted to investigate whether it was possible to recreate the exponential-like profiles seen in the experimental data. To do this, we simulated profiles for a few values of $\sigma_1, \sigma_2, \Delta\mu$ ($\Delta\mu = \mu_2 - \mu_1$) and f_2 over a wide range. The standard deviation of both curves had values of 1, 2, 5, 10 and 20 mJ/m² and the values of $\Delta\mu$ were 5, 10, 15, 20 and 40 mJ/m². Finally, we varied the relative fraction (f_2) through a large number (over 20) of values from 0 to 1. Profiles were simulated for all of the combinations within this space, numbering at 2500! For clarity, we have shown six representative distributions in figure 4.2(A,B,C,G,H,I). They cover a wide range of possible variations; two narrow curves close together, two broad curves set apart from one another and distributions containing a mix of broad and narrow curves. Underneath each of the distributions are the profiles generated for a number of relative populations of each of the curves. While not every distribution generates profiles that match the shape of experimentally observed profiles we can see that as the gap ($\Delta\mu$) between the two curves is increased some of the profiles start to take on the characteristic concave shape (see figure 4.2(E, K)). Also, if the standard deviation of the low energy curve is kept relatively narrow ($\sigma_1 \approx 1$ mJ/m²) and the standard deviation of the high energy curve, σ_2 , is increased the profiles bear a very close resemblance to experimental profiles. In general, these profiles have an exponential-like decay to them (except in the trivial cases where $f_2 = 0$ or 1).

Broadly speaking, we can say that there are two criteria that need to be fulfilled: the first is that the high energy curve is at least 20 mJ/m² higher than the lower curve, and second, that the low and high energy curves have narrow ($\sigma_1 \approx 1$ mJ/m²) and broad ($\sigma_1 \approx 20$ mJ/m²) standard deviations respectively.

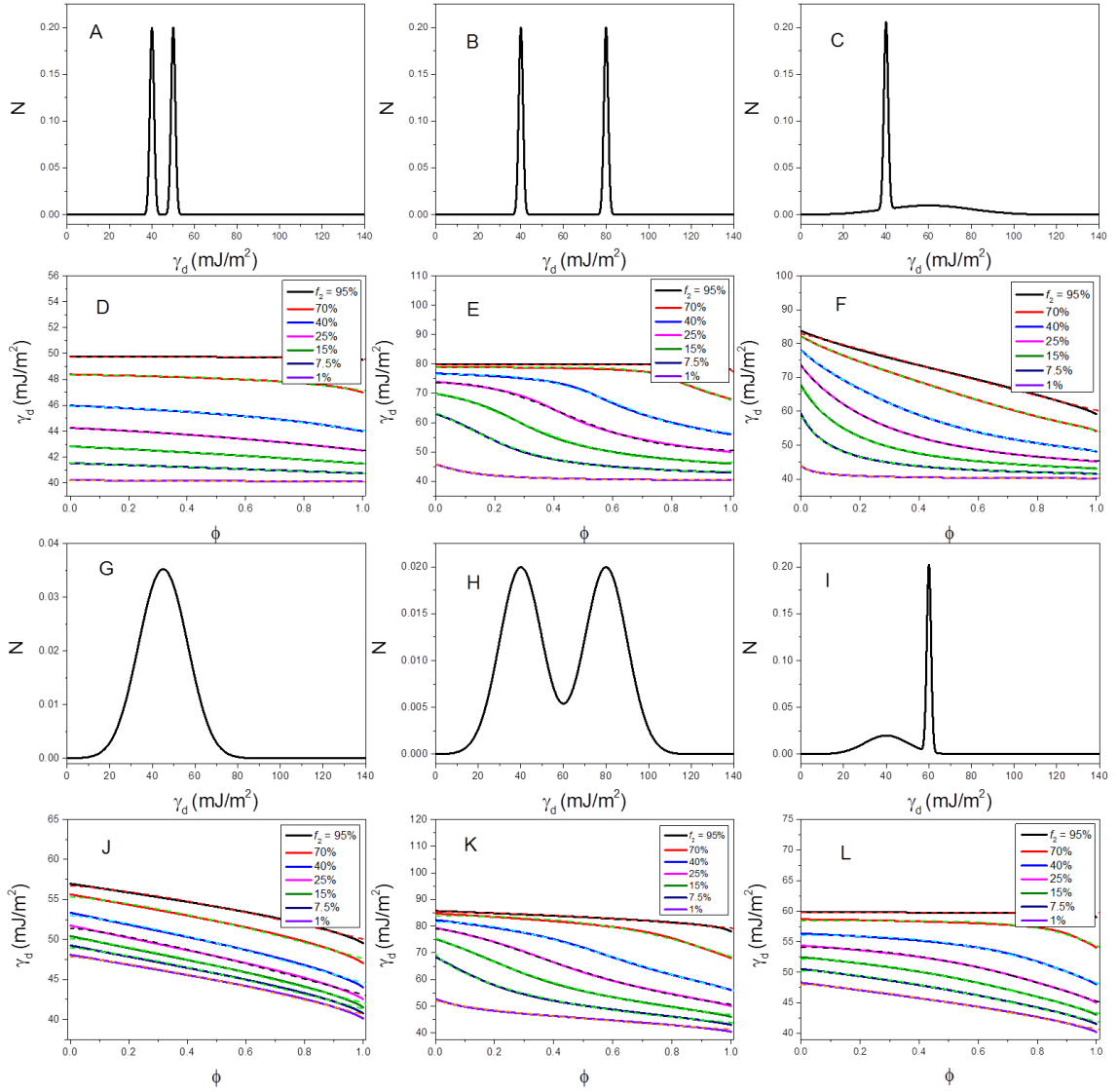


Figure 4.2. (A) Two neighbouring narrow curves. (B) Two narrow curves separated by a large gap. (C) A narrow and a wide curve. (D) Simulated surface energy profiles of the distribution shown in (A) for various weightings of the curves. (E) Simulated surface energy profiles of the distribution shown in (B) for various weightings of the curves. These somewhat resemble experimentally observed profiles. (F) Simulated surface energy profiles of the distribution shown in (C) for various weightings of the curves. These resemble closely the experimentally observed profiles. (G) Two neighbouring broad curves. (H) Two broad curves separated by a large gap. (I) A broad and a narrow curve. (J) Simulated surface energy profiles of the distribution shown in (G) for various weightings of the curves. (K) Simulated surface energy profiles of the distribution shown in (H) for various weightings of the curves. (L) Simulated surface energy profiles of the distribution shown in (I) for various weightings of the curves.

(D,E,F,J,K,L) Each set of surface energy profiles is fitted to a stretched exponential function.

The third and final extracted parameter from equation (4.1), the decay constant, ϕ_0 , is a measure of how quickly the surface energy falls with coverage, ϕ . It is therefore related to the fraction of high energy sites in the distribution. The more high energy sites, the greater the coverage required to fill the high energy sites and begin probing the low energy sites. Thus we would expect to find some relationship between the fraction of high energy sites and the decay constant. In figure 4.3, the decay constant, ϕ_0 , is plotted against the fraction of high energy sites, f_2 , for the same distributions shown in figure 4.2. Across all the distributions, there is clearly some relationship between the two. Most distributions have erratic trends, likely due to the stretched exponential function not being able to describe the shapes of the profiles and the decay constant losing its physical meaning. If we turn our focus on the distribution shown in figure 4.3(C), the distribution that produced exponential-like profiles, we see the clearest trend. Below a value for f_2 of ≈ 0.4 there is a linear trend between ϕ_0 and f_2 , with $\phi_0 = \beta * f_2$. This means that it is possible to use the decay constant as a proxy for the fraction of high energy sites. This relationship will be particularly useful when analysing experimental data from real-world samples as it serves as a proxy for the fraction of high energy sites.

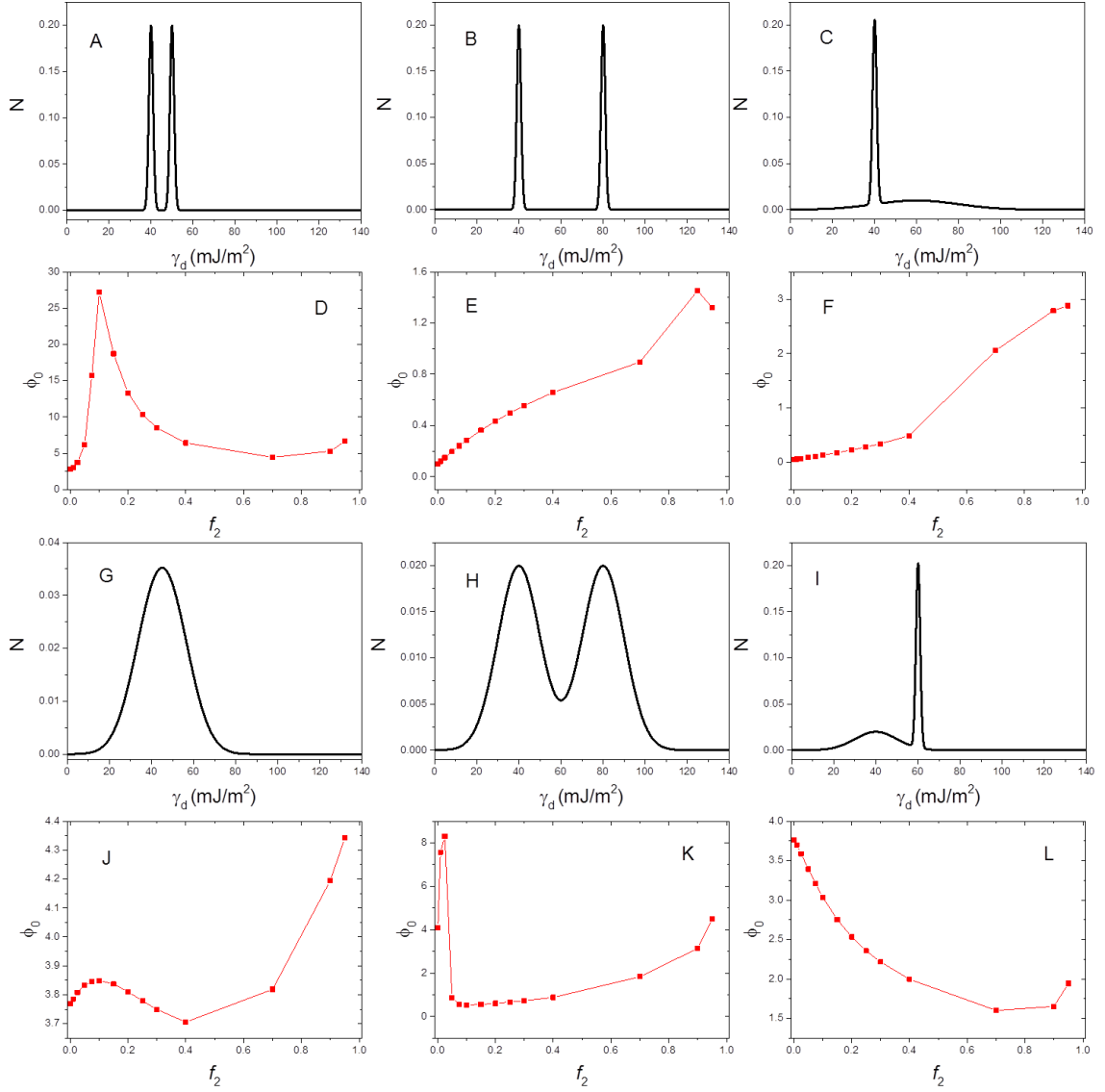


Figure 4.3. (A) Two neighbouring narrow ($\sigma = 1$ mJ/m²) distributions (B) Two narrow ($\sigma = 1$ mJ/m²) distributions separated by a large gap ($\mu_2 - \mu_1 = 40$ mJ/m²). (C) A narrow and a wide distribution. (G) Two neighbouring broad ($\sigma = 20$ mJ/m²) distributions. (H) Two broad distributions separated by a large gap. (I) A broad and a narrow distribution. (D,E,F,J,K,L) Plot of the decay constant, ϕ_0 , of the simulated profiles against the fraction of the high energy sites, f_2 .

The linear relationship and threshold of $f_2 \approx 0.4$ is seen only in distributions where there is a narrow low energy curve and a broad high energy curve. Within that constraint however, the relationship is maintained across a wide range of values of μ and σ .

Plotted in figure 4.4(A) are decay constant values for distributions where $\mu_2 - \mu_1 = 20$ mJ/m². It shows how that the relationship is maintained across a wide variety of standard deviations. We see that ϕ_0 decreases as the standard deviation of the high energy curve is increased. This can be explained since as the standard deviation, σ_2 , is increased the fraction of sites at a surface energy much higher than curve 1 is decreased. Thus the fraction of sites at a high energy is reduced causing the decay constant to fall also.

Shown in figure 4.4(B) is a plot of the proportionality constant, β , versus the standard deviation of the high energy curve for different values of $\mu_2 - \mu_1$. We can see that β varies between 0.5 and 5. It decreases with increasing standard deviation of the high energy curve. Above $\sigma_2 = 10$ mJ/m², β increases as the gap between the low energy and high energy curves is widened. We believe β to be an intrinsic material property dependent on the surface energy distribution. This is a first step in determining its relation to the surface energy distribution. Knowing the typical range for β and what value it should take for a given distribution can provide us with a reality check when analysing our experimental data.

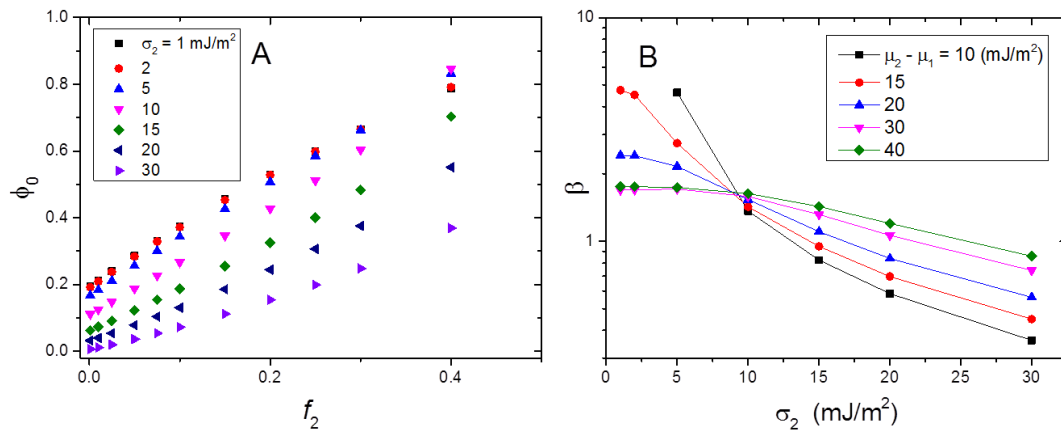


Figure 4.4. (A) Decay constant, ϕ_0 , plotted against the fraction of high energy sites, f_2 . The standard deviation of the high energy curve, σ_2 , was varied between 1 and 30 mJ/m². (B) The proportionality constant β plotted against the standard deviation of the high energy sites, σ_2 . The distance between the centres of the two curves ($\mu_2 - \mu_1$) was increased from 0 to 40 mJ/m².

In an earlier section, we demonstrated that the surface energy at full coverage, $\gamma_{d,\phi=1}$, is equal to the mean of the distribution. Shown in figure 4.5(A) are five distributions with σ_2 increasing. The surface energy profile of each distribution is simulated for a range of values of f_2 between 0 and 1. Since $\gamma_{d,\phi=1}$ is the mean of the distribution we expect to find a linear dependence on f_2 , which is what we see in figure 4.5(B). This can be stated more generally as $\gamma_{d,\phi=1} = \sum_i^n f_i \gamma_i$, where f_i and γ_i are the fraction and the surface energy of site “i”.

It should be noted that the plot of $\gamma_{d,\phi=1}$ vs f_2 in figure 4.5(A) for each of the five distributions in figure 4.5(A) are identical and overlap. This is expected since it has already been shown in figure 4.1(C) that there is no dependence of $\gamma_{d,\phi=1}$ on the standard deviation of the Gaussian curves. The values of $\gamma_{d,\phi=1}$ at $f_2 = 0$ and 1 are equal to the centres of the low and high energy Gaussians. In the case shown in figure 4.5(B) they have a value of $\mu_1 = 40 \text{ mJ/m}^2$ and $\mu_2 = 60 \text{ mJ/m}^2$. We can see that these values agree with the centre of the curves shown in figure 4.5(A). Using this knowledge it is possible to infer from any plot of $\gamma_{d,\phi=1}$ versus f_2 the values of μ of the two Gaussian curves in a distribution.

In figure 4.5(C), we have plotted $\gamma_{d,\phi=0}$ versus f_2 ; immediately it is clear that the behaviour of $\gamma_{d,\phi=0}$ is less straightforward to analyse. It rises sharply from a minimum value at $f_2 = 0$ before plateauing to its maximum value at $f_2 = 1$. The shape of this plot shows the strong dependence of $\gamma_{d,\phi=0}$ on the highest energy sites. The sensitivity of $\gamma_{d,\phi=0}$ on the standard deviation of the Gaussian representing the high energy site is obvious from figure 4.5(C). Recalling the behaviour of a single Gaussian distribution, we know that the value of $\gamma_{d,\phi=0} - \gamma_{d,\phi=1}$ is dependent mainly on the standard deviation of the Gaussian curve according to equation (4.4). This means that using the values of $\gamma_{d,\phi=0}$ and $\gamma_{d,\phi=1}$ at $f_2 = 0$ and 1 (where the distribution becomes a single Gaussian) it is possible to calculate the values of σ and μ for each of the two curves in the distribution.

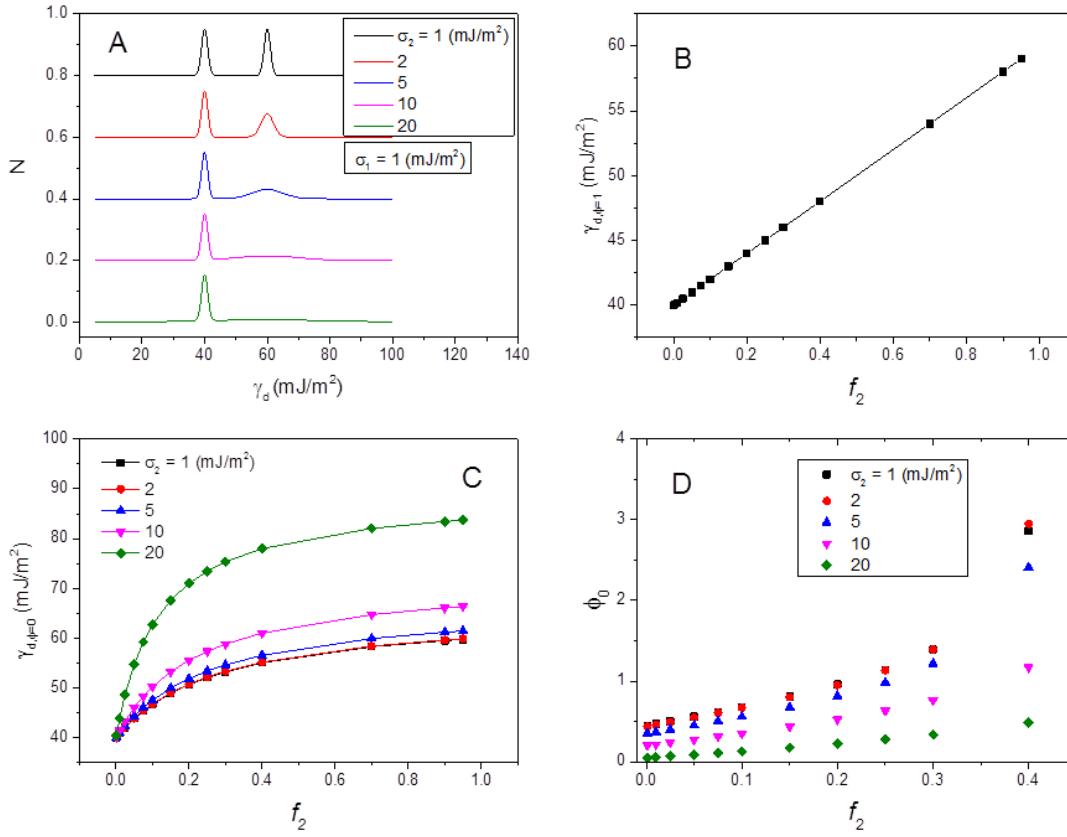


Figure 4.5. (A) Examples of distributions comprised of a low energy and a high energy curve. Shown here equally weighted. The standard deviation of the low energy curve, σ_1 , is held constant. The standard deviation of the high energy curve, σ_2 , is varied. (B) Plot of the surface energy at full coverage, $\gamma_{d,\phi=1}$, against the fraction of high energy sites, f_2 . This is unchanged by the varying standard deviation. (C) Plot of the surface energy at zero coverage, $\gamma_{d,\phi=0}$, against the fraction of high energy sites, f_2 . The value at $f_2 = 0$ is unchanged while the value at $f_2 = 1$ depends on the standard deviation of the high energy distribution, σ_2 . Combining the plots (B) and (C) gives a unique ID for any distribution. (D) Decay constants (found by fitting surface energy profiles) plotted against the fraction of high energy sites. Below a threshold of roughly $f_2 = 0.4$ the decay constant has a linear dependence on f_2 .

Using the relationships outlined above of both $\gamma_{d,\phi=1}$ and $\gamma_{d,\phi=0}$ with f_2 , the plots shown in figure 4.5(B) and (C) can be used as a unique identifier of a surface energy distribution comprised of two Gaussian curves. By changing the particle size of a sample, the fraction of high energy sites will change. This means it is possible to determine the

distribution of real samples by plotting the $\gamma_{d,\phi=0}$ and $\gamma_{d,\phi=1}$ against particle size and the decay constant, ϕ_0 , which we found could be used as a proxy for f_2 . Figure 4.5(D) demonstrates this again for the distributions of figure 4.5(A). It shows the decay constant, ϕ_0 , following a linear relationship with f_2 . This method will be developed further by incorporating an additional Gaussian curve. Chapters 5 and 6 will show how it can be applied to the real samples of molybdenum disulphide and boron nitride.

We also investigated the behaviour of two overlapped curves. Shown in figure 4.6(A) are the same single Gaussian distributions from figure 4.1(A). Figure 4.6(E) shows the corresponding surface energy profiles. The standard deviation, σ , of the Gaussian curve is increased and we observe the $\gamma_{d,\phi=0}$ increasing. The shape of the profile is convex. The following plots (B, C, D) show two overlapped Gaussians where the standard deviation, σ_1 , of one curve (denoted by a subscript “1”) is held constant at 1 mJ/m² while the value of the standard deviation of the second (denoted by a subscript “2”), σ_2 , is increased. The weightings of the curves are changed from f_2/f_1 ; 0.9/0.1 0.5/0.5 and 0.1/0.9 for the plots (B), (C) and (D) respectively. Here, the subscripts refer to the broad and narrow curves respectively. The corresponding surface energy profiles are plotted in (F), (G) and (H). Almost all show similar behaviour to that of the single Gaussian profiles shown in figure 4.6(E). They remain convex, the $\gamma_{d,\phi=0} - \gamma_{d,\phi=1}$ values behave in a similar manner and the $\gamma_{d,\phi=1}$ value is still equal to the centre of the two Gaussian curves. That two overlapping curves can be approximated to a single curve is useful when considering distributions comprised of three Gaussian curves. However, when most of the sites are concentrated in the narrow curve with a small amount of sites at a higher energy the profiles begin to take on the concave shape associated with experimental profiles. This too will become relevant in the next section.

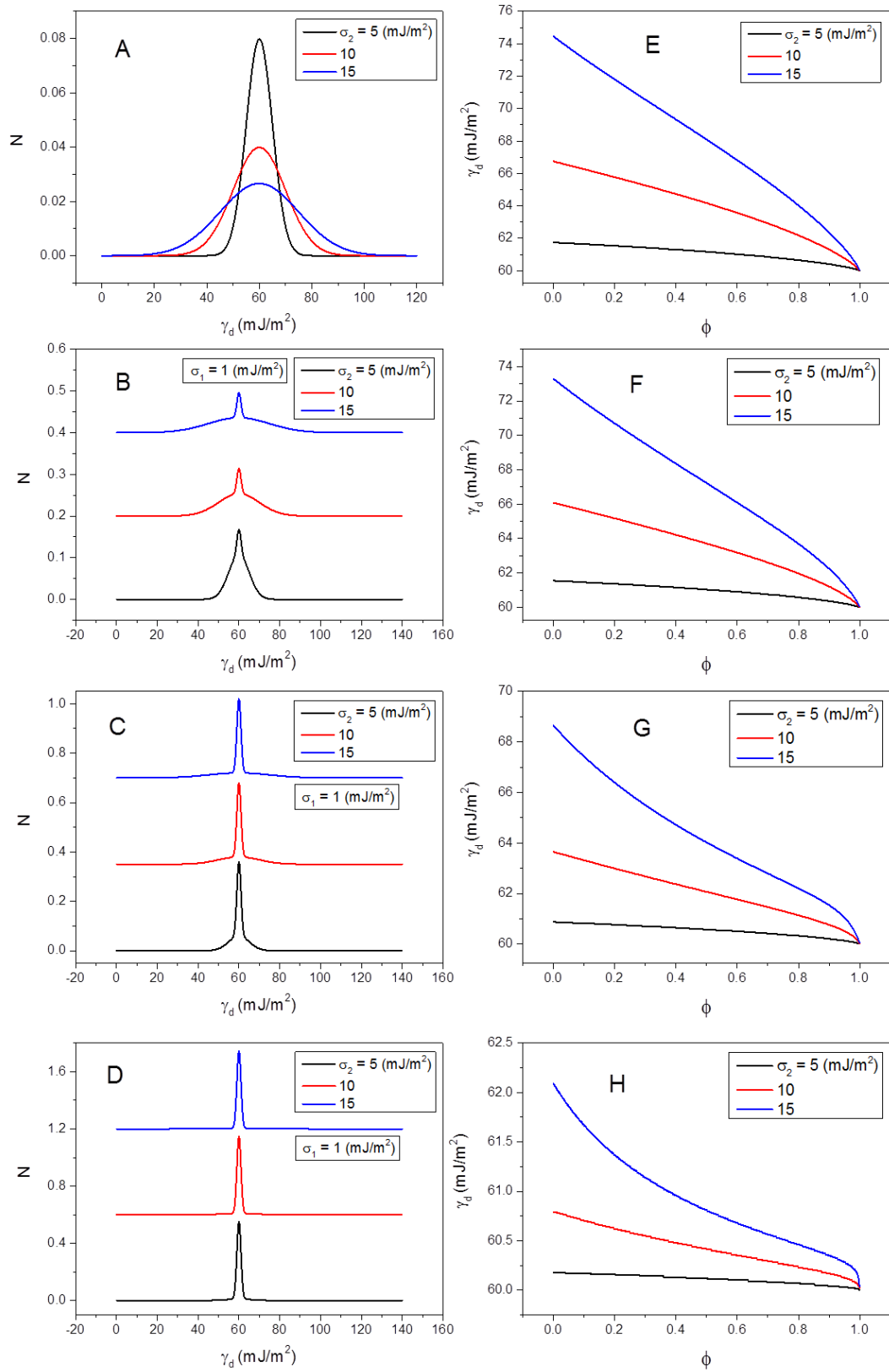


Figure 4.6. Showing the similar behaviour of a distribution comprised of two overlapping Gaussian functions to the behaviour of a single Gaussian function. (A)

Three sample distributions centred at 60 mJ/m^2 with different standard deviations. (B, C, D) Each plot shows three distributions comprised of a narrow ($\sigma_1 = 1 \text{ mJ/m}^2$) curve and a broad ($\sigma_2 = 5, 10, 15 \text{ mJ/m}^2$) curve. The curves are denoted with a subscript 1 and 2 respectively. The weighting of the two distributions is varied accordingly (B): $f_2/f_1 = 10\%/90\%$, (C): $f_2/f_1 = 50\%/50\%$, (D): $f_2/f_1 = 90\%/10\%$. (E, F, G, H) Simulated surface energy profiles of the distributions shown in (A, B, C, D).

4.2.3 Surface Energy Distributions with three Gaussian curves

Most two dimensional nanomaterials can be thought of as having three distinct aspects to their surface energy distribution; these can be roughly divided into Basal Plane sites, Defects in the basal plane and Edge sites. Each of these sites may have a distinct Gaussian curve associated with them. In addition, while a system consisting of two Gaussian curves can successfully emulate the behaviour seen in materials being studied in this thesis. Work carried out previously in this group by Ferguson et al. has shown it to fall short when describing graphite and graphene [198]. As such, we wanted to study distributions comprised of three Gaussian curves.

As there are nine different parameters in such a system, the parameter space is incredibly large. In order to manage the complexity of the system, we divided the parameter space into three different categories. For each we set out to study the dependence of the resultant profiles and their characteristic parameters on the values of μ , σ and f of each curve. These three categories are defined as follows; each of the three Gaussian curves are completely separate, two curves overlapping with one separate, and all three curve overlapping. Within each of those three categories the standard deviations can be varied creating new subcategories and then within each subcategory the relative populations of the Gaussian curves can be varied.

We first consider the category of completely separate curves. The curves are numbered 1, 2 and 3 with ascending values of μ_1 , μ_2 , and $\mu_3 = 40, 60$ and 80 mJ/m^2 . We varied the standard deviation of each curve independently and then changed the relative populations of the curves. The standard deviations, $\sigma_{1,2,3}$, are varied as $\sigma = 2, 5, 10$ and 20 mJ/m^2 , starting with curve 1 then moving to curves 2 and 3. Again, we simulated all the possible combinations of these parameters. Several examples of this first category

are shown in figure 4.7(A-E). Each plot shows a set of four distributions; together they attempt to convey the range of possible distributions. In each set the standard deviation of one of the three curves is increasing. Shown in figure 4.7(A, B) are distributions where only one of the curves is broad. The plots in figure 4.7(D-E) show distributions consisting of two and three curves with large standard deviations.

The first step is to check whether the profiles generated have the characteristic exponential shape similar to that observed experimentally. For each plot of four distributions, we have plotted the corresponding set of profiles for a range of relative populations. They are shown to the right of the distributions. The number of relative fractions shown has been reduced for the sake of clarity. It is clear from the profiles shown in figure 4.7 that most do not have the desired concave shape. Those profiles that do display this shape are a result of surface energy distributions that have a very small fraction of one of the curves. Thus the distribution may resemble the successful surface energy distributions consisting of two curves discussed earlier.

None of the distributions simulated within this category showed the characteristic exponential-like shape. No further study was carried out on these distributions because of this.

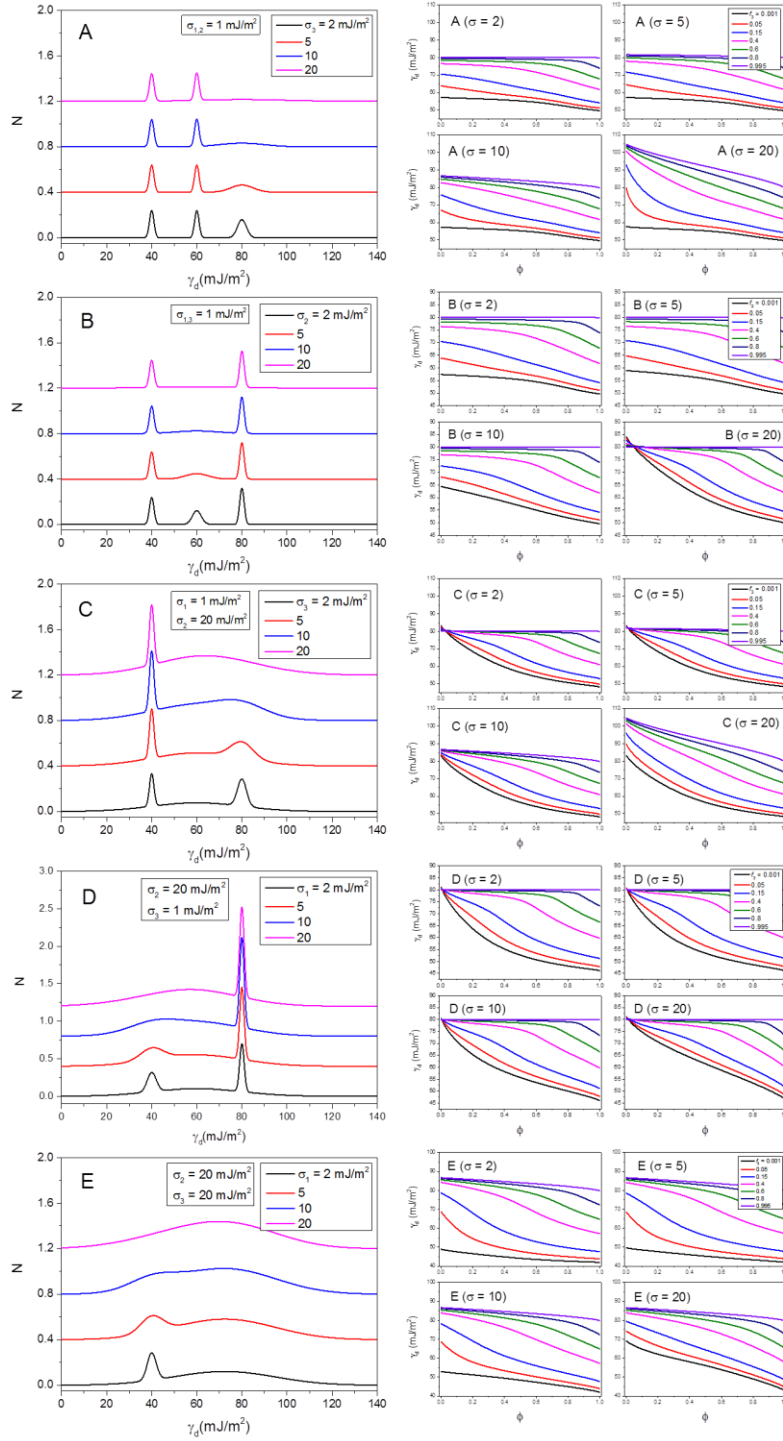


Figure 4.7. (A-E) Surface energy distributions consisting of three Gaussian curves, the curves are centred at $\mu_{1,2,3} = 40, 60$ and 80 mJ/m². The curves are labelled curves 1, 2 and 3 respectively and are identified with a subscript of their number; for example, σ_1 , refers to the standard deviation of the curve centred at 40 mJ/m². Each plot shows a set of four distributions where σ of one of the curves is varied. To the right of each plot are

the corresponding sets of surface energy profiles for different fractions of the curves. Each set shows a variety of distributions with separated curves.

The second category consists of distributions in which two of the curves are overlapping. Curve 1 is centred at $\mu_1 = 40 \text{ mJ/m}^2$, curve 3 is centred at $\mu_{2,3} = 60 \text{ mJ/m}^2$ and curve 2 has a mean value of either 40 or 60 mJ/m^2 . Since two of the Gaussian curves overlap, these distributions can be thought of as distributions with only two Gaussian curves. Earlier some of the permutations that such a distribution can take were listed; two narrow curves, two broad curves, and a mix of broad and narrow curve at either low or high energy. Most of those were already ruled out since they didn't produce suitable profiles. The same principles apply in this case.

Figure 4.8 below aims to show again those types of distributions that are not successful. In other words, those with broad and narrow curves at the low and high energy respectively, and those with two broad curves. Figure 4.8(A-E) shows five sets of four distributions; in each plot two of the curves have a constant standard deviation of either 2 or 20 mJ/m^2 , while the standard deviation of the other curve takes the values of 2, 5, 10 or 20 mJ/m^2 . The relative fraction of each curve was varied between 0 and 1. Surface energy profiles for all possible combinations of these parameters were simulated. Once again we have shown several examples of distributions from this category in figure 4.8(A-E). As before, the set of surface energy profiles are shown to right of the distributions. Of the examples shown, most do not have profiles with shapes that match experimental profiles, as with the previous example those that do display the desired shape are those with a small fraction of one of the curves. Causing the surface energy distribution to resemble the successful surface energy distributions discussed in section 4.2.2.

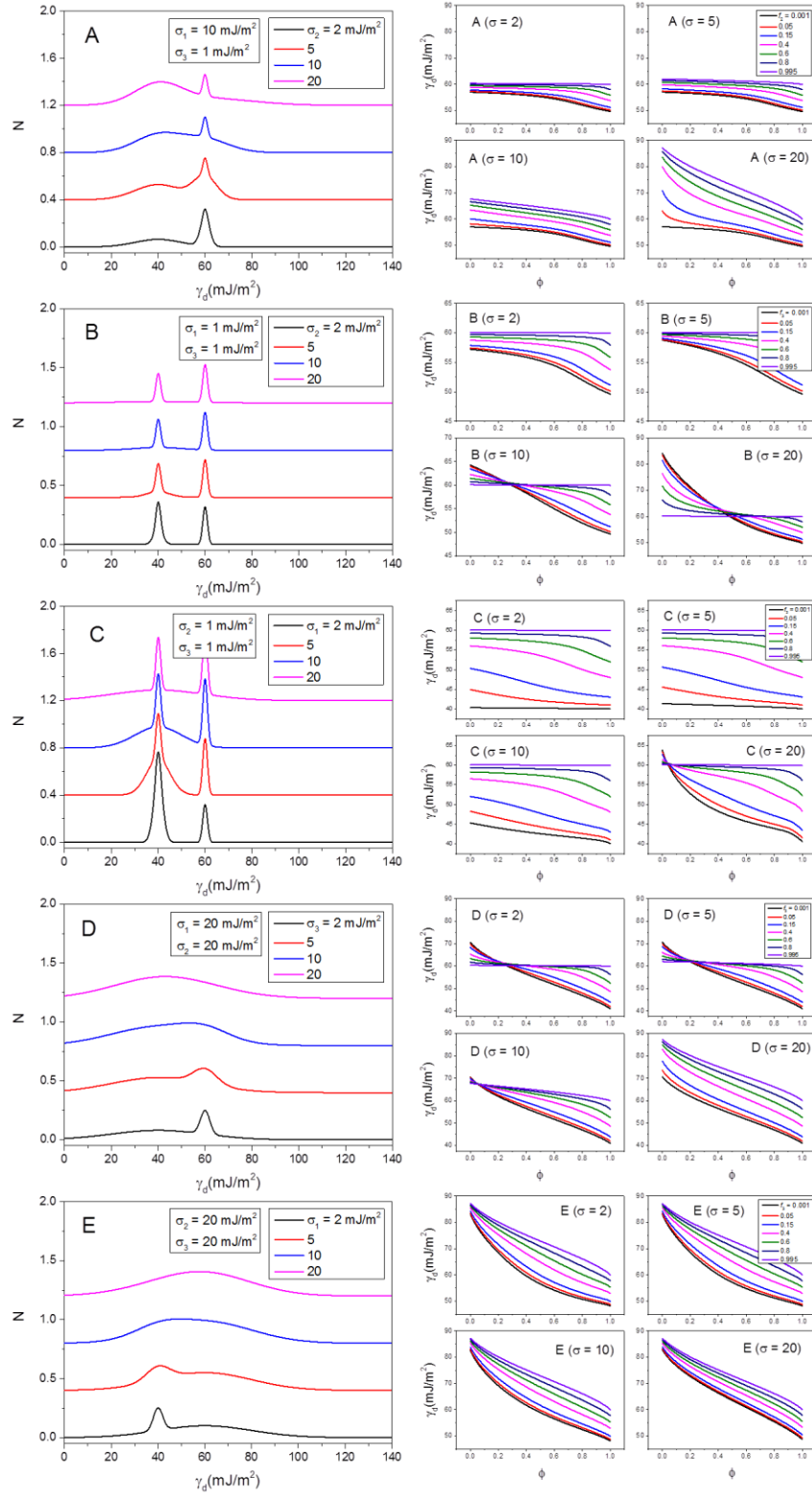


Figure 4.8. (A-E) Surface energy distributions consisting of three Gaussian curves, the curves are centred at $\mu_{1,2,3} = 40, 60$ and 60 mJ/m^2 . The curves are labelled curves 1, 2 and 3 respectively and are identified with a subscript of their number; for example, σ_1 , refers to the standard deviation of the curve centred at 40 mJ/m^2 . Each plot shows a set

of four distributions where σ of one of the curves is varied. To the right of each plot are the corresponding sets of surface energy profiles for different fractions of the curves. Each set shows a variety of distributions from this category.

We were, however, able to find two types of distributions from this category (two curves overlapped) which generated profiles matching the characteristic exponential-like shape. These distributions and their corresponding profiles are shown below in figure 4.9. If we first consider the distribution shown in (A), the distribution is of a narrow curve ($\sigma_1 = 1 \text{ mJ/m}^2$) at $\mu_1 = 40 \text{ mJ/m}^2$ and two curves (curve 2 and 3) at $\mu_{2,3} = 60 \text{ mJ/m}^2$. The standard deviation of curve 2 is equal to 1 mJ/m^2 and the standard deviation of curve 3, σ_3 , is changed from 1 to 20 mJ/m^2 . Recalling the result from section 4.2.2, the two overlapping curves can be approximated as a single Gaussian curve of a similar standard deviation. So as the standard deviation of curve 3 is increased the distributions shown in figure 4.9(A) become equivalent to those shown in figure 4.5(A), where there is a narrow low energy curve and a broad high energy curve. The profiles plotted in figure 4.9(B) are for the distribution where $\sigma_3 = 10 \text{ mJ/m}^2$ (pink line). These profiles have the exponential-like shape that we are searching for.

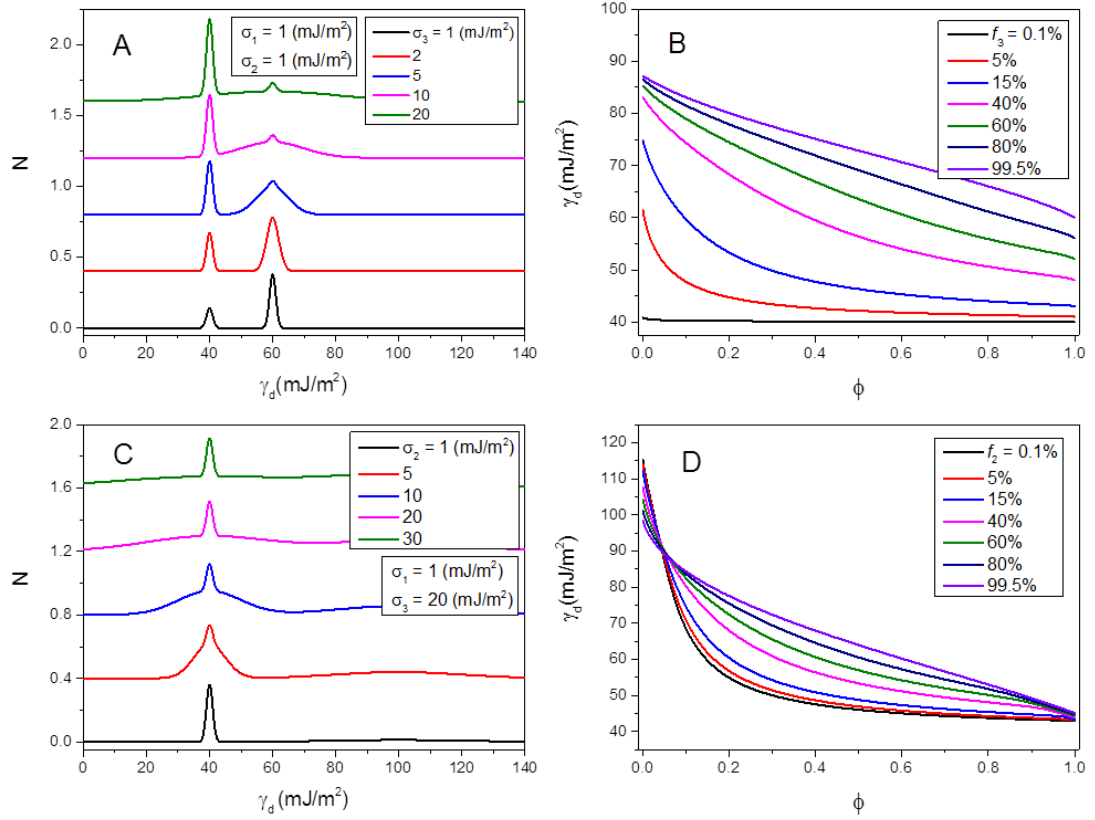


Figure 4.9. (A) Plot of five distributions where the standard deviation of curve 3, centred at 60 mJ/m² is changed. (B) Plot of the surface energy profiles generated from the distribution shown with the pink line, ($\sigma_3 = 10$ mJ/m²). They exhibit the characteristic exponential-like shape of experimental profiles. (C) Plot of five distributions where the standard deviation of curve 2, centred at 40 mJ/m² is changed. (D) Plot of the surface energy profiles generated from the distribution shown with the green line, ($\sigma_2 = 30$ mJ/m²).

As mentioned earlier, in previous work we have seen $\gamma_{d,\phi=0}$ fall exponentially with decay constant. The distributions in figure 4.9(C) have two curves at 40 mJ/m², curve 1 is kept narrow while the standard deviation, σ_2 , of curve 2 is changed from 1 to 30 mJ/m². The third curve is centred at 100 mJ/m² and has a constant standard deviation of 20 mJ/m². The profiles shown in figure 4.9(D) correspond to the distribution in figure 4.9(C) where $\sigma_2 = 30$ mJ/m² (green line). Note that the decay constant of the profile increases with fraction of sites belonging to curve 2. This indicates that curve 2 should be regarded as a high energy set of surface sites. We would then expect $\gamma_{d,\phi=0}$ to rise

with increasing fraction of curve 2. Unusually though, the value of $\gamma_{d,\phi=0}$ drops with increasing fraction of curve 2 sites, f_2 .

The third and final category consists of distributions with all three Gaussian curves overlapping. It has a much smaller parameter space as much of it is redundant since changing the standard deviation, σ , of one curve has the same effect as changing the σ of any of the other curves.

We chose a mean value, μ , of 40 mJ/m^2 for all of the curves. When all three have a narrow ($\sim 1 \text{ mJ/m}^2$) standard deviation, the resulting profiles are very similar in shape to the profiles generated from a single Gaussian curve shown in section 4.2.1. This is to be expected as the three curves can be reduced down to a single curve. However, as the standard deviation of one the curves is increased there is a distinct change in the shape of the profiles which begin to take on the characteristic exponential-like shape seen experimentally. This behaviour was mentioned in section 4.2.2 when discussing overlapped curves (see Figure 4.6).

To illustrate this, we have plotted two distributions shown in figure 4.10(A,C). The first distribution has values for $\sigma_{1,2,3}$ of 1, 1 and 10 mJ/m^2 . The second has values of 1, 1 and 20 mJ/m^2 . Shown in figure 4.10(B) and (D) are the corresponding profiles of the two distributions for various values of f_3 between 0 and 1. The profiles shown in figure 4.10(B) have a convex shape that closely resembles those from section 4.2.1 generated from a single Gaussian curve, while the profiles in figure 4.10(D) have a shape that matches a stretched exponential decay. This means that this second type of distribution can be added to the other distributions that generate desirable profiles.

There is a common quality that links each of these three successful types of distribution. It is that the majority of the sites are concentrated at the low end of the distribution and the rest are spread out in a long tail at higher energies. The shape of this can be roughly approximated as lognormal. This makes sense if we consider the shape of the experimental profiles and how sites are filled according to their surface energies. For a profile to fall to a plateau it follows that the majority of the sites are concentrated around a surface energy with the value of the plateau. Also, if the measured surface energy is to have a high initial value quickly followed by a drop to lower values it makes sense then that there are only a small fraction of sites at a high surface energy which are the very first to be measured.

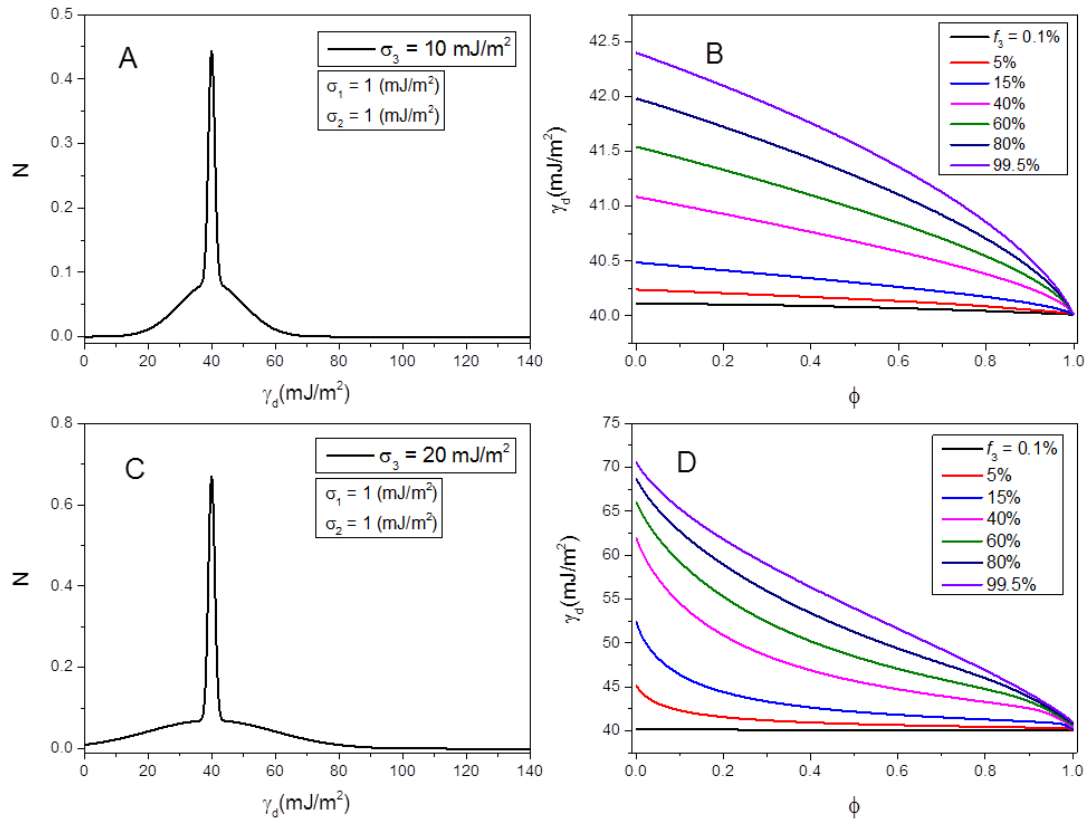


Figure 4.10. (A) Distribution with all three curves overlapped, centred at 40 mJ/m². The standard deviation of curve 3 is 10 mJ/m², while the other two curves have a standard deviation of 1 mJ/m². (C) Plot of the generated surface energy profiles, they exhibit the same behaviour as seen in distributions consisting of a single Gaussian curve. (B) Plot of a distribution with all three curves overlapped, centred at 40 mJ/m². The standard deviation of curve 3 is 20 mJ/m², while the other two curves have a standard deviation of 1 mJ/m². (D) Plot of the generated surface energy profiles, increasing the standard deviation has caused them to now exhibit the exponential-like behaviour of experimental profiles.

4.2.4 Further study of surface energy distributions

To summarise, there were three types of distribution that produced simulated profiles with behaviour similar to that of experimental profiles. Each is described by three Gaussian curves, one curve for each aspect of the material. These distributions are shown in figure 4.11(A-C). The first distribution has a narrow curve at low energy and

a broad curve at high energy. The third curve is overlapped with one of the other two and has a narrow standard deviation. The second type of distribution has all three curves at the same centre, μ , but one of the curves having a particularly broad standard deviation. The third distribution is similar to the first in that there is a narrow low energy curve and a broad high energy curve. Unlike that first distribution, there is also a broad curve at the same energy as the narrow curve. Chapters 5 and 6 will refer back to these distributions as “Type” “A, B or C” as labelled in figure 4.11(A-C).

Their corresponding surface energy profiles are shown in figure 4.11(D-F). Now we turn our attention to studying the descriptive parameters ($\gamma_{\phi=1}$, $\gamma_{\phi=0}$ and ϕ_0) of these surface energy profiles. In figure 4.11(G-I) the $\gamma_{d,\phi=0}$ values for each distribution are plotted against the fraction of either curve 2 or 2 and 3. For the plots in figure 4.11(G) and (H), the behaviour of the $\gamma_{d,\phi=0}$ values is the same as seen in section 4.2.2 which discussed distributions with two curves, i.e. $\gamma_{d,\phi=0}$ increases steeply before plateauing to its final value. The more interesting behaviour is seen in figure 4.11(I). As mentioned previously, we have observed that the $\gamma_{d,\phi=0}$ rather than increasing, can decay exponentially as the fraction of high energy sites is increased. This behaviour was seen in previous work by Ferguson et al. when studying graphite and graphene [199]. Of the three distributions, only “Type C” shown in figure 4.11(C) is able to generate this behaviour. So for cases such as graphene and graphite, which exhibit this behaviour it is a strong indication of the overall shape of the distribution.

The values of $\gamma_{d,\phi=1}$ still have a linear relationship with the relative fractions of the curves. figure 4.11(J-L) shows this behaviour being conserved across all the distributions. Interestingly, the linear trend between the decay constant and the fraction of high energy sites is also conserved across distributions; showing that it is a robust and general relationship. In figure 4.11(M-O) the decay constant is plotted against the fraction of high energy sites. The linear behaviour is clear to see. Even more surprising, is that the same threshold for linear behaviour is also maintained. Since we cannot know a priori the relative fraction of the high energy sites of a sample, this makes the decay constant an extremely useful proxy for fraction of high energy sites when studying real samples. This means that as stated at the end of section 4.2.2 it is possible to use the extracted parameters to identify the unique surface energy distribution that produced the profiles and apply it to real world samples.

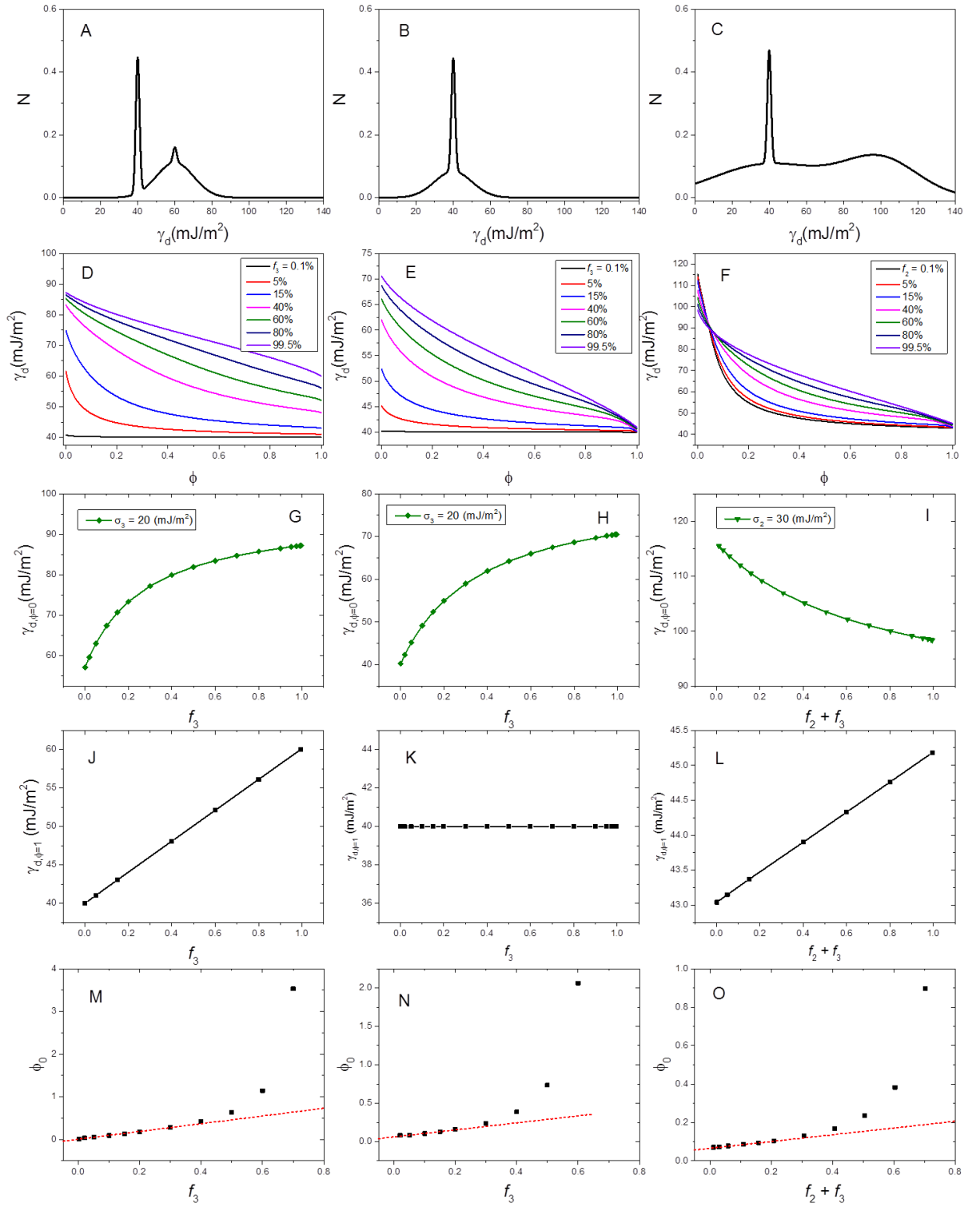


Figure 4.11. Showing the distributions and plots of the corresponding surface energy profiles and their descriptive characteristics. Plots are grouped into columns. (A) Surface energy distribution consisting of three Gaussian curves. The curves have values of $\mu_{1,2,3} = 40, 60$ and 60 mJ/m². The standard deviations are $\sigma_{1,2,3} = 1, 1$ and 20 mJ/m².

(B) Surface energy distribution consisting of three Gaussian curves. The curves have values of $\mu_{1,2,3} = 40 \text{ mJ/m}^2$. The standard deviations are $\sigma_{1,2,3} = 1, 1$ and 20 mJ/m^2 . (C) Surface energy distribution consisting of three Gaussian curves. The curves have values of $\mu_{1,2,3} = 40, 40$ and 100 mJ/m^2 . The standard deviations are $\sigma_{1,2,3} = 1, 30$ and 20 mJ/m^2 . (D) Set of the corresponding surface energy profiles of the distribution shown in (A), for different fractions of curve 3, f_3 . (E) Set of the corresponding surface energy profiles of the distribution shown in (B), for different fractions of curve 3, f_3 . (F) Set of the corresponding surface energy profiles of the distribution shown in (C), for different fractions of curves 2 and 3, $f_2 + f_3$. (G) Plot of the surface energy at zero coverage, $\gamma_{d,\phi=0}$, against f_3 . The shape is related to the standard deviation, σ_3 , of curve 3. (H) Plot of the surface energy at zero coverage, $\gamma_{d,\phi=0}$, against f_3 . The shape is related to the standard deviation, σ_3 . (I) Plot of the surface energy at zero coverage, $\gamma_{d,\phi=0}$, against $f_2 + f_3$, the fraction of curves 2 and 3. The shape is related to the standard deviation, σ_2 . (J, K, L) Plots of the surface energy at full coverage, $\gamma_{d,\phi=1}$, plotted against f_2 or $f_2 + f_3$ as appropriate. (M, N) Plots of the decay constant against the fraction of curve 3 (broad high energy curve). (O) Plot of the decay constant against the fraction of the two broad curves (2 and 3).

4.3 Conclusion

This chapter began by using the method outlined by Smith et al for simulating surface energy profiles for a specified surface energy distribution to examine the simplest form of energy distribution, a single Gaussian curve. [194] We were able to gain some useful insights but found that its simplicity limited its applicability. We then moved gradually to more complex distributions comprised of two and three Gaussian curves.

To uncover the relationship between the surface energy distribution and the changing shape of the surface energy profiles, we systematically varied the parameters of each distribution and studied the generated profiles. By fitting the profiles to a stretched exponential, we were able to extract some descriptive parameters, examine their behaviour and relate them to the surface energy distribution. This provided us with a deeper understanding of the shape of the profiles and which types of distributions give rise to profiles with the characteristic exponential decay.

We found that $\gamma_{d,\phi=1}$ can be used to find the centre, μ , of the Gaussian curves. That $\gamma_{d,\phi=0}$ - $\gamma_{d,\phi=1}$ is related to the standard deviation of the curve, and that the decay constant, ϕ_0 , can be used as a proxy for the fraction of high energy sites. We found that overlapping curves can in most cases be simplified to a single curve. This enabled us to reduce the complexity of the more complicated surface energy distributions.

We were also able to use the relationship between $\gamma_{d,\phi=0}$ and the fraction of high energy sites to identify an unusual case where the $\gamma_{d,\phi=0}$ decays exponentially rather than increasing. This behaviour was seen in previous work on graphene and graphite by Ferguson et al. [198], [199]

Using these relationships we have developed a method to derive the surface energy distribution of a material from its surface energy profiles. Using multiple surface energy profiles measured with samples of different particle size makes the method more robust. It is less likely to arrive at a local minimum and we can ascribe surface energies to the different aspects of the material being studied.

In the following two chapters we will put this method into practice by inferring the surface energy distributions and ascribing surface energies to the material aspects of molybdenum disulphide and boron nitride.

Chapter 5

Molybdenum Disulphide

5.1 Introduction

Molybdenum Disulphide (MoS_2) has been used and studied for a long time. It's most commonly used as a dry or solid lubricant. Since the discovery and exfoliation of graphene there has been renewed interest in two dimensional materials. MoS_2 belongs to a class of 2D materials known as Transition Metal Dichalcogenides, of which MoS_2 is one example. Due to the increase in research of these materials many properties of MoS_2 have been tested and measured: conductivity, mobility, photoluminescence and even surface energy. Surface energy values have been published previously, with good agreement around 45 mJ/m^2 [193], [200]. These measurements were made using contact angle, which will measure only the average surface energy, so quoting a single value neglects the heterogeneity of a material.

Many more measurements have been carried out on graphene. There is a much wider variation in quoted surface energy values. This is largely due to the use of different techniques and how they interact with the sample surface and to what extent it probes the different aspects of a surface. These differences were explained in an earlier chapter. This dependence on technique illustrates the shortcomings of using a single value to describe surface energy.

Lack of a complete description of a surface's heterogeneity will hinder the understanding of its interactions with its surroundings. An example important to this group is that of liquid phase exfoliation, which is used to produce defect free thin sheets of layered materials including graphene and MoS_2 [71], [191], [201]. It has been shown through theoretical studies that this technique works best when the difference between the surface energy of the solvent and the material is minimised [66], [202]. Currently,

finding the optimal solvent is an empirical process, thus having a complete understanding of a material's surface energy would help greatly in the search for suitable, non-toxic solvents. The best solvents for exfoliating MoS₂ have been found to be those with a surface energy of 70 mJ/m² [191], but as already discussed this value cannot fully represent the surface energy of MoS₂ or other materials.

This chapter will attempt to use the method detailed in the previous chapter to infer the surface energies of the different aspects of MoS₂; Basal Plane, Defects in the Basal Plane and Edges. Coverage dependent inverse gas chromatography is used to measure the surface energy profiles of MoS₂ at a range of different flake lengths. Changing the flake length changes the relative proportion of edge and basal plane enabling the deconvolution of the surface energy in to their separate contributions. The surface energy at high surface coverage was found to be independent of flake length with a value around 40 ± 4 mJ/m²; closely matching the values from the literature. This should be no surprise as the value at full coverage comes from interacting with the entire sample surface just like contact angle measurements. On the other hand, surface energy at low coverage showed a clear dependence on flake length indicating a relationship between the number of high energy sites and flake length, varying quite a bit between 42 and 96 mJ/m². By analysing this dependence on length we are able to extract the contributions to the surface energy. We also observed that the basal defect content varied with flake length. We were able to determine values for the fraction of defects in the basal plane at zero and infinite flake lengths of 0.015 and 0.42. This is a surprising result but there is additional published work which corroborates it. Findings by Vega-Mayoral et al. used the optoelectronic properties of MoS₂ to infer the density of defects in flakes of different lengths [203]. They found that as the length of the flakes of MoS₂ was increased the defect density rose by an order of magnitude. The reported values for the defect density in MoS₂ fall over a wide range from 6×10^{11} cm⁻² to 3.5×10^{13} cm⁻² [54], [204]. The values obtained as part of this work fall within this range and show close agreement.

This work will help to further develop and generalise the framework initially set out in previous work on graphite and graphene; helping the analysis of many more nanomaterials.

5.2 Experimental Methods

5.2.1 Materials:

Molybdenum disulphide was sourced from two suppliers: Sigma-Aldrich and Alfa Aesar.

5.2.2 Methods:

The central premise of this work relies on being able to alter the flake length of MoS_2 . In order to be able to do this reliably and minimise other changes to the distribution caused by effects such as mining or production processes; it was decided that we would obtain more consistent and reliable results if we were to select for the flake length of the samples ourselves. We found centrifugation to be the simplest and most time efficient method. The theory behind centrifugation sedimentation has already been discussed in chapter 3 but to briefly reiterate, it has the ability to size select samples because the larger flakes fall out of the solvent more quickly than the smaller flakes. Thus by adjusting the angular velocity and the centrifugation time we are able to produce samples with different mean flake lengths. We can also be confident that the sample is otherwise quite similar to the original sample. In other words that the number of defects in the basal plane will be unaffected and that the chemical composition is unchanged.

All samples were produced in a similar manner. Each time starting with 1 g of MoS_2 powder from Sigma Aldrich. This was added to 200 mL of deionised water and shaken vigorously, resulting in a dispersion with a concentration of 5 mg/mL. This dispersion was added to four 50 mL centrifuge tubes, which were then subjected to a force of ~ 28 G (500 rpm) for the following lengths of time; 0.5, 1, 2, 4, 6 and 8 minutes. The supernatant from each tube was collected and then dried in a vacuum oven for 48 hours at 80°C . After drying the sample was collected and stored in a sealed vial while awaiting measurement.

To obtain the mean flake size, $\langle L \rangle$, of each sample a small amount of each was placed onto a sticky carbon tab and sputtered with Gold-Palladium to prevent charge build-up on the sample. Images of the samples were taken with a Zeiss Ultra Plus Field Emission SEM at 5 keV. The resulting images were imported into the software ImageJ which was used to measure the length and width of individual flakes. A minimum of 200 flakes

were measured for each sample so that a statistically reliable distribution could be obtained.

The surface area and surface energy profile of each sample was measured using a Surface Energy Analyser (SEA) IGC (Surface Measurement Systems, UK). Each sample was packed into a silanised glass column with an internal diameter of 2mm and length 30 cm. In order to keep the material in place both ends of the tube were plugged with silanised glass wool. To measure the specific surface area, 15 to 20 mg of sample was packed into a glass column and preconditioned at 110 °C for 2 hours at a flow rate of 10 mL/min to remove any weakly adsorbed contaminants present on the surface. Octane was injected at increasing concentrations into the glass column at 20 °C and flow rate of 20 mL/min. Peak max was taken as the retention time. These retention times were used to produce an adsorption isotherm, from which using the BET equation the SMS Cirrus software is able to calculate the specific surface area. (see chapter 3). To measure the surface energy profile of a sample a mass corresponding to an area of 0.5 m² was packed into a glass column. The sample is preconditioned in the same manner as the specific surface area measurements. The alkanes; Hexane, Heptane, Octane, Nonane and Decane were used as probe molecules. Coverages ranged from 0.004 to 0.4. Chromatograms were measured using a flame ionising detector (FID). The peak centre of mass (COM) was used as the retention time. Measurements were made at a temperature of 25 °C. The included SMS Cirrus software was used to carry out all calculations. Errors were calculated using the method of REF and automated using a python script. Briefly, the error depends on the quality of the linear fit of the alkane line. To ensure the accuracy of our measurements we aimed to use only measurements where the R² value of the alkane line fit was greater than 0.999, unfortunately for some measurements we were unable to achieve this standard.

5.3 Results and Discussion

5.3.1 Basic Characterisation

To begin our study of how surface energy depends on flake size we carried out SEM on each sample and measured the mean flake length. This was done using the method outlined above in chapter 3. Figure 5.1 shows representative images of the flakes from each sample. The flakes were determined to be made up of platelets stacked together

rather than being monoliths. Flake length was defined as a flakes largest dimension. The histograms of each sample are shown in figure 5.2. We found the mean lengths to vary between 0.525 and 44 μm .

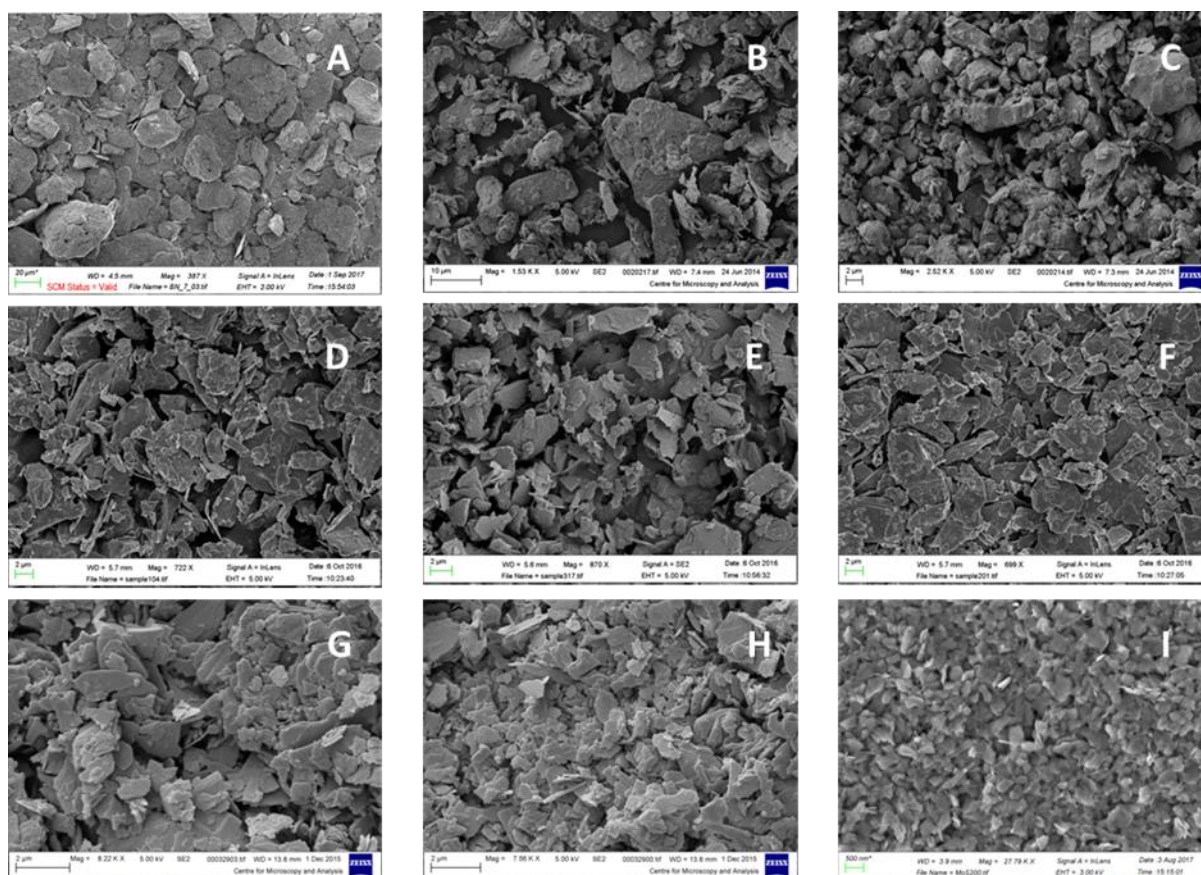


Figure 5.1. Representative SEM images of the molybdenum disulphide samples. A) Alfa Aesar, B) Sigma Aldrich, C) 30 sec, D) 1 min, E) 2min, F) 4 min, G) 6 min, H) 8 min, I) Exfoliated.

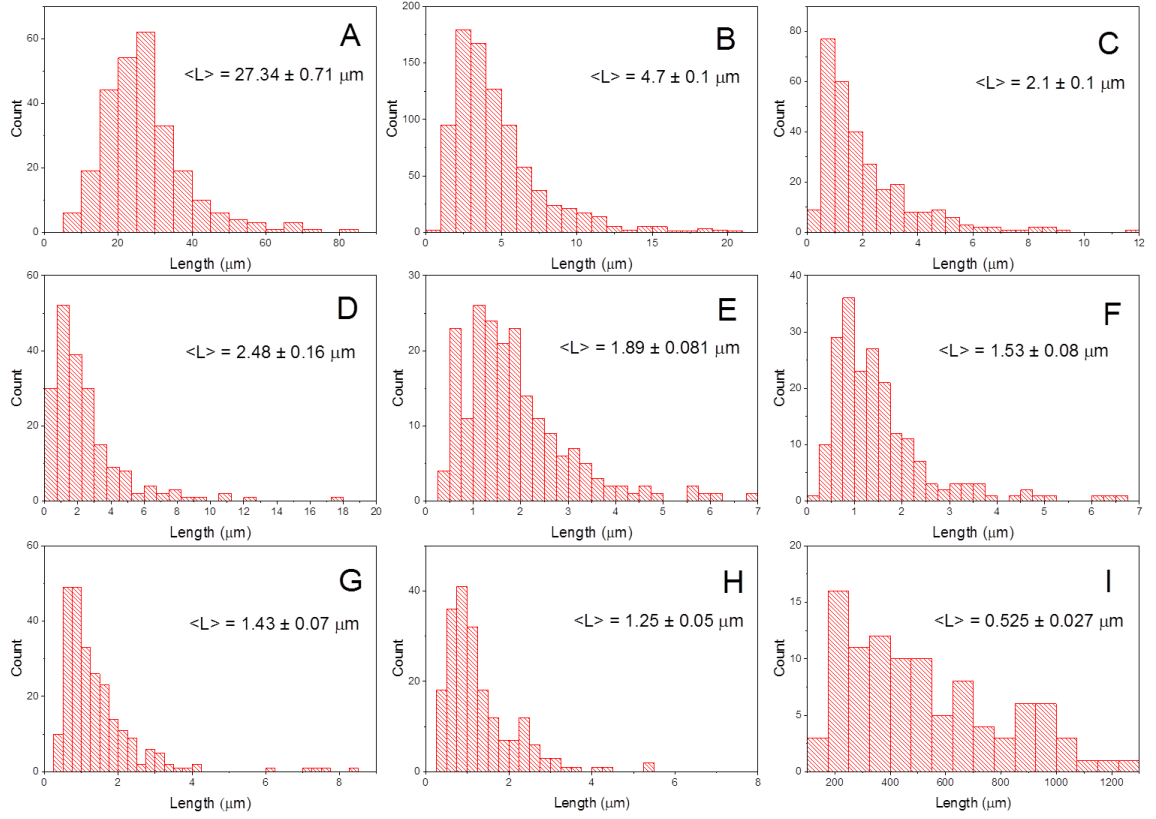


Figure 5.2. SEM histograms of the molybdenum disulphide samples. A) Alfa Aesar, B) Sigma Aldrich, C) 30 sec, D) 1 min, E) 2min, F) 4 min, G) 6 min, H) 8 min, I) Exfoliated.

The measured specific surface area values fall between 5 and 60 m²/g. They have a clear linear dependence on $1/L$. This is shown in figure 5.4. This relationship can be explained by considering the following. The specific surface area, S_{BET} , of a flake can be described in terms of the flake area, A , perimeter length, P , and thickness, t , with the following expression:

$$S_{BET} = \frac{2A + Pt}{\rho At} = \frac{2}{\rho t} + \frac{P}{\rho A} \quad (5.1)$$

where ρ is the density of the platelet. The first term on the *RHS* represents the contribution of the basal plane to the surface area and the second term represents the edge contribution. As we only have data on the length and width of the flakes we need

to re-express equation (5.1) in these terms. The ratio of the length to the width of the flake is represented as $k = L/W$. The width is defined as the length of the flake in the axis perpendicular to the length. This ratio was found to be independent of L with an average value of $k = 1.25$. The platelets are modelled as a rhombus as shown in figure 5.3. We can now re-express the ratio of P/A .

$$P = 2L\sqrt{1 + k^{-2}} \quad (5.2)$$

$$A = \frac{L^2}{2k} \quad (5.3)$$

Combining these equations we arrive at:

$$\frac{P}{A} = \frac{4}{L}\sqrt{1 + k^2} \quad (5.4)$$

Combining equations (5.1) and (5.4) to get:

$$S_{BET} = \frac{2A + Pt}{\rho At} = \frac{2}{\rho t} + \frac{4\sqrt{1 + k^2}}{\rho L} \quad (5.5)$$

This equation describes the linear trend in the data observed in figure 5.4. With S_{BET} rising as L decreases, indicating that the edge is contributing to the surface area as expected. From a linear fit of the data we can use the intercept to calculate a value for the flake thickness. That the data fits to a linear model indicates that flake thickness, t , is constant and independent of L . We calculated a value of 95 nm for the flake thickness.

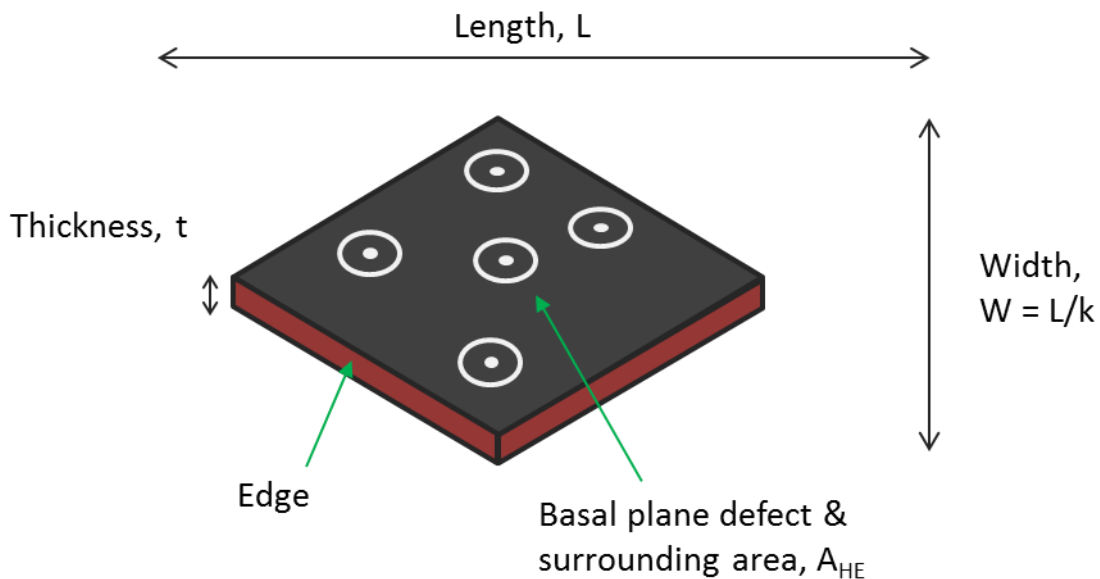


Figure 5.3. Diagram of a flake modelled as a rhombus. Edges are shown in red and the defects in the basal plane are surrounded by an area where atoms are dislocated from there equilibrium position (shown in white).

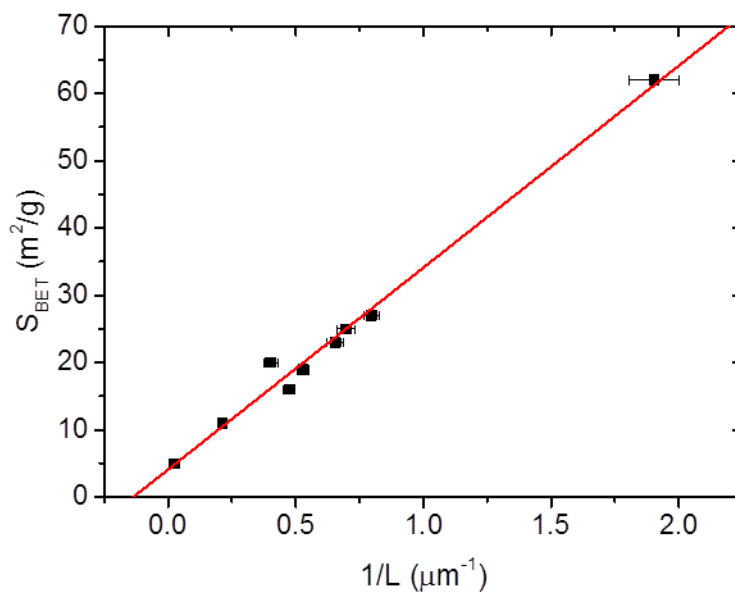


Figure 5.4. Plot of the measured surface area plotted against the reciprocal of the flake length. The plot shows a clear linear relationship.

5.4 IGC Measurements

To measure the surface energy profiles of each sample we used coverage dependent IGC. These profiles are built up by measuring the surface energy at a series of specified coverages. At each coverage a series of alkanes are injected. The surface coverage is calculated as a fraction of the monolayer capacity which is calculated from the specific surface area using the formula:

$$S_{BET} = N_a a n_m \quad (5.6)$$

The plot of the measured Gibbs free energy of adsorption for each alkane is plotted against the alkane carbon number and is known as an alkane line. Two sample alkane lines are shown figure 5.5(A); both are from the same sample but at different surface coverages, note the reduction of the slope as the coverage is increased. Using the slope of this plot, the Dorris-Gray method and equation (5.7) a surface energy profile is built up. Two sample surface energy profiles are shown in figure 5.5(B) are of MoS₂, immediately apparent is their characteristic concave, exponential-like shape.

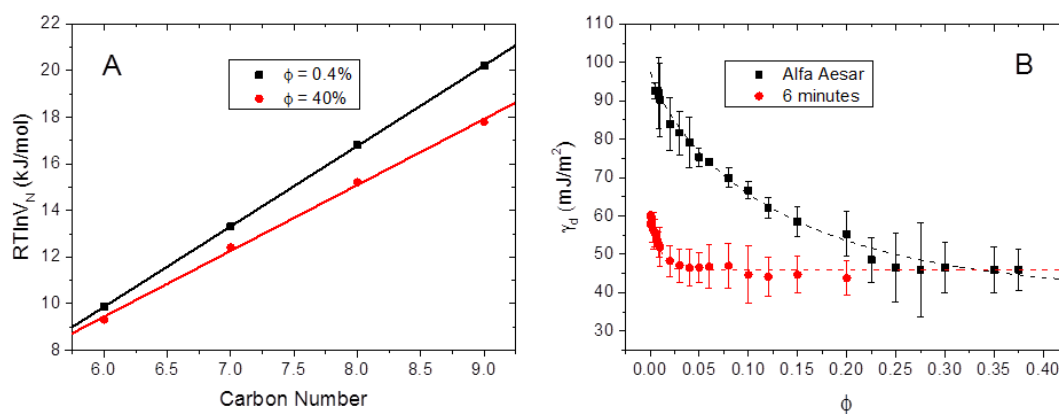


Figure 5.5. (A) Plot of the Gibbs free energy of adsorption ($RT\ln V_N$) against the alkane number. Shown are two “alkane lines” for the same sample (Alfa Aesar) at different coverages. They are fitted to equation (5.7). (B) γ_d plotted as a function of surface coverage (ϕ) for two samples (Alfa Aesar and 6 minutes) of MoS₂. Note the decrease of γ_d with surface coverage and that it reaches a plateau value ($\gamma_{d,\phi=1}$). These plots have been fitted to a stretched exponential equation (5.9).

$$\gamma_d = \frac{1}{4\gamma_d^{CH_2}} \left[\frac{RT \ln(V_{N,n+1}/V_{N,n})}{N_A a_{CH_2}} \right]^2 \quad (5.7)$$

At low coverages a high surface energy is measured, which then falls as coverage is increased, eventually reaching a plateau value which is taken to be the surface energy at full coverage. In the study of energetic heterogeneity, previous authors have fitted γ_d profiles have to an empirical exponential function [205], [206].

$$\gamma_d(\varphi) = \gamma_{d,\varphi=1} + (\gamma_{d,\varphi=0} - \gamma_{d,\varphi=1}) e^{-\left(\frac{\varphi}{\varphi_0}\right)} \quad (5.8)$$

where $\gamma_{d,\varphi=1}$ is the dispersive surface energy at full coverage, $\gamma_{d,\varphi=0}$ is the dispersive surface energy at zero coverage, φ is the coverage and φ_0 is a constant which describes how the surface energy decays with increasing coverage. We have found that a stretched/compressed exponential describes the data much more closely and gives more consistent results, as well as this the fitted parameters of simulated profiles behave in a more coherent manner using this function.

$$\gamma_d(\varphi) = \gamma_{d,\varphi=1} + (\gamma_{d,\varphi=0} - \gamma_{d,\varphi=1}) e^{-\left(\frac{\varphi}{\varphi_0}\right)^j} \quad (5.9)$$

where j is the stretching ($0 < j < 1$) or compressing ($j > 1$) exponent. Plotted in figure 5.6(A-I) are all the surface energy profiles of MoS₂; each has been fitted to equation (5.9). Their fit parameters are listed in Table 5.1 below and will be used in a later section.

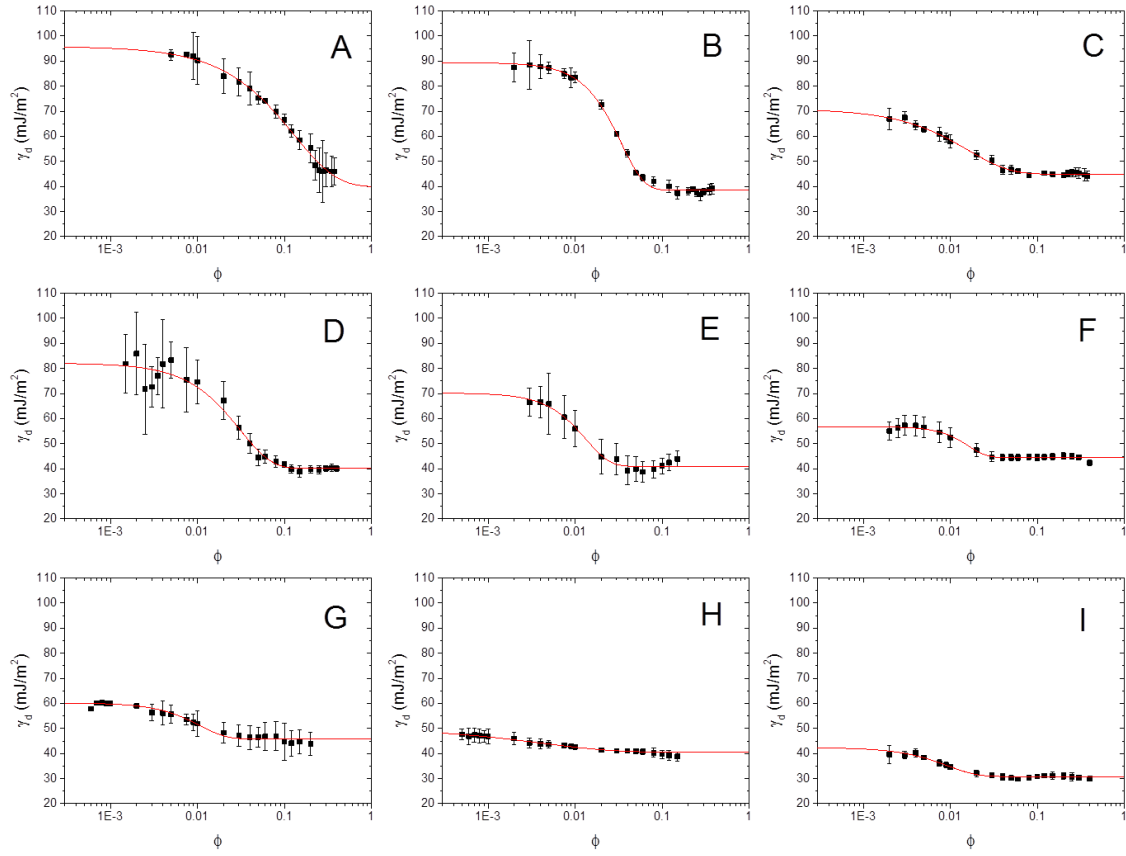


Figure 5.6. γ_d plotted as a function of surface coverage (ϕ) for all samples of MoS_2 used in this work. A) Alfa Aesar, B) Sigma Aldrich, C) 30 sec, D) 1 min, E) 2min, F) 4 min, G) 6 min, H) 8 min, I) Exfoliated. Each profile has been fitted to a stretched exponential function as shown in equation (5.9).

Table 5.1. Fitting parameters of the surface energy profiles of the MoS₂ profiles shown in figure 5.6.

Sample	$\gamma_{d,\varphi=0}$ (mJ/m ²)	$\gamma_{d,\varphi=1}$ (mJ/m ²)	Φ_0	j	$\langle L \rangle$ (μm)
Alfa Aesar	95.84 $\pm$ 1.95	39.89 $\pm$ 3.66	0.129 $\pm$ 0.017	0.886	27.34 $\pm$ 0.71
Sigma Aldrich	89.36 $\pm$ 1.08	38.56 $\pm$ 0.32	0.034 $\pm$ 0.0006	1.647	4.7 $\pm$ 0.1
0.5 minutes	70.94 $\pm$ 2.38	44.92 $\pm$ 0.11	0.016 $\pm$ 0.0023	0.91	2.1 $\pm$ 0.1
1 minute	82.11 $\pm$ 2.72	40.09 $\pm$ 0.26	0.0309 $\pm$ 0.0029	1.195	2.48 $\pm$ 0.16
2 minute	70.12 $\pm$ 3.01	40.99 $\pm$ 0.64	0.0134 $\pm$ 0.0015	1.604	1.89 $\pm$ 0.08
4 minute	56.7 $\pm$ 0.559	44.51 $\pm$ 0.25	0.016 $\pm$ 0.0013	2.16	1.53 $\pm$ 0.08
6 minute	60.2 $\pm$ 0.417	45.84 $\pm$ 1.39	0.0107 $\pm$ 0.0025	1.448	1.43 $\pm$ 0.07
8 minute	50.4 $\pm$ 1.62	40.5 $\pm$ 0.3	0.0041 $\pm$ 0.0012	0.521	1.25 $\pm$ 0.05
Exfoliated	42.41 $\pm$ 6.43	30.83 $\pm$ 0.01	0.0094 $\pm$ 0.044	1.3	0.525 $\pm$ 0.027

For $\gamma_{d,\varphi=0}$ we measured values between 42 and 96 mJ/m². The values we found for $\gamma_{d,\varphi=1}$ were in the range of 30 to 45 mJ/m². These values agree with contact angle measurements done on MoS₂ [193], [200]. This agreement stands to reason due to the similarity between contact angle measurements and full coverage IGC measurements.

Plotted in figure 5.7(A) are the values of the surface energy at zero and full coverages against the mean flake length. The values of the surface energy at full coverage are independent of flake length with an average value of 40.6 mJ/m². There is a clear trend between the $\gamma_{d,\varphi=0}$ values and the flake length. As with the simulated values of $\gamma_{d,\varphi=0}$ discussed in the previous chapter they rise sharply before reaching a plateau value. That

the values reach their maximum at large flake lengths indicates that the high energy sites are associated with the basal plane or more likely its defects. At small flake lengths, where the edge sites dominate the $\gamma_{d,\varphi=0}$ fall to a minimum value close to that of the values for $\gamma_{d,\varphi=1}$. The plot in figure 5.7(B) of the decay constant versus flake length demonstrates that the ability of φ_0 to stand in as a proxy for defect fraction still holds for real-world samples.

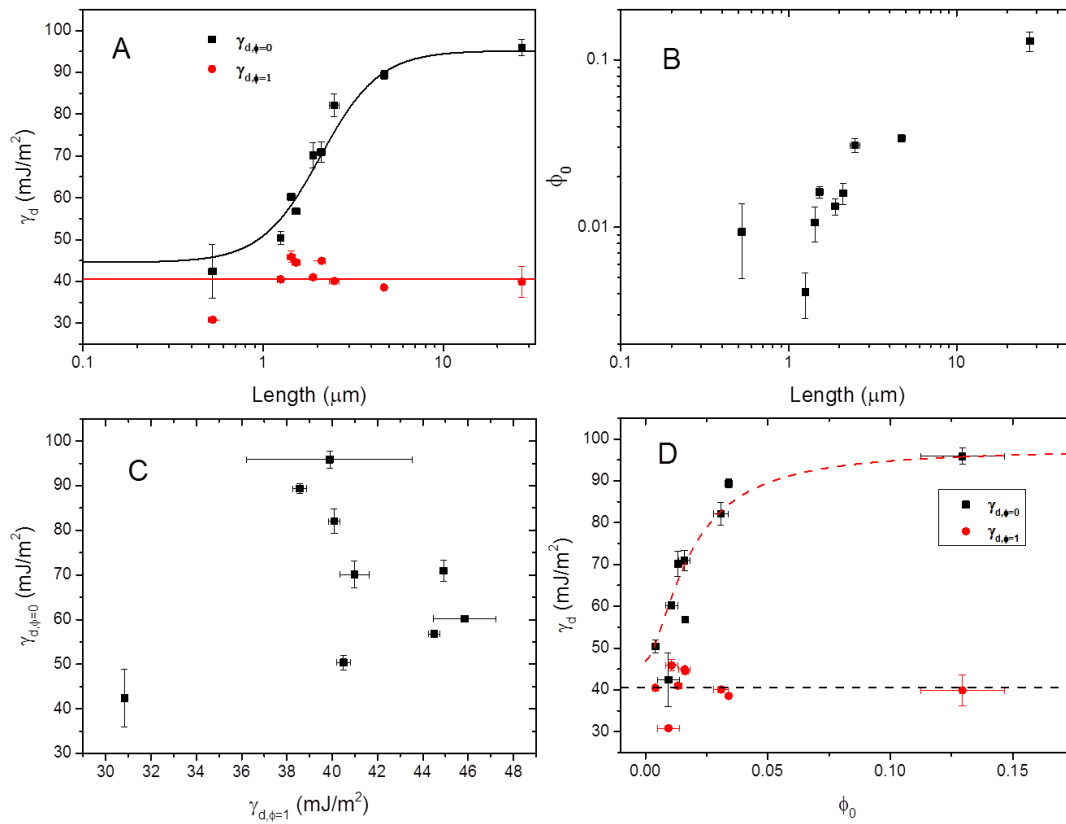


Figure 5.7. (A) Plot showing the zero and full coverage surface energies plotted against mean flake length. (B) Plot of the decay constant against mean flake length. (C) $\gamma_{d,\varphi=0}$ plotted against $\gamma_{d,\varphi=1}$ shows no correlation between the two indicating they are independent. (D) The zero and full coverage surface energies plotted against the decay constant, ϕ_0 . The zero coverage fits to a logistic function while the full coverage values are roughly constant at mean value of 40.6 mJ/m².

The plot in figure 5.7(C) is of $\gamma_{d,\varphi=0}$ vs $\gamma_{d,\varphi=1}$ showing no correlation between the two, implying that measuring just one or the other has little to no information to give about the other and about the surface energy of a material as a whole. This highlights the necessity of coverage dependent-IGC in analysing the surface energy of materials compared to other techniques. Plotting in figure 5.7(D) $\gamma_{d,\varphi=0}$ and $\gamma_{d,\varphi=1}$ against φ_0 we can see that $\gamma_{d,\varphi=1}$ and φ_0 are independent of one another. On the other hand $\gamma_{d,\varphi=0}$ shows an obvious relationship with φ_0 , indicating that the two are related and have a basis in the same phenomena.

5.5 Fitting characteristic parameters

Previous work in this group developed a semi-empirical model to interpret the behaviour of the parameters and their relationships to flake length.[199] It was shown that $\gamma_{d,\varphi=0}$ decayed exponentially with φ_0 . This behaviour was demonstrated to only occur for a certain type of surface energy distribution consisting of three Gaussian curves (see chapter 4). The simulations were able to show that the decay of $\gamma_{d,\varphi=0}$ with the increasing fraction of a broad low energy component of the surface energy distribution could be adequately described by an exponential function. In figure 5.8(A) is the experimental data of graphene and graphite showing this decay of $\gamma_{d,\varphi=0}$ with φ_0 , while in figure 5.8(B) is a plot of simulated data replicating this behaviour. The simulated data is generated with the following distribution. The means of the Gaussian curves are equal to, $\mu_{1,2,3} = 100, 60, 70 \text{ mJ/m}^2$. The standard deviations are equal to, $\sigma_{1,2,3} = 20, 2, 30 \text{ mJ/m}^2$. The relative population of the third Gaussian curve ($\mu_3 = 70 \text{ mJ/m}^2$, $\sigma_3 = 30 \text{ mJ/m}^2$) was varied. The relative populations of the other two curves were kept at a constant ratio. The Gaussian curve with a mean, $\mu_2 = 60 \text{ mJ/m}^2$ was kept at a ratio of 5:1 to the curve with a mean, $\mu_1 = 10 \text{ mJ/m}^2$. Both plots are fitted using an exponential decay showing good agreement. In the work of Ferguson et al the broad ($\sigma = 30 \text{ mJ/m}^2$) low energy ($\mu = 60 \text{ mJ/m}^2$) Gaussian curve was ascribed to the edge sites.

Using the same model as earlier in section 5.3.1, where we assume the flake to be a rhombus of area A , perimeter P and thickness t , we can write

$$\varphi_0 = \beta f_{HE} = \beta \times \frac{A_{HE}(N_{D,B}/A)2A + Pt}{2A + Pt} \quad (5.10)$$

The fraction of edges sites scales approximately as $f_{\text{edge}} \approx Pt/2A$ which is proportional to $1/L$. Since the decay constant falls exponentially with the fraction of high energy sites this implies that $\gamma_{d,\varphi=0}$ scales with L as $\gamma_{d,\varphi=0} = \gamma_{d,\varphi=0}(L=0) + [\gamma_{d,\varphi=0}(L=\infty) - \gamma_{d,\varphi=0}(L=0)] \times \exp(-L_{BD=ED} \ln 2/L)$. Where BD and ED are the basal plane and edge defects, so $L_{BD=ED}$ is the length where two populations of each are equal. This form was justified because the flake length $L_{BD=ED}$ represents the flake length where $\gamma_{d,\varphi=0}$ is midway between its limits at large and small L . This is consistent with the two populations of BD and ED being equal at $L_{BD=ED}$. $L_{BD=ED}$ can be written in terms of flake aspect ratio, thickness and basal plane defect fraction as $2\sqrt{1+k^2}[A_{HE}(N_{D,B}/A)]^{-1}$ using equation (5.11). Where $2\sqrt{1+k^2}t/L$ is the term representing the edge fraction.

$$\varphi_0 = \beta \frac{A_{HE}(N_{D,B}/A) + 2\sqrt{1+k^2}t/L}{1 + 2\sqrt{1+k^2}t/L} \quad (5.11)$$

Combining these results we arrived at equation (5.12), which was successful in fitting the experimental data. It is also possible to use equation (5.11) to avoid the reliance on measurements of L and t . Giving equation (5.13), these two equations allowed us to interpret the data and calculate values for the surface energies of the edge ($L = 0$) and defect ($L = \infty$) sites.

$$\begin{aligned} \gamma_{d,\varphi=0} = & \\ \gamma_{d,\varphi=0}(L = 0) + & \\ [\gamma_{d,\varphi=0}(L = \infty) - \gamma_{d,\varphi=0}(L = 0)]e^{-2\ln 2\sqrt{1+k^2}[A_{HE}(N_{D,B}/A)]^{-1} \times t/L} & \end{aligned} \quad (5.12)$$

$$\begin{aligned} \gamma_{d,\varphi=0} \approx & \gamma_{d,\varphi=0}(L = 0) \\ & + 2[\gamma_{d,\varphi=0}(L = \infty) \\ & - \gamma_{d,\varphi=0}(L = 0)]e^{-\ln 2 \times \varphi_0 [\beta A_{HE}(N_{D,B}/A)]^{-1}} \end{aligned} \quad (5.13)$$

Where $\gamma_{d,\varphi=0}(L = 0)$ and $\gamma_{d,\varphi=0}(L = \infty)$ are the $\gamma_{d,\varphi=0}$ values at zero and infinite flake length respectively, corresponding to surface energy values associated with either the edges or the basal plane defects. Equation (5.13) is used to fit both experimental and simulated data shown in figure 5.8(A) and (B) respectively. The equation shows good agreement with both experimental and simulation.

While this behaviour was seen in graphite and graphene, it was not observed in MoS₂. In figure 5.8(C) and (D) are simulated $\gamma_{d,\varphi=0}$ data with similar behaviour to the MoS₂ data shown in figure 5.7(D). The simulated data are generated with the following parameters; the means of the Gaussian curves are $\mu_{1,2,3} = 40, 40, 60 \text{ mJ/m}^2$ and the standard deviations are equal to $\sigma_{1,2,3} = 2, 2, 10 \text{ mJ/m}^2$, the relative population of the curve with a mean of $\mu = 60 \text{ mJ/m}^2$ is varied. The remaining fraction of the population was split equally between the two curves with a mean of $\mu = 40 \text{ mJ/m}^2$. In figure 5.8(C) the blue line represents an exponential fit, it is close but clearly doesn't fully capture the shape of the data; this required us to rethink the semi-empirical model used previously. The data has a sigmoidal shape as it transitions between its minimum and maximum values. So we tried a logistic function of the form

$$y = A_2 + \frac{(A_1 - A_2)}{1 + \left(\frac{x}{x_0}\right)^p} \quad (5.14)$$

In figure 5.8(D) the red line represents a fit to a logistic function and more accurately describes the shape of the data. The parameters A_1 and A_2 are the lower and upper limits of the y-variable. X_0 is the value of x for which the y-variable has a value halfway between the limits A_1 and A_2 , $y_0 = (A_2 - A_1)/2$. The final variable p controls how sharply the y values rise. The higher the value of p the more closely the logistic function resembles a step function.

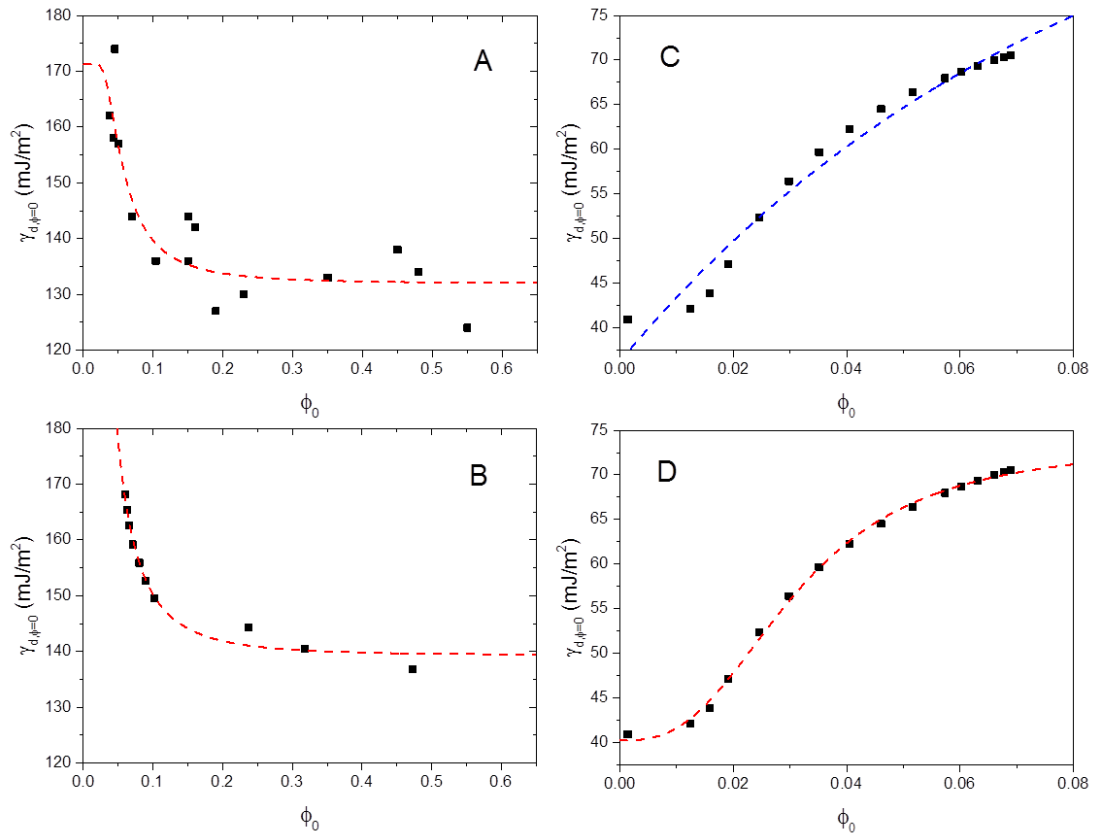


Figure 5.8. (A, B) Plot of zero coverage surface energy values for (A) experimental and (B) simulated data from graphite and graphene against decay constants. Dashed red lines represent a fit to an exponential decay. (C,D) Plot of simulated zero coverage surface energy values against decay constant, ϕ_0 . (C, red line) Shows a fit to logistic function, showing good matching. (D, blue line) Shows a fit to an exponential, showing a poorer fit.

The zero coverage surface energy data of MoS_2 are plotted against the decay constant, ϕ_0 and t/L . These are shown in figure 5.9(A) and (B), the red lines show fits to equations (5.12) and (5.13). The resulting fit parameters are nonsensical and disagree with each other. For example the fitted values for $\gamma_{d,\phi=0}$ at zero flake length were 20 mJ/m^2 and 35 mJ/m^2 for equations (5.12) and (5.13) respectively. Both these values are lower than the value of 40 mJ/m^2 for $\gamma_{d,\phi=1}$, which cannot be the case. Perhaps this is to be expected as these equations were developed to model a different system.

Given that the logistic function managed to more accurately capture the behaviour of the simulated data we developed an equation of that form. We want to find values for $\gamma_{d,\varphi=0}$ at the limits of zero and infinite flake length where the edge and the basal plane dominate respectively. Figure 5.7(A) shows $\gamma_{d,\varphi=0}$ plotted against flake length, the data has a sigmoidal shape which is possible to fit to a logistic function. $\gamma_{d,\varphi=0}$ transitions between the upper and lower limits of $\gamma_{d,\varphi=0}(L=\infty)$ and $\gamma_{d,\varphi=0}(L=0)$. So we can write equation (5.15). L_0 is the flake length at which the $\gamma_{d,\varphi=0}$ is halfway between its upper and lower limits.

It is possible to avoid the reliance on length measurements by using the decay constant, φ_0 . We already know that φ_0 and length are related. In Chapter 4 we explained that the fraction of edge and basal plane depends on length, we also demonstrated that φ_0 can be used as a proxy for the fraction of high energy sites. In figure 5.7(B) we have shown the relationship between flake length and φ_0 and figure 5.7(D) shows the same sigmoidal dependence of $\gamma_{d,\varphi=0}$ on φ_0 . Thus, applying the same logic as before; at zero and infinite values of φ_0 we can find the lower and upper limits of $\gamma_{d,\varphi=0}$, $\varphi_{0,0}$ is the value of the decay constant where $\gamma_{d,\varphi=0}$ is halfway between its two limits.

$$\gamma_{d,\varphi=0} = \gamma_{d,\varphi=0}(L=0) + \frac{(\gamma_{d,\varphi=0}(L=\infty) - \gamma_{d,\varphi=0}(L=0))}{1 + \left(\frac{L}{L_0}\right)^p} \quad (5.15)$$

$$\gamma_{d,\varphi=0} = \gamma_{d,\varphi=0}(\varphi_0=0) + \frac{(\gamma_{d,\varphi=0}(\varphi_0=\infty) - \gamma_{d,\varphi=0}(\varphi_0=0))}{1 + \left(\frac{\varphi_0}{\varphi_{0,0}}\right)^p} \quad (5.16)$$

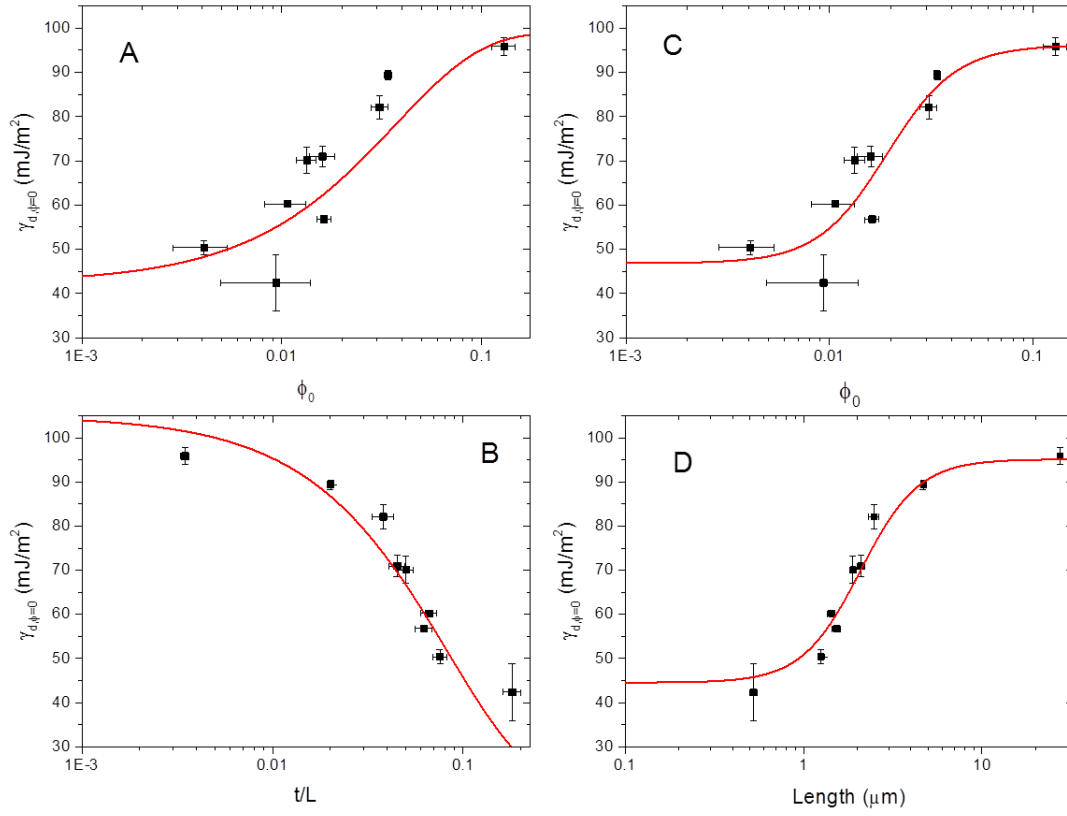


Figure 5.9. (A,B) Plot of measured (MoS_2) zero coverage surface energy values against decay constant, ϕ_0 and t/L . Red line is a fit to the equations (5.12) and (5.13). The fit parameters do not agree and do not seem reasonable. (C,D) Plot of measured (MoS_2) zero coverage surface energy values ϕ_0 and Length. The red lines are fits to equations (5.15) and (5.16). The fit parameters agree and are more sensible than the fit parameters from equations (5.12) and (5.13).

In figure 5.9(C) and (D) show the same $\gamma_{d,\varphi=0}$ data plotted against mean flake length and $1/\phi_0$. The red lines are the fits to equations (5.15) and (5.16). Fitting to these new equations we get fit parameters of $\gamma_{d,\varphi=0}(L = 0) = 44.5$ and 46.8 mJ/m^2 and $\gamma_{d,\varphi=0}(L = \infty) = 95.1$ and 96.2 mJ/m^2 . These values show much better agreement. They are also much more reasonable than the values from equations (5.12) and (5.13) since the surface energy value at zero coverage is higher than at full coverage. We also find L_0 to have a value of $1.86 \mu\text{m}$ and $\phi_{0,0}$ to have a value of 0.019 .

It should be noted that $\gamma_{d,\varphi=0}$ rises as flake length increases; this is consistent with edges having a low surface energy and defects having a higher surface energy.

5.6 Determining the distribution

In chapter 4 we explained how it is possible to use the extracted parameters from fitting to the stretched exponential function to infer the surface energy distribution. We will now make use of the methods outlined in that section to infer the surface energy distribution of MoS₂. We showed that the value of $\gamma_{d,\varphi=1}$ is identical to that of the mean of the entire γ_d distribution. We can put this fact to use by extrapolating the value of $\gamma_{d,\varphi=1}$ to the extremes of L and φ_0 . Plotting $\gamma_{d,\varphi=1}$ against length and φ_0 , shown in figure 5.10(A) and (B), we see that it is independent of flake length and the data have a mean value of 40.6 ± 4.0 mJ/m². At $L = 0$ a flake is composed entirely of edge sites. Thus we can conclude that the Gaussian curve representing edge sites is centred at 40.6 ± 4.0 mJ/m². A similar argument can be made as we move toward an infinite flake length, at $L = \infty$, the value of $\gamma_{d,\varphi=1}$ is 40.6 ± 4.0 mJ/m². At this length, the flake is composed entirely of the basal plane and defects. We can make the conclusion that the mean value of the two Gaussian curves representing the basal plane and defects is 40.6 ± 4.0 mJ/m². Recalling the three types of distributions that were found to produce profiles that matched experiment; it's clear the surface energy distribution of MoS₂ cannot be “Type C” since the behaviour of the $\gamma_{d,\varphi=0}$ data does not match. Returning to the $\gamma_{d,\varphi=1}$ plots we see that the data matches the behaviour of the “Type B” distribution, remaining flat over the measured range. From this we can conclude that all three curves are overlapped each with a centre close to the value 40.6 ± 4.0 mJ/m².

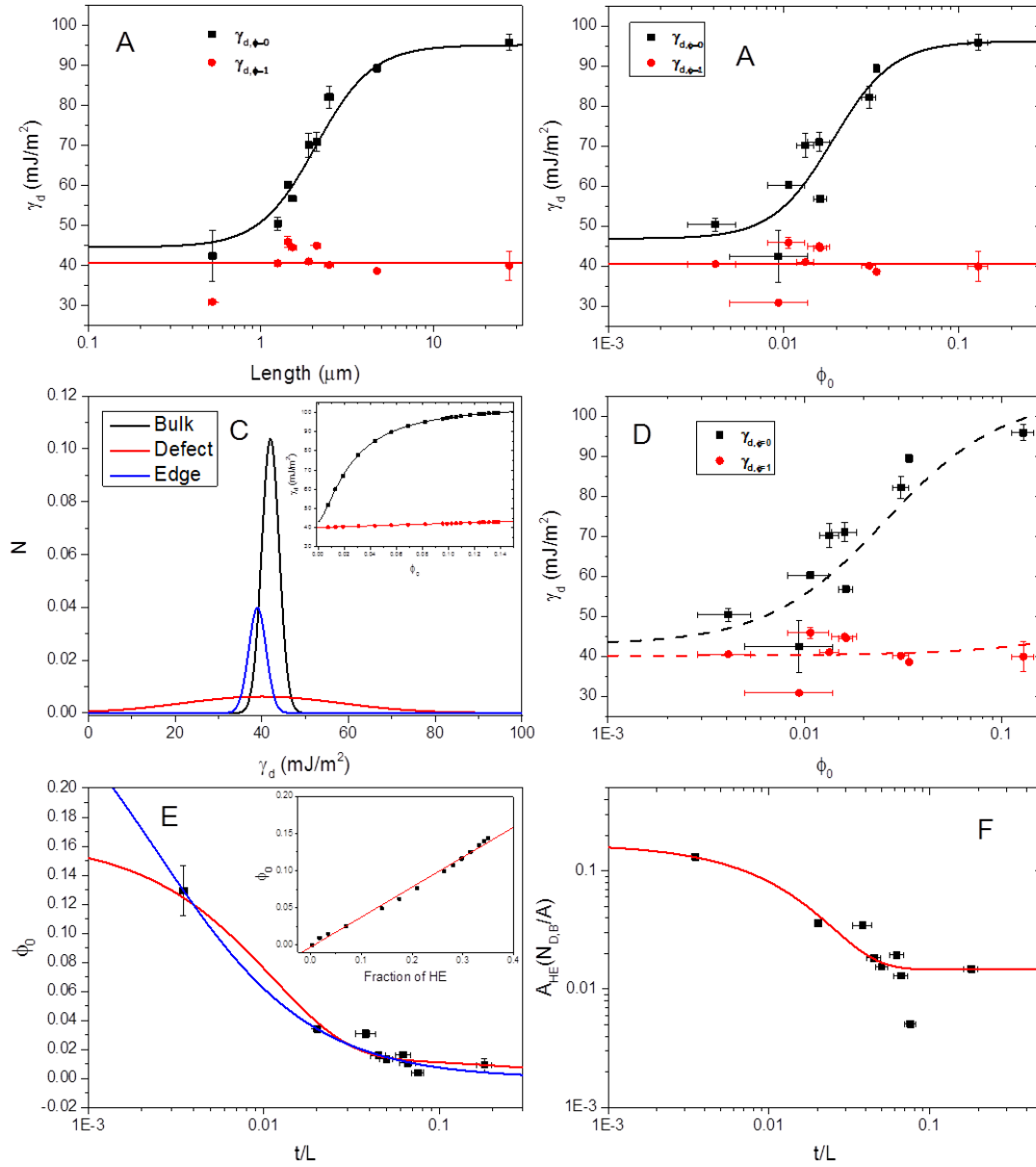


Figure 5.10. (A) Plot of zero and full surface coverage values plotted against mean flake length. The red line is a fit to equation (5.15). The black line represents the mean of the full coverage values of 40.6 mJ/m². (B) Zero and full coverage values plotted against ϕ_0 . The black line is a fit to equation (5.16), again the red line represents the mean value of 40.6 mJ/m². (C) Plot of the surface energy distribution found to have the best agreement between simulated and experimental values of $\gamma_{d,\phi=0}$ and $\gamma_{d,\phi=1}$. Inset shows the resulting $\gamma_{d,\phi=0}$ and $\gamma_{d,\phi=1}$ values from this distribution plotted against their corresponding ϕ_0 values. (D) Plot of the zero and full coverage data plotted against, ϕ_0 . Dashed lines represent the simulated values of the inferred distribution. (E) Decay

constant plotted as a function of t/L . The blue line is a fit to equation (5.20). The red line is a fit to equation (5.23). Inset shows the simulated decay constant as a function of fraction high energy (HE) sites. (F) Plot of the defect area as a function of t/L . Fit is to equation (5.21). Showing the defect area changing with flake length.

A Gaussian function is defined by two parameters; the mean and the standard deviation. Now that we have found the value for the means of the three curves we can turn to the standard deviations. In chapter 4, when analysing the behaviour of single Gaussian systems; we showed that the difference between $\gamma_{d,\varphi=0}$ and $\gamma_{d,\varphi=1}$ is dependent on the standard deviation of the Gaussian. From the fits of the two equations (5.16) and (5.17) we found an average value of 45.65 mJ/m^2 for $\gamma_{d,\varphi=0}$ in the edge dominated regime and 95.65 mJ/m^2 in the basal plane defect dominated regime. Using these values and a value of $\gamma_{d,\varphi=1} = 40.6 \text{ mJ/m}^2$ we find $\gamma_{d,\varphi=0} - \gamma_{d,\varphi=1}$ to be 5.05 and 55.05 mJ/m^2 for the edge and basal plane regimes respectively. In chapter 4 the dependence of $\gamma_{d,\varphi=0} - \gamma_{d,\varphi=1}$ on the standard deviation of a Gaussian curve was demonstrated in figure 4.1(D). Using that relationship and the values above we can find the standard deviations of the curve representing the edge ($\sim 5 \text{ mJ/m}^2$) and basal plane defects ($\sim 17 \text{ mJ/m}^2$).

The situation regarding the curves representing the basal plane and its defects is slightly more complicated as they are two curves overlapping. But as we showed in section 4.2.2 it is possible to approximate two overlapping curves as a single curve. We make the assumption that the curve corresponding to the basal plane is narrow ($\sim 2 \text{ mJ/m}^2$) and the curve corresponding to the defects is broad.

Now considering how the shapes of the profiles (figure 5.6) change as the flake length moves from infinite to zero. At infinite flake length the surface energy distribution will consist solely of the two Gaussian curves corresponding to the Basal Plane and its defects. We have shown already that two overlapping curves can generate exponential-like surface energy profiles if most of the sites are concentrated in a narrow curve and the remainder are spread out in a broad curve. The inferred distribution has exactly this property and generates profiles with the characteristic exponential shape. Moving to zero flake length, the distribution consists of a single narrow Gaussian curve. This should cause the surface energy profiles to lose the distinctive exponential shape and take on a more convex appearance; which is what we observe as the length flake approaches zero.

To summarise the previous paragraphs we arrived at a surface energy distribution described by the following parameters; $\mu_{\text{Basal}}, \mu_{\text{Defect}}, \mu_{\text{Edge}}, = 40.6 \text{ mJ/m}^2$, $\sigma_{\text{Basal}}, \sigma_{\text{Defect}}, \sigma_{\text{Edge}} = 2, 17$ and 5 mJ/m^2 respectively. This distribution is shown in figure 5.10(C), inset is the combined distribution. The relative fractions of the Gaussian curves change with flake length. Most obviously the fraction of edge sites will drop with increasing flake length. We will also show that the fraction of defects within the basal plane changes with flake length.

It seems prudent to try to verify the distribution inferred from the above method by running the values through the simulation and checking the resulting relationships between the extracted parameters to see if they match those of the measured data. Shown in figure 5.10(D) is a plot of the experimental values of $\gamma_{d,\varphi=0}$ and $\gamma_{d,\varphi=1}$ versus φ_0 . For clarity, the simulated data was fitted to a logistic function (inset of figure 5.10(C)) and the fit line then superimposed onto the experimental data. It shows that the simulated data lie directly on top of the measured data. This strongly indicates that the inferred distribution is accurate.

Given that the decay constant scales with the fraction of high energy sites and that defects are the only high energy sites present in the distribution we would expect the decay constant to fall with the inverse of the flake length. This is what is observed when φ_0 is plotted against t/L as in figure 5.10(E). It is possible to model decay constant as a function of the number of high energy sites present in a flake. If we first consider both edges and basal plane defects to be high energy sites, assume that there are $N_{D,B}/A$ defects per unit area of the basal plane and that around each defect there is an area of dislocation A_{HE} that acts as a high energy site. Using the same model as earlier in section 5.3.1, where we assume the flake to be a rhombus of area A , perimeter P and thickness t , we can write

$$\varphi_0 = \beta f_{HE} = \beta \times \frac{A_{HE}(N_{D,B}/A)2A + Pt}{2A + Pt} \quad (5.17)$$

where β is the proportionality constant relating decay constant, φ_0 , to the fraction of high energy sites, f_{HE} . Substituting equation (5.16) into equation (5.17).

$$\frac{P}{A} = 4\sqrt{1 + k^2}/L \quad (5.18)$$

Resulting in:

$$\varphi_0 = \beta \frac{A_{HE}(N_{D,B}/A) + 2\sqrt{1 + k^2}t/L}{1 + 2\sqrt{1 + k^2}t/L} \quad (5.19)$$

However, this equation will increase monotonically with t/L which is not the behaviour observed in the data. The reason this function increases with t/L is the edge term, $2\sqrt{1 + k^2}t/L$, removing it we arrive at the following

$$\varphi_0 = \beta \frac{A_{HE}(N_{D,B}/A)}{1 + 2\sqrt{1 + k^2}t/L} \quad (5.20)$$

Shown in figure 5.10(E) is the decay constant versus t/L , the blue line shows the fit to equation (5.20). This equation fits the data quite well, adding further weight to the conclusion that edges do not behave as high energy sites and lending credence to our inferred surface energy distribution. We find that when $t/L = 0$, $\beta^* A_{HE}(N_{D,B}/A) = 0.31$. Unfortunately, the value of $k \approx 200$, so something must be amiss. We know that our samples have an average value of k of 1.25. This implies that φ_0 is falling more quickly than expected with t/L . To account for this we believe that the defect fraction of the basal plane is increasing with flake length. There have been other reports of a similar relationship between flake length of MoS_2 and defect fraction [203]. This work showed that larger flakes of MoS_2 had an order of magnitude higher defect density than smaller flakes.

Using the inferred surface energy distribution we simulated the decay constants for different fractions of edge sites. These simulated values of decay constant are plotted in the inset of figure 5.10(E) against f_{HE} , from this we extract a value of $\beta = 0.4$. We know this is a reasonable value of β from earlier work in chapter 4 (see figure 4.4). Using this value for β , as well as experimental values of k and φ_0 we can calculate $A_{HE}(N_{D,B}/A)$ with the following expression:

$$A_{HE}(N_{D,B}/A) = \frac{\varphi_0}{\beta} \left(1 + 2\sqrt{1 + k^2}t/L \right) \quad (5.21)$$

These values are shown plotted in figure 5.10(F), we observe $A_{HE}(N_{D,B}/A)$ increasing with flake length. This was expected as the fit of equation (5.20) implied that the defect fraction in the basal plane increases with increasing flake length. To find the values of $A_{HE}(N_{D,B}/A)$ at $L = 0$ and ∞ we can empirically fit to an exponential function:

$$A_{HE}(N_{D,B}/A) = A_{HE}(N_{D,B}/A)_0 + Ae^{-[t/L/x_0]} \quad (5.22)$$

We find $A_{HE}(N_{D,B}/A)$ at infinite flake length and zero flake length to be 0.42 and 0.015 respectively. There is a wide diversity of possible defects in MoS_2 ; vacancies, interstitials and dopants [53], [204], [207]. They have sizes in the range of 0.5 nm across. If we assume the area of effect of the defect is roughly double this, we can approximate $A_{HE} \approx 1 \text{ nm}^2$. Now we can estimate defect density to change between $1.5 \times 10^{16} \text{ m}^{-2}$ and $4.2 \times 10^{17} \text{ m}^{-2}$. This agrees reasonably well to literature values of $6 \times 10^{15} \text{ m}^{-2}$ and $3.5 \times 10^{17} \text{ m}^{-2}$ [54], [204].

Equation (5.22) can then be substituted back into equation (5.20)

$$\varphi_0 = \beta \frac{A_{HE}(N_{D,B}/A)_0 + Ae^{[t/L/x_0]}}{1 + 2\sqrt{1 + k^2 t/L}} \quad (5.23)$$

This equation has been fitted to the decay constant data and is plotted in figure 5.10(E). β was found to have a value of 1, which shows a reasonable agreement with the simulated value of $\beta = 0.4$.

From equations (5.15) and (5.16) we can use the parameters L_0 and $\varphi_{0,0}$ to cross validate our models. They correspond to the value of the x-variable where the y-variable is at halfway between its upper and lower limits. The fitted value of $L_0 = 1.86 \text{ } \mu\text{m}$, $t = 0.095 \text{ } \mu\text{m}$, so $t/L = 0.051$. Substituting this value into equation (5.23) we calculate $\varphi_0 = 0.014$. This closely matches the value of $\varphi_{0,0} = 0.019$. This process can be repeated by using equation (5.22) to calculate the value of $A_{HE}(N_{D,B}/A)$ for $t/L_0 = 0.051$. At this point we find $A_{HE}(N_{D,B}/A) = 0.016$. The decay constant, φ_0 , has been shown to relate to $A_{HE}(N_{D,B}/A)$ via the proportionality constant β , $\varphi_{0,0} = \beta * A_{HE}(N_{D,B}/A)$. So by dividing $\varphi_{0,0} = 0.019$ by $A_{HE}(N_{D,B}/A) = 0.016$ we arrive at $\beta = 1.2$, which shows good agreement

with the values for β obtained through simulating the inferred distribution and through fitting the decay constant data, 0.4 and 1 respectively.

5.7 Conclusion

This chapter set out to show that the method detailed in Chapter 4 for inferring the surface energy distribution could be applied to real materials. We started by using centrifugation to produce samples of various mean flake lengths. This length was found by imaging each sample using SEM to individually measure flakes. We showed that the surface area of the samples had a linear dependence on $1/L$. This behaviour was explained by modelling the flakes as a rhombus and allowed us to calculate the thickness of the flakes which we found to be constant at $0.095 \mu\text{m}$. Using Finite Dilution IGC we measured the surface energy profiles of each of the nine samples. We found that the surface energy at full coverage to be roughly constant across the flake lengths measured with a value of 40.6 mJ/m^2 . This value has a close agreement with literature values obtained using contact angle [193], [200]. The surface energy at zero coverage we found to have a very different behaviour ranging from 45 mJ/m^2 at the smallest flake lengths to 95 mJ/m^2 for the largest flakes. This low value at small flake lengths implies that the edge sites have a low surface energy, which leads us to conclude they must have been passivated during the production process.

We were able to model the behaviour of $\gamma_{d,\varphi=0}$ using two logistic functions which we were able to use to find values for $\gamma_{d,\varphi=0}$ at zero and infinite flake length. Using the findings from Chapter 4 we used these values as well as the value of $\gamma_{d,\varphi=1}$ to infer the surface energy distribution of MoS_2 . The simulated and experimental values for $\gamma_{d,\varphi=0}$ and $\gamma_{d,\varphi=1}$ showed good agreement.

Then using the values of the decay constant of the surface energy profiles we showed that defect density is increasing with mean flake length. We found the lower and upper bounds on the defect density to be $1.5 \times 10^{16} \text{ m}^{-2}$ and $4.2 \times 10^{17} \text{ m}^{-2}$ at zero and infinite flake length respectively. We found corroborating evidence in the literature which used the optoelectronic properties of MoS_2 to show a change of an order of magnitude in the

defect density as flake length changed [203]. We also found close agreement between these defects densities and those in the literature [54], [204].

Having successfully applied the lessons from Chapter 4 to MoS_2 the following chapter will attempt the same with boron nitride.

Chapter 6

Boron Nitride

6.1 Introduction

As with MoS₂, the discovery of single layer graphene has led to renewed interest in Boron Nitride (BN). This work focussed on the allotrope; hexagonal boron nitride (h-BN). It has an equal number of boron and nitrogen atoms arranged in a lamellar structure similar to that of graphene. Layers of hexagonally arranged boron and nitrogen bound are strongly together within the plane by sp² hybridised orbitals. Interaction between the layers is mediated by weak Van der Waals forces. Just like MoS₂ this weak interlayer bonding makes the bulk form soft and suitable for dry lubrication, and it is commonly used in cosmetics. [208][209] Boron nitride is similar to MoS₂ in that it is a layered 2-dimensional nanomaterial but it has a structure and chemistry distinct to that of TMDs. By studying a material with a different structure and chemical composition we are demonstrating the generalisability of the method to other materials.

Values for the surface energy of boron nitride have been quoted between 35 and 78 mJ/m². [210][211] Rathod et al. measured a value of 35 mJ/m² using contact angle and reflects the average value for the surface energy. Garnier et al. simulated the surface energy of few layer boron nitride and found a value of 78 mJ/m². As explained previously in chapter 5, quoting a single value for the surface energy of a material neglects its heterogeneity. In order to determine the surface energy distribution of boron nitride this chapter will apply the method described in chapter 4. It will ascribe surface energies to each of the aspects of the material; Basal Plane, Defects in the basal plane and Edges. We found that at large flake lengths where the basal plane dominates the surface, the values at full and zero coverage both have a value of roughly 40 mJ/m². This indicates that the defects have a similar energy to the basal plane. It isn't known if

the defects have been passivated or if the defects of boron nitride do not have an elevated surface energy. At small flake lengths we see the full coverage surface energy increase to 70 mJ/m^2 , indicating that the edge sites have a higher mean surface energy than those of the basal plane. The zero coverage surface energy is much higher at 100 mJ/m^2 , implying a wide range of energies for the edge sites.

The thickness of the flakes was found to be constant at 207 nm. We were able to infer a distribution which displayed reasonable agreement between simulated and the experimental $\gamma_{d,\varphi=0}$ and $\gamma_{d,\varphi=1}$ values.

6.2 Experimental Methods

6.2.1 Materials

The majority of Boron Nitride was sourced from Henze Boron Nitride Products to ensure chemical homogeneity between samples. An additional sample from Alfa Aesar was used as well.

6.2.2 Methods

To reiterate from the previous chapter; the premise of this work depends on changing the relative populations of each aspect of the surface. Ideally without the surface energies of the material changing due to alterations in chemical composition. We characterised nine samples altogether. A single sample was from Alfa Aesar. Five were measured as purchased from Henze BNP. To increase the number of datapoints, an additional three samples were made using the boron nitride from Henze BNP. Using the largest sample (HeBo 501); two samples with a smaller flake length were created. 1 g of HeBo 501 was added to 200 ml of deionised water and shaken vigorously creating dispersion with a concentration of 5 mg/ml. It was centrifuged at 500 rpm ($\sim 28 \text{ G}$) for either 5 or 10 seconds. The supernatant of each dispersion was collected and dried in a vacuum oven at 80°C for 48 hours. A third sample with an intermediate flake length was created by mixing the together the two samples (HeBo 501 and 490) with the largest flake lengths. These three new samples are referred to as sample A, sample B, and sample C respectively.

To obtain the mean flake size, $\langle L \rangle$, of each sample a small amount of each was placed onto a sticky carbon tab and sputtered with Gold-Palladium to prevent charge build-up on the sample. Images of the samples were taken with a Zeiss Ultra Plus Field Emission SEM at 5 keV. The resulting images were imported into the software ImageJ which was used to measure the length and width of individual flakes. A minimum of 200 flakes were measured for each sample so that a statistically reliable distribution could be obtained.

The surface area and surface energy profile of each sample was measured using a Surface Energy Analyser (SEA) IGC (Surface Measurement Systems, UK). Each sample was packed into a silanised glass column with an internal diameter of 2mm and length 30 cm. In order to keep the material in place both ends of the tube were plugged with silanised glass wool. To measure the specific surface area, 15 to 20 mg of sample was packed into a glass column and preconditioned at 110 °C for 2 hours at a flow rate of 20 mL/min to remove any weakly adsorbed contaminants present on the surface. Octane was injected at increasing concentrations into the glass column at 20 °C and flow rate of 20 mL/min. Peak max was taken as the retention time. These retention times were used to produce an adsorption isotherm, from which using the BET equation the SMS Cirrus software is able to calculate the specific surface area (see chapter 3). To measure the surface energy profile of a sample a mass corresponding to an area of 0.5 m² was packed into a glass column. The sample is preconditioned in the same manner as the specific surface area measurements. The alkanes; Hexane, Heptane, Octane, Nonane and Decane were used as probe molecules. Coverages ranged from 0.004 to 0.4. Chromatograms were measured using a flame ionisation detector (FID). The peak centre of mass (COM) was used as the retention time. Measurements were made at a temperature of 25 °C. The included SMS Cirrus software was used to carry out all calculations. Errors were calculated using the method of REF and automated using a python script. Briefly, the error depends on the quality of the linear fit of the alkane line. To ensure the accuracy of our measurements we aimed to use only measurements where the R² value of the alkane line fit was greater than 0.999, unfortunately for some measurements we were unable to achieve this standard.

6.3 Results and Discussion

6.3.1 Basic Characterisation

We carried out SEM on each sample and measured the mean flake length, $\langle L \rangle$. This was done using the method outlined above in chapter 3. Figure 6.1 shows representative images of flakes from each sample. The flakes are quite circular in shape, this made it challenging to determine the longest axis which we defined earlier as the flake length. The aspect ratio $k = L/W$ was very close to 1 at $k = 1.08$. Histograms of the flake length measurements of each sample are shown in figure 6.2. We found the mean lengths of the flakes to vary between 0.82 and 38 μm .

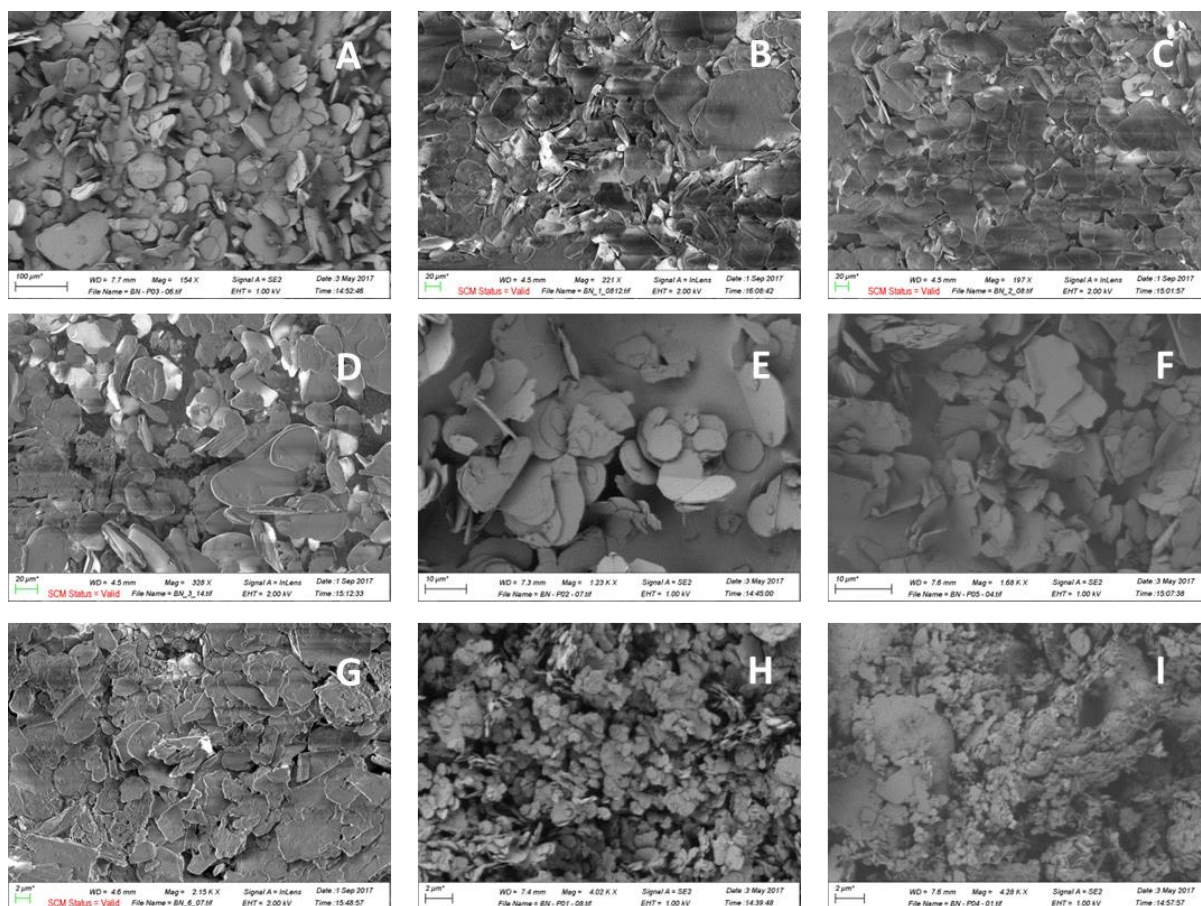


Figure 6.1. Representative SEM images of the molybdenum disulphide samples. A) HeBo 501, B) sample A, C) sample B, D) sample C, E) HeBo 490, F) HeBo 641, G) Alfa Aesar, H) HeBo 110, I) HeBo 511.

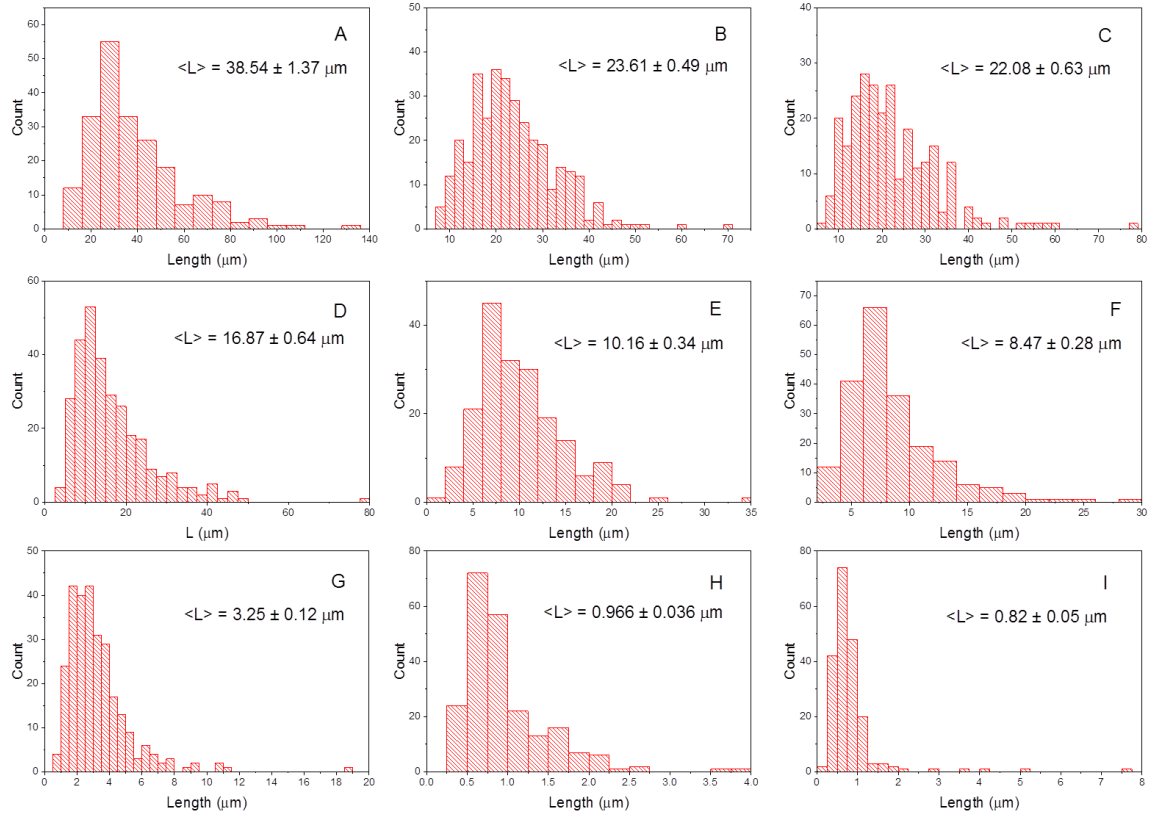


Figure 6.2. SEM histograms of the molybdenum disulphide samples. A) HeBo 501, B) sample A, C) sample B, D) sample C, E) HeBo 490, F) HeBo 641, G) Alfa Aesar, H) HeBo 110, I) HeBo 511.

The measured specific surface area values fall between 2 and 15 m²/g. These are plotted in figure 6.3 against 1/L. As before, the specific surface area, S_{BET} , of a flake can be described in terms of the flake area, A , perimeter length, P , and thickness, t , with the following expression:

$$S_{BET} = \frac{2A + Pt}{\rho At} = \frac{2}{\rho t} + \frac{4\sqrt{1 + k^2}}{\rho L} \quad (6.1)$$

where ρ is the density of the platelet and k is the ratio between flake length and flake width.

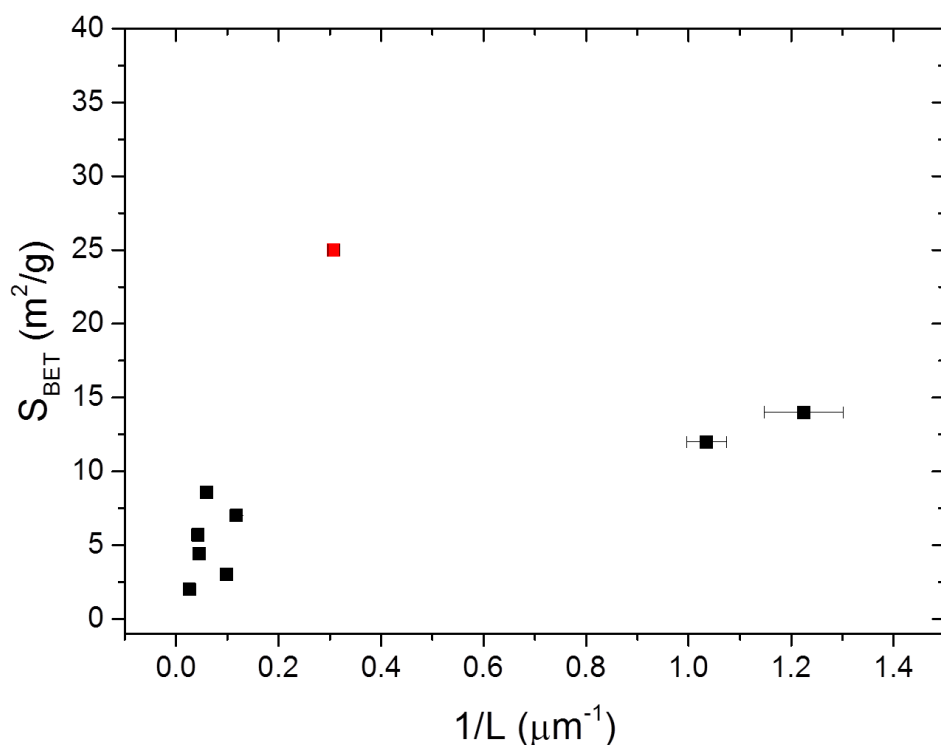


Figure 6.3. *Plot of the measured surface area plotted against the reciprocal of the flake length.*

The trend is not well defined as in MoS_2 . The lack of a strong linear trend suggests that the flake thickness is not constant. This outlier marked in red belongs to the sample Alfa Aesar, all other samples are from the same supplier. The large difference may be due to a higher porosity or rougher flakes, either of which would increase the surface area of a sample.

Using equation (6.1) and the measured values of k and L it is possible to calculate values for the flake thickness t . These values are plotted against flake length in figure 6.4. There is a clear dependence of the thickness on flake length. Examining the images from figure 6.1 the values seem to be reasonable estimates for the flake thickness.

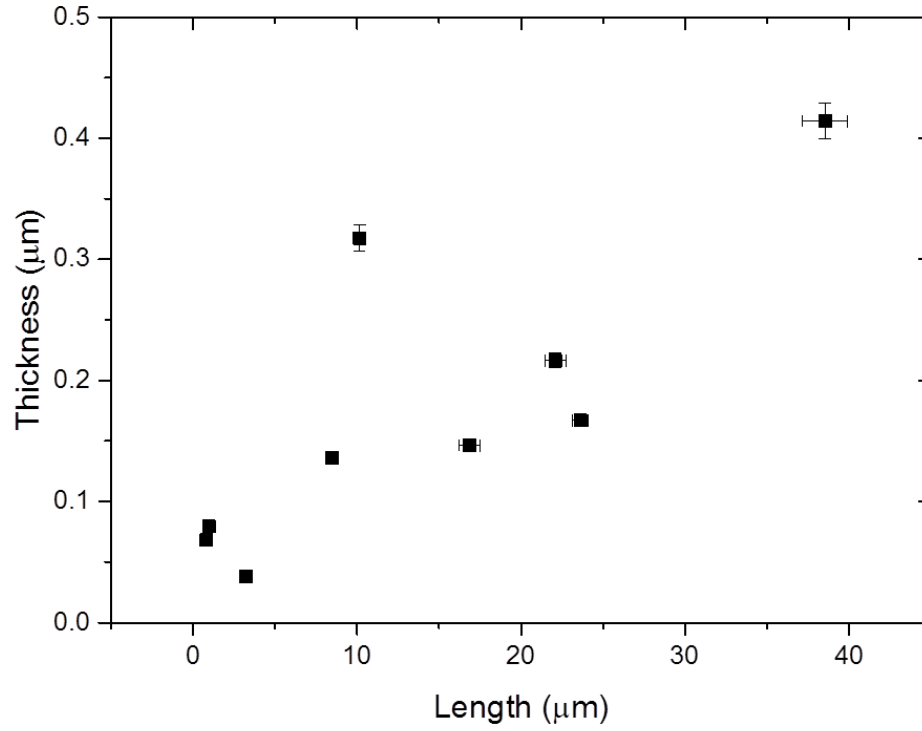


Figure 6.4. Plot of flake thickness against flake length. Displaying a clear positive trend between the two.

6.4 IGC Measurements

To measure the surface energy profiles of each sample we used coverage dependent IGC. These profiles are built up by measuring the surface energy at a series of specified coverages. The measured profiles have the same exponential-like shape seen in other materials. They are shown in figure 6.5, with a fit (red line) to the stretched exponential function in equation (6.2).

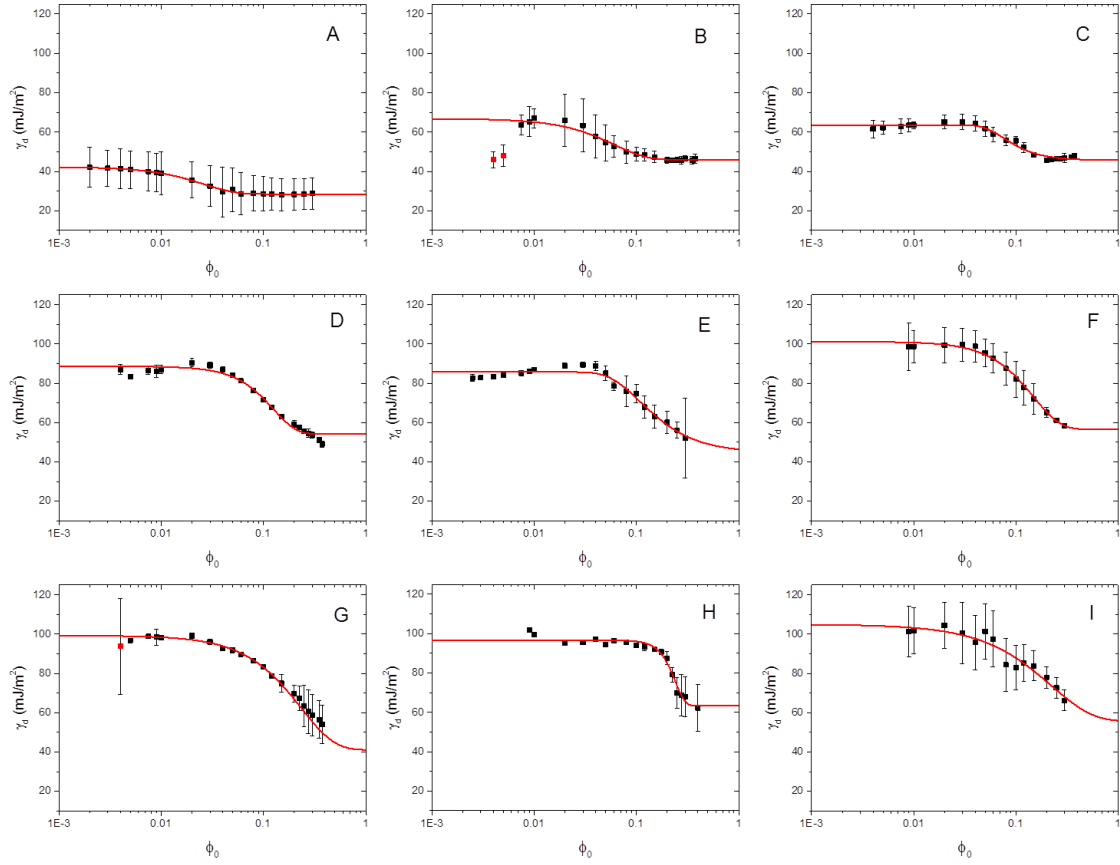


Figure 6.5. Measured surface energy profiles of each sample of boron nitride. A) HeBo 501, B) sample A, C) sample B, D) sample C, E) HeBo 490, F) HeBo 641, G) Alfa Aesar, H) HeBo 110, I) HeBo 511. Each profile has been fitted to a stretched exponential function shown in equation (6.2).

$$\gamma_d(\varphi) = \gamma_{d,\varphi=1} + (\gamma_{d,\varphi=0} - \gamma_{d,\varphi=1})e^{-\left(\frac{\varphi}{\varphi_0}\right)^j} \quad (6.2)$$

The fit parameters are listed in Table 6.1 below. Most of the profiles are well-behaved and have fits with small errors.

Table 6.1. *Fitting parameters of the surface energy profiles of the Boron Nitride samples.*

Sample	$\gamma_{d,\varphi=0} \text{ (mJ/m}^2\text{)}$	$\gamma_{d,\varphi=1} \text{ (mJ/m}^2\text{)}$	Φ_0	j	$\langle L \rangle \text{ (}\mu\text{m)}$
HeBo 501	42.25 ± 0.35	28.52 ± 0.13	0.0263 ± 0.00112	1.404	38.54 ± 1.37
Sample A	66.79 ± 1.46	45.89 ± 0.15	0.0607 ± 0.0068	1.36	23.61 ± 0.49
Sample B	63.49 ± 0.51	45.66 ± 1.04	0.0761 ± 0.0052	2.178	22.08 ± 0.63
Sample C	88.61 ± 1.34	54.07 ± 1.05	0.125 ± 0.006	1.939	16.87 ± 0.64
HeBo 490	85.74 ± 0.81	44.63 ± 8.59	0.1087 ± 0.0199	1.418	10.16 ± 0.34
HeBo 641	101.19 ± 1.03	56.57 ± 0.58	0.1499 ± 0.004	1.664	8.47 ± 0.28
Alfa Aesar	99.28 ± 1.03	41.01 ± 21.3	0.32 ± 0.006	1.32	3.25 ± 0.12
HeBo 110	96.64 ± 0.82	63.24 ± 2.22	0.24 ± 0.0092	4.52	0.966 ± 0.036
HeBo 511	104.95 ± 4.75	55.61 ± 39.08	0.25 ± 0.018	1.069	0.82 ± 0.05

It was shown in chapter 4 and 5 that the decay constant, φ_0 , is linearly proportional to the fraction of high energy sites. Since $\gamma_{d,\varphi=1}$ is proportional to the weighted mean of the surface energy distribution $\gamma_{d,\varphi=1}$ should then increase linearly with the fraction of high energy sites.

$\gamma_{d,\varphi=0}$ and $\gamma_{d,\varphi=1}$ are shown plotted figure 6.6(A) against flake length. The values of the surface energy at full coverage display a dependence on the flake length indicating that the mean of the Gaussian curve representing the edges and the basal plane are different. This is in contrast to the MoS₂ data. As in the previous on MoS₂ and as demonstrated in Chapter 4 the values of $\gamma_{d,\varphi=0}$ rise sharply before reaching a plateau. On this occasion the maximum value of $\gamma_{d,\varphi=0}$ is reached at small flake lengths. Indicating the edge sites of BN are heterogeneous, compare this to MoS₂ where the edge sites were shown to all

have a similar surface energy. The plot in figure 6.8(B) of the decay constant versus flake length demonstrates that the ability of ϕ_0 to stand in as a proxy for defect fraction still holds for boron nitride.

We have plotted $\gamma_{d,\phi=0}$ versus $\gamma_{d,\phi=1}$, shown in figure 6.6(C), there is a clear correlation between the two values. Plotting $\gamma_{d,\phi=0}$ and $\gamma_{d,\phi=1}$ against ϕ_0 (figure 6.6(D)) we can see that $\gamma_{d,\phi=1}$ has the expected linear dependence on ϕ_0 . The plot of the surface energy at zero coverage, $\gamma_{d,\phi=0}$, versus the decay constant displays the same logistic behaviour seen in simulations and in MoS₂.

The behaviour of both $\gamma_{d,\phi=0}$ and $\gamma_{d,\phi=1}$ was examined in chapter 4 when describing the three possible types of surface energy distributions. The distribution referred to as “Type A”, in which there is a narrow curve at low energy and a broad curve at a higher energy produced $\gamma_{d,\phi=0}$ and $\gamma_{d,\phi=1}$ data with the behaviour seen here. Later, when we infer the surface energy distribution we will see if this prediction is borne out.

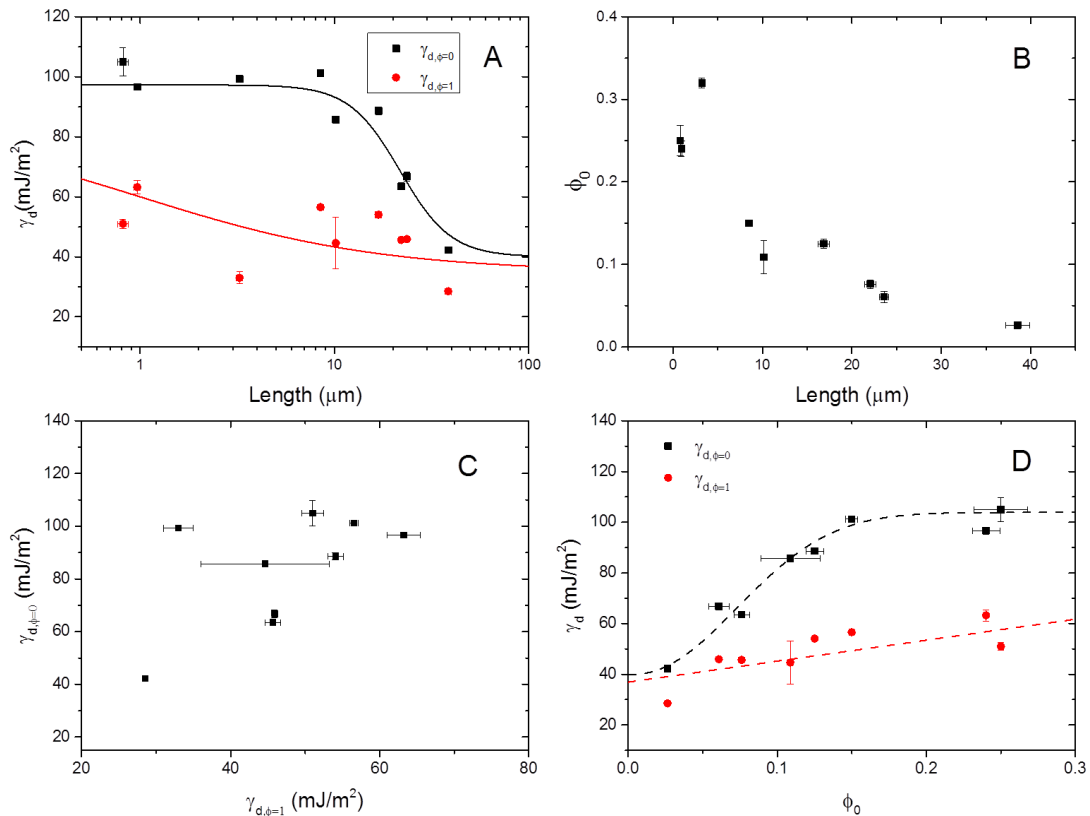


Figure 6.6. (A) The surface energies at zero and full coverage plotted against flake length. (B) The decay constant, ϕ_0 , plotted against flake length. (C) $\gamma_{d,\phi=0}$ plotted against $\gamma_{d,\phi=1}$. This shows some positive correlation between the two parameters. (D)

The zero and full coverage surface energies plotted against the decay constant, φ_0 . The zero coverage, $\gamma_{d,\varphi=0}$, fits to a logistic function while the full coverage, $\gamma_{d,\varphi=1}$, values increase linearly with decay constant.

The decay constant is related to the fraction of high energy sites through a constant, β .

$$\varphi_0 = \beta \times f_{HE} \quad (6.3)$$

where the subscript ‘‘HE’’ refers to high energy. Using the model developed in chapter 5 and equation (6.4) it is possible to describe the relationship between the decay constant and flake length.

$$\varphi_0 = \frac{\beta(A_{HE}(N_{D,B}/A) + 2\sqrt{1+k^2}t/L)}{(1 + 2\sqrt{1+k^2}t/L)} \quad (6.4)$$

where $A_{HE}(N_{D,B}/A)$ is the defect density. This equation assumes that both defects in the basal plane and edges are high energy sites. The assumption of high energy defects does not conform to the conclusion drawn from the $\gamma_{d,\varphi=0}$ and $\gamma_{d,\varphi=1}$ data. Removing the $A_{HE}(N_{D,B}/A)$ term from the top line modifies the equation to take this into account. Resulting in equation (6.5)

$$\varphi_0 = \frac{\beta(2\sqrt{1+k^2}t/L)}{(1 + 2\sqrt{1+k^2}t/L)} \quad (6.5)$$

Plotted in figure 6.7 is the decay constant against t/L . The decay constant rises as the value of t/L increases demonstrating that the edges are high energy sites. That the decay constant falls so close to zero in the region of the plot dominated by the basal plane implies that the defects in the basal plane do not have an elevated surface energy associated with them, in other words that the Gaussian curve associated with the defects has a narrow standard deviation, σ_{def} .

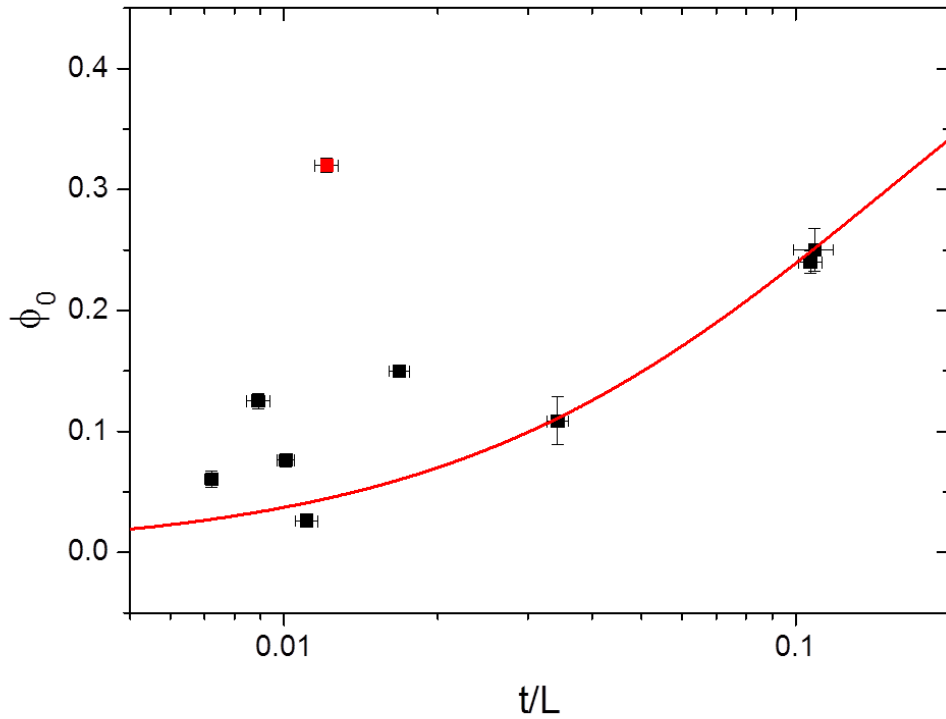


Figure 6.7. Plot of the decay constant, ϕ_0 , versus t/L . The data has been fitted to equation (6.5). It displays an increasing decay constant and hence fraction of high energy sites as the edges dominate at large values of t/L .

While the data in figure 6.7 have a lot of scatter associated with them they are still consistent with the model and imply that the edges are the high energy sites. This is because the decay constant rises with larger values of t/L where the edges dominate.

From fitting the data to equation (6.5) a value of 0.5 for β can be calculated. This seems like a reasonable value according to the simulations carried out in chapter 4. It will be compared to the value gotten from fitting the $\gamma_{d,\phi=0}$ data in the following section.

It is also possible to calculate a value for the aspect ratio, k , of 3. This value is very similar to the value from fitting surface area to equation (6.1) of 3.8. Unfortunately it is larger than the experimental value of 1. A possible explanation for this higher value of k could be caused by the standard deviation of the Gaussian curve representing the edges narrowing. This would cause the decay constant to increase more sharply with t/L . This

narrowing of the edge curve will be mentioned again when comparing the simulated and the experimental $\gamma_{d,\varphi=0}$ values.

6.5 Fitting Characteristic Parameters

In the previous chapter we demonstrated how the $\gamma_{d,\varphi=0}$ data could be modelled with logistic functions when plotted against decay constant and mean flake length. These equations are shown again as equations (6.6) and (6.7). Equation (6.7) has a slight modification; the term referring to the defect density has been changed to the fraction of edge sites. This is to reflect the fact that it is the edge sites not the defects which have a high surface energy.

$$\gamma_{d,\varphi=0} = \gamma_{d,\varphi=0}(L = 0) + \frac{(\gamma_{d,\varphi=0}(L = \infty) - \gamma_{d,\varphi=0}(L = 0))}{1 + \left(\frac{L}{L_0}\right)^p} \quad (6.6)$$

$$\begin{aligned} \gamma_{d,\varphi=0} = \gamma_{d,\varphi=0}(\varphi_0 = 0) \\ + \frac{(\gamma_{d,\varphi=0}(\varphi_0 = \infty) - \gamma_{d,\varphi=0}(\varphi_0 = 0))}{1 + \left(\frac{\varphi_0}{\beta f_{edge}}\right)^p} \end{aligned} \quad (6.7)$$

Fitting the data in figures 6.8(A) and (B) to equations (6.6) and (6.7) respectively gives two values for $\gamma_{d,\varphi=0}$ in the edge dominated domain (97 and 100 mJ/m²) and in the domain dominated by the basal plane (40 and 42 mJ/m²). Then taking the average of each pair of values results in a value of $\gamma_{d,\varphi=0} @ (L = 0) = 98.5$ mJ/m² and $\gamma_{d,\varphi=0} @ (L = \infty) = 41$ mJ/m².

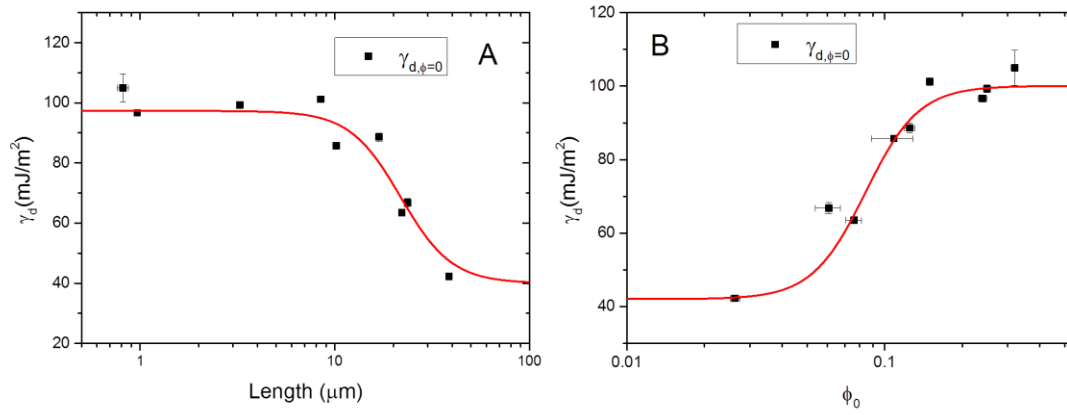


Figure 6.8. Plots showing the behaviour of $\gamma_{d,\phi=0}$. (A) $\gamma_{d,\phi=0}$ plotted against mean flake length. The $\gamma_{d,\phi=0}$ drops as flake length increases; indicating that the edges have a high surface energy and the defects have a low surface energy. (B) $\gamma_{d,\phi=0}$ plotted against the reciprocal of the decay constant. The decay constant is a measure of the fraction of high energy sites; so the $\gamma_{d,\phi=0}$ value increases with increasing ϕ_0 . These plots are fitted to equations (6.6) and (6.7); their fit parameters are then used to infer the surface energy distribution of boron nitride.

The midpoint of the equation (6.7) (βf_{edge}) is used to calculate β . The midpoint of the fitted function in figure 6.8(B) has a value of $\beta f_{edge} = 0.084$. If we then approximate this midpoint as the point at which there is an equal fraction of high and low energy sites, i.e. $f_{edge} = 0.5$ we can find β . In reality high energy sites have an outsized effect on the $\gamma_{d,\phi=0}$ compared to low energy sites; if we were to weight their effects on $\gamma_{d,\phi=0}$ appropriately we would expect f_{edge} to have a smaller value at the midpoint and for β to be larger. This being said if we use the value of $f_{edge} = 0.5$ we find β to equal 0.16, which is quite close to the value (0.5) found from fitting the decay constant data in figure 6.7 to equation (6.5).

The $\gamma_{d,\phi=1}$ data for MoS₂ was independent of flake length and decay constant. This meant it was possible to take the average value of the $\gamma_{d,\phi=1}$ data as the mean of all three curves representing Edge, Defect and Basal Plane sites. Since the boron nitride $\gamma_{d,\phi=1}$ data exhibits a dependence on flake length and decay constant, it is necessary to model this behaviour in order to find the $\gamma_{d,\phi=1}$ values for the edge and basal plane dominated regimes.

Recalling $\varphi_0 = \beta f_{HE}$ and using equation (6.5) results in

$$f_{Edge} = \frac{(2\sqrt{1+k^2}t/L)}{(1+2\sqrt{1+k^2}t/L)} \quad (6.8)$$

where the top line represents the edge sites and the bottom represents the total number of sites. Using the fact that $\gamma_{d,\varphi=l}$ is the weighted average of the means, μ , of the high and low energy curves we can write

$$\gamma_{d,\varphi=1} = (f_{edge} \times \mu_{edge}) + (f_{basal} \times \mu_{basal}) \quad (6.9)$$

where the subscripts edge and basal refer to the edge sites and the basal plane (including defects). Rearranging we get

$$\gamma_{d,\varphi=1} = \mu_{basal} + (\mu_{edge} - \mu_{basal}) \times (f_{edge}) \quad (6.10)$$

Combining this with equations (6.3) and equation (6.8) results in:

$$\gamma_{d,\varphi=1} = \mu_{basal} + (\mu_{edge} - \mu_{basal}) \times \left(\frac{(2\sqrt{1+k^2}t/L)}{(1+2\sqrt{1+k^2}t/L)} \right) \quad (6.11)$$

$$\gamma_{d,\varphi=1} = \mu_{basal} + (\mu_{edge} - \mu_{basal}) \times \left(\frac{\varphi_0}{\beta} \right) \quad (6.12)$$

The values of $\gamma_{d,\varphi=l}$ in the basal and edge dominated regimes can be found from the intercepts and slopes of equations (6.11) and (6.12). In the case of equation (6.11), a value for β needs to be used. The value, 0.5, obtained from fitting the decay constant data to equation (6.7) was used. Shown in figure 6.9 are the plots of $\gamma_{d,\varphi=l}$ against the fraction of edge sites calculated using the values of flake length (A) and the decay

constant (B). The plots shown in figure 6.9(A) and (B) are fitted to equation (6.11) and (6.12) respectively.

They return values of $\gamma_{d,\varphi=1} = 74 \text{ mJ/m}^2$ and 82 mJ/m^2 for the edge dominated regime and values of $\gamma_{d,\varphi=1} = 48 \text{ mJ/m}^2$ and 42 mJ/m^2 for the regime dominated by the basal plane and its defects; resulting in averages of 78 mJ/m^2 and 45 mJ/m^2 for the mean values of the edge and basal plane curves respectively. Since the data suggests that the sites of the basal plane and the defects have such similar surface energies we will approximate them as a single Gaussian curve.

Using the above values for $\gamma_{d,\varphi=1}$ as well as the values for $\gamma_{d,\varphi=0}$ of 99 mJ/m^2 and 41 mJ/m^2 we calculate $\gamma_{d,\varphi=0} - \gamma_{d,\varphi=1} \approx 20 \text{ mJ/m}^2$ and 1 mJ/m^2 for the edge and basal plane regimes respectively.

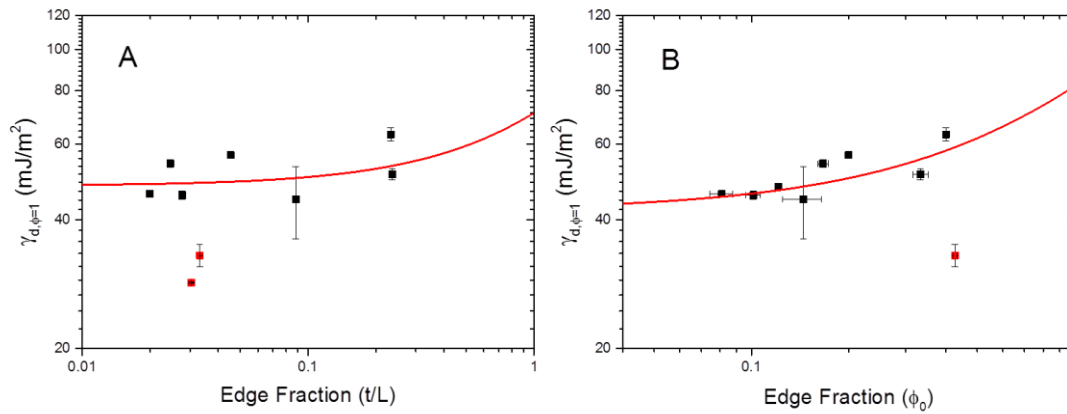


Figure 6.9. $\gamma_{d,\varphi=1}$ plotted against the edge fraction calculated from the flake length and the decay constant, ϕ_0 , to show how the $\gamma_{d,\varphi=1}$ is changing indicating that the edge sites sit at a higher mean surface energy than the basal plane sites. By fitting plots (A) and (B) to equations (6.11) and (6.12) we can calculate values of the mean of the curves representing edge and basal plane sites.

6.6 Determining the distribution

The surface energy distribution of boron nitride can be inferred using the method outlined in chapter 4 and the values found in this chapter for the parameters; $\gamma_{d,\varphi=0}$, $\gamma_{d,\varphi=1}$ and ϕ_0 .

Using the $\gamma_{d,\varphi=1}$ data shown in figure 6.9(A) and (B) it is possible to infer the means, μ , of the Gaussian curves representing the edge and basal plane. As the defects of the basal plane do not act as high energy sites and appear indistinguishable from the rest of the basal plane we have considered them together as a single Gaussian curve.

Fitting the $\gamma_{d,\varphi=1}$ versus edge fraction data to equations (6.11) and (6.12) the mean of the curve representing the basal plane and its defects, μ_{basal} , has been determined to lie at 45 mJ/m² and the mean value of the curve representing the edges, μ_{edge} , lies at 78 mJ/m². Fitting the $\gamma_{d,\varphi=0}$ data to equations (6.6) and (6.7) gives values for $\gamma_{d,\varphi=0}$ in the edge and basal plane dominated regimes of 99 and 41 mJ/m². Using these values we can calculate $\gamma_{d,\varphi=0} - \gamma_{d,\varphi=1}$ for the edge and basal plane dominated regimes to be approximately 20 and 1 mJ/m² respectively.

We have shown in chapter 4 that it is possible to relate the value of $\gamma_{d,\varphi=0} - \gamma_{d,\varphi=1}$ to the standard deviation of a Gaussian curve (see figure 4.1(D)). As before, when analysing the MoS₂ data we can use this relation to find values for the standard deviation of the Gaussian curve representing the edge sites (σ_{edge}) and the Gaussian curve representing the basal plane (σ_{basal}). We find values of $\sigma_{edge} = 20$ mJ/m² and $\sigma_{basal} = 1$ mJ/m². Using this inferred distribution and varying the relative fraction of the edge sites; the surface energy profiles are simulated and the resulting values of $\gamma_{d,\varphi=0}$ and $\gamma_{d,\varphi=1}$ were plotted against the decay constants. The behaviour of this plot was compared with the plot of the experimental values. By decreasing the mean value of the basal plane sites, μ_{basal} to 40 mJ/m² we were able to slightly improve the match between the experimental and simulated plots of $\gamma_{d,\varphi=0}$.

Even so, we were unable to generate $\gamma_{d,\varphi=0}$ data that rose as quickly with φ_0 as the experimental data. This comparison is shown in figure 6.10(A). The parameters providing the closest match to the experimental data were μ_{basal} , $\mu_{edge} = 40, 70$ mJ/m² and σ_{basal} , $\sigma_{edge} = 1, 20$ mJ/m². This inferred distribution is shown in figure 6.10(B). It was stated earlier in section 6.4 that from the behaviour of $\gamma_{d,\varphi=0}$ and $\gamma_{d,\varphi=1}$, a type A distribution was expected and this has proven to be the case.

The difficulty in fitting the experimental data may indicate that there is something other than a change in relative populations at play as the flake length changes. It may be possible to replicate the $\gamma_{d,\varphi=0}$ behaviour with simulations if we were to allow the standard deviation of the edge curve to become narrower as the fraction of edges is

increased. This conclusion links back to the unusually large value for the aspect ratio, k , of 3. A possible cause for this may be a change in the ratio of armchair to zigzag edges which have different surface energies associated to them. [212]

Plotted in figure 6.10(C) are the simulated values of decay constant versus the fraction of edge sites. The data can be fit to a line, the slope of which is β which equals 0.8. This value is in close agreement with the other values for β of 0.5 and 0.16 from fitting equations (6.5) and (6.7). The agreement of these three values for β demonstrates the consistency between the models, lending them credibility. It also suggests the inferred distribution is similar to the actual surface energy distribution of boron nitride.

Earlier, the midpoint value of equation (6.7), $\phi_{0,0}$ was found to equal 0.084. Taking the midpoint from equation (6.6), L_0 is found to equal 22 μm , and the value $t = 0.207 \mu\text{m}$ from equation (6.1), then $t/L_0 = 0.009$. Substituting this value into equation (6.5) produces a decay constant with a value of 0.05. These two values for ϕ_0 are in close agreement again demonstrating the robustness of the models used to fit the two datasets.

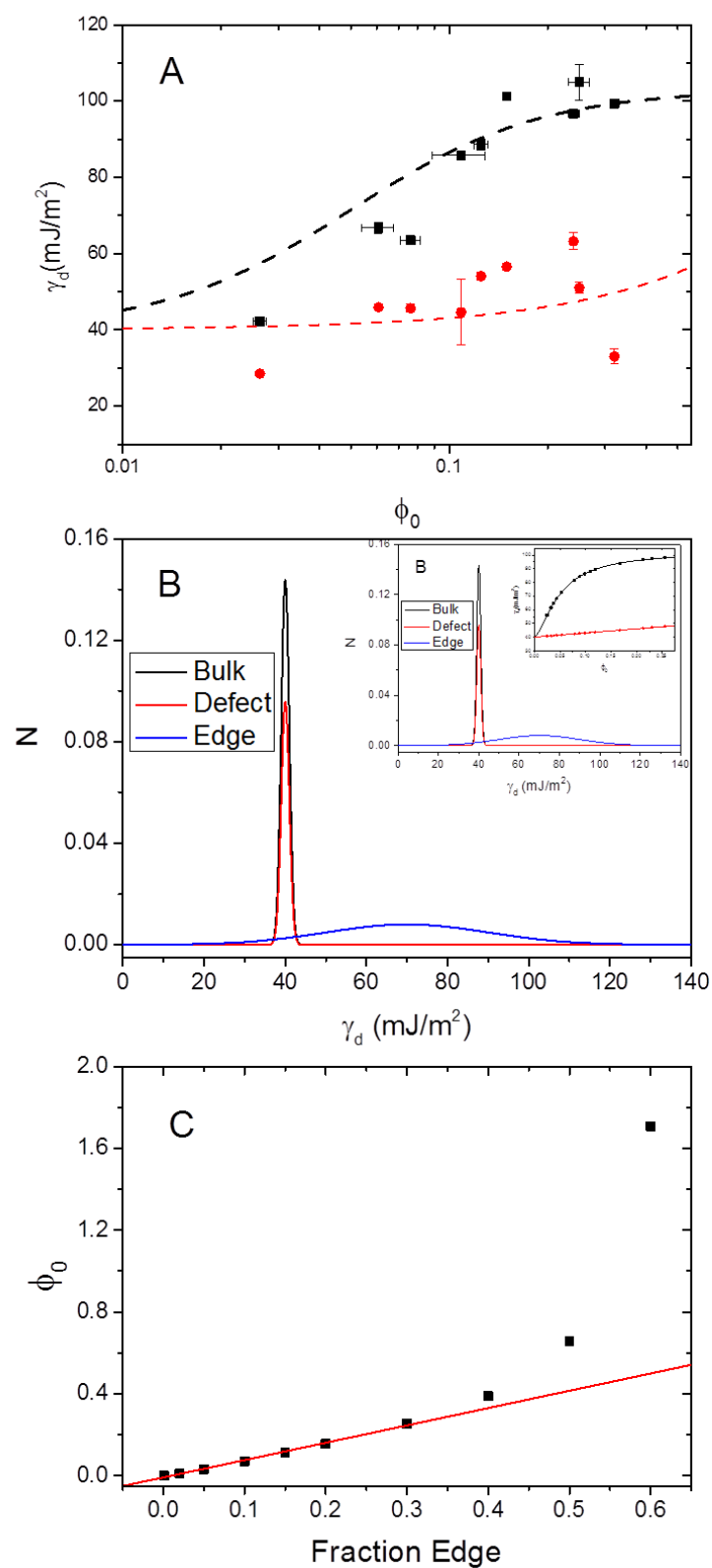


Figure 6.10. (A) Zero and full coverage surface energy values plotted against $1/\phi_0$. The dashed lines are fits to the simulated data and are there to allow a clear comparison between experimental and simulated data. (B) The inferred distribution of boron

nitride, the basal plane and its defects are centred 40 mJ/m² and have a narrow curve ($\sigma = 1 \text{ mJ/m}^2$) while the edge sites are represented by a broad curve ($\sigma = 20 \text{ mJ/m}^2$) with a mean of 70 mJ/m². (C) Plot of the simulated decay constant values against the fraction of edge sites. The slope corresponds to β and has a value of 0.8.

6.7 Conclusion

The intention of this chapter was to extend the methodology demonstrated in chapters 4 and 5 to another material with a different structure and chemistry. Nine samples of boron nitride were used in this study. The surface area of the samples was found to have a linear dependence on mean flake length; implying a constant value of 207 nm for flake thickness. The surface energy profiles of each sample was measured using finite dilution inverse gas chromatography. The surface energy at full coverage was found to rise with decreasing flake length, indicating that edges have a higher surface energy than the basal plane. Using simple models to fit the data the edge sites were found to have a mean surface energy of 69 mJ/m² and the basal plane to have a mean surface energy of 40 mJ/m². This value has a close agreement with literature values obtained using contact angle. [210], [211]

The behaviour of the surface energy at zero coverage was modelled with two logistic functions. From the fits of these equations values of 41 mJ/m² and 99 mJ/m² were found for the basal plane and edge regimes respectively. The value of 41 mJ/m² implies that the defects in the basal plane have been passivated in some manner and do not have an elevated surface energy associated with them.

Despite using a slightly modified version of the inferred distribution to fit the experimental values of the surface energy at zero and full coverages an exact match was not found. This may be due to the standard deviation of the edge curve narrowing as flake length falls. The very high value of the aspect ratio, k , found from the fitting the decay constant data may also be explained by this narrowing.

By applying the method from chapter 4 to a second material it has been demonstrated to be a generalizable and robust method for inferring the surface energy distribution of a material. This should be of great utility to applications for which knowledge of the surface energy is important.

Chapter 7

Conclusions and Future Work

7.1 Conclusions

The surface energy of a material plays an important role in the interactions a material has with its environment and therefore an accurate description of the surface energy is essential for certain applications such as creating composites. In the literature it is quoted as a single value, neglecting the inherent heterogeneity of a material's surface and hence its surface energy. It would be more accurately described as a distribution of surface energies, with contributions from the different aspects of the material surface.

Several methods for measuring surface energy were discussed, but only Finite Dilution Inverse gas chromatography (FD-IGC) has the ability to provide information about the entire surface. FD-IGC measures the surface energy at a range of surface coverages; the data are then plotted as a surface energy profile. The shape of this profile is directly influenced by the surface energy distribution.

This motivation of this thesis was to gain a more fundamental understanding of the relationship between the profiles and the distributions. Then, using this knowledge to construct and demonstrate a method for inferring the surface energy distribution of a material.

Distributions were approximated with Gaussian curves. Distributions comprised of one, two or three curves were studied. These curves can each be described with three parameters; their mean value, standard deviation and their relative fractions. The effect of changing these parameters on the profiles was systematically studied. The first task was to find distributions that would give rise to profiles that had a similar shape to the experimentally measured profiles. We found that only distributions with a shape that can be roughly approximated to a lognormal produced the desired profile shape.

For profiles that had the exponential-like shape we found that it was possible to accurately fit them to a stretched exponential function. The fit parameters ($\gamma_{d,\varphi=0}$, $\gamma_{d,\varphi=1}$ and φ_0) were used to describe the shape of the profiles. By plotting these fit parameters against the parameters describing the distribution some useful relationships were found.

It was shown that the surface energy at full coverage is equal to the average surface energy value of the whole distribution, the decay constant is proportional to the fraction of high energy sites and that the difference between $\gamma_{d,\varphi=0}$ and $\gamma_{d,\varphi=1}$ depends on the standard deviation of the Gaussian curve. It was demonstrated that it is possible to infer the surface energy distribution from plots of $\gamma_{d,\varphi=0}$ and $\gamma_{d,\varphi=1}$ versus the fraction of high energy sites.

The decay constant and mean flake length were used as proxies for the fraction of high energy sites so that the method could be applied to the real world materials molybdenum disulphide and boron nitride. We were able successfully determine the surface energy distribution of the two materials and ascribe surface energy values to the different aspects of the surface; basal plane, defects in the basal plane and the edges. These materials have distinct structures and chemistries, illustrating the generalisability of this method.

When analysing molybdenum disulphide we found that the $\gamma_{d,\varphi=1}$ had a constant value across flake lengths indicating that all the curves had the same mean value of ~ 40 mJ/m². The $\gamma_{d,\varphi=0}$ values however, showed a maximum at large flake lengths implying that the defects have a broad surface energy curve associated with them. While at small flake lengths the $\gamma_{d,\varphi=0}$ fell close to the value of $\gamma_{d,\varphi=1}$ implying a narrow surface energy curve associated with the edges. We surmise that the edges are passivated in some manner, possibly as a result of the size selection procedure but we are unsure as to why the defects remain unaffected. Fitting the $\gamma_{d,\varphi=0}$ data to logistic models we were able to find values for $\gamma_{d,\varphi=0}$ at infinite and zero flake lengths. Using these values we were able to infer the following parameters μ_{Basal} , μ_{Defect} , μ_{Edge} , = 40.6 mJ/m², σ_{Basal} , σ_{Defect} , σ_{Edge} = 2, 17 and 5 mJ/m² for the surface energy distribution of molybdenum disulphide. We were also able to demonstrate that the simulated values of $\gamma_{d,\varphi=0}$, $\gamma_{d,\varphi=1}$ and φ_0 resulting from this distribution behaved identically to experiment.

By modelling the flakes as a rhombus we derived an equation relating the surface area to the mean flake length. The linear fit of the data suggests that flake thickness is

independent of flake length with a constant value of 95 nm. Using this rhombus model we were also able to relate the decay constant, ϕ_0 , to t/L . While attempting to fit this model to the data we found that to achieve a close fit, the edges needed to be considered as sites with a low surface energy. This conclusion is consistent with the conclusion drawn from the $\gamma_{d,\phi=0}$ data that showed the defects must be described by a narrow surface energy curve. This illustrates the reliability of the results from the method presented in this work. The data also suggest that the defect density rises with increasing flake length. This result has been corroborated with other work in the literature using spectroscopic techniques. Using the relaxation behaviour of the excited states provided insight into the defect trap density. This could allow the systematic study of samples from growth or exfoliation processes. [203]

Our attention then turned to boron nitride and we applied the method in much the same manner. One clear difference between the two materials is the behaviour of the $\gamma_{d,\phi=0}$ data. Unlike before, the $\gamma_{d,\phi=1}$ changes value with flake length, reaching minimum and maximum values of 40 and 69 mJ/m² at infinite and zero flake length respectively. This implies that the edge sites are high energy sites described by a curve with an average value of 69 mJ/m² and that the basal plane and defects are described by a curve with an average value of 40 mJ/m².

Fitting the $\gamma_{d,\phi=0}$ data to the same logistic models as before, we found values for $\gamma_{d,\phi=0}$ at infinite and zero flake length of 41 and 98.5 mJ/m². Using these values we arrived at a distribution with the following parameters $\mu_{\text{basal}}, \mu_{\text{edge}} = 40, 70$ mJ/m² and $\sigma_{\text{basal}}, \sigma_{\text{edge}} = 1, 15$ mJ/m² but found that increasing the σ_{edge} to 20 mJ/m² gave a slightly improved fit when comparing the behaviour of the simulated and experimental values of $\gamma_{d,\phi=0}$ and $\gamma_{d,\phi=1}$. The surface energy data suggest that the defects do not have a high surface energy and behave in much the same way as the rest of the basal plane. We found evidence in support of this when plotting the decay constant, ϕ_0 , versus t/L . We observe the decay constant increasing with t/L ; implying that the defects have a low surface energy and the edges have a high surface energy. We also found results that might suggest the ratio of armchair to zigzag edges is changing with flake length.

Quickly summarising the methodology of this work; several samples of the material of interest with different particle dimensions are either bought or prepared. The IGC profiles of each sample is measured and fitted to a stretched exponential. The fitted

parameters $\gamma_{d,\varphi=1}$ and $\gamma_{d,\varphi=0}$ are plotted against φ_0 flake length. These plots can be fitted to straight line and logistic equations respectively. The fit values of these equations are then used to infer the parameters describing the distribution (μ and σ). This is done by making use of the relationships we found between μ and σ , and $\gamma_{d,\varphi=1}$ and $\gamma_{d,\varphi=0}$.

Not only did this thesis detail a method for inferring the surface energy distribution of material but one that can also ascribe surface energies to the different aspects of the material. This is invaluable for applications where a complete description of the surface energy is required. It could also be of use when the surface energy of a single aspect of a material is required. Being able to measure the surface energy at full coverage would be of use for applications such as liquid phase exfoliation and being able to measure the defect density would also be useful for picking an ideal starting material before processing.

7.2 Future Work

There are several avenues for possible future research. This thesis and the work carried out by Ferguson et al. have only shown this method to work for the 2D nanomaterials; graphene, molybdenum disulphide and boron nitride. One of the most obvious routes to take is to apply the technique to materials that are not part of this class. Materials with multiple crystallographic planes and that cannot be described by three Gaussian curves. Deconvolution may be more time-consuming but should still be possible. The general relations laid out in this work would still apply. This would conclusively demonstrate the wide applicability of this method. This method is not limited to the experimental parameters laid out in this work. It is possible to change flow rate, temperature etc. and still apply the procedure detailed in this thesis.

We showed that there are three “types” of distribution that can produce surface energy profiles with the exponential like shape seen in experiment. Including the graphite work we are able to show a real-world example of each. Each of these “types” can be roughly approximated as a lognormal distribution. It may be possible to find a material or even construct a sample with a distribution distinct from this shape. It would be

interesting to see if the experimental profiles would retain the exponential like shape or match those generated by the simulation.

Returning to 2D nanomaterials, it would be worthwhile to repeat a similar set of experiments to those carried out here but, instead of varying flake length to induce different degrees of defect density using lasers. This would hopefully show that we are indeed measuring the surface energy and concentration of the defects.

Appendix A

The following is the Python code used to define a distribution of surface energies and simulate the IGC surface energy profile that would result from a real-world experiment.

The code is also available at <https://github.com/caffreit>

```
1. # -*- coding: utf-8 -*-
2. """
3. Created on Wed Jun 22 10:28:25 2016
4.
5. @author: Administrator
6. """
7.
8. import math
9. import numpy as np
10. import scipy.stats
11. from scipy.optimize import curve_fit
12. import csv
13. from more_itertools import unique_everseen
14. #import matplotlib.pyplot as plt
15. import winsound
16.
17.
18. def func(cov,gam0,gam1,k,d):
19.     return (gam0-((gam0-gam1)*(np.exp(-((k*cov)**d)))))
20.
21.
22. split_list = [0.3]#, 0.02, 0.03, 0.04, 0.05, 0.07, 0.1, 0.2, 0.3, 0.4, 0.5, 0.
    6, 0.7, 0.8, 0.9, 0.95, 0.99]#Defect in Basal, i.e. % of Not Edge that is defe
    ctive
23. Temp_list = [25]#, 0.96, 0.955, 0.95, 0.945, 0.94, 0.92, 0.9, 0.85, 0.8, 0.75,
    0.7, 0.6, 0.5, 0.4]
24. mu_3_list = [0.04]#, 0.05, 0.06, 0.07, 0.08, 0.09] #Defect
25. mu_2_list = [0.042] #Bulk
26. mu_1_list = [0.039]#, 0.06, 0.07, 0.08, 0.09] #Edge
27. sigma_3_list = [0.0175]#, 0.002, 0.005, 0.01, 0.012, 0.015, 0.0175, 0.02] #De
    fect
28. sigma_2_list = [0.002] #Bulk
29. sigma_1_list = [0.002]#, 0.01, 0.015, 0.02] #Edge
30. for split in split_list:
31.     for mu_3 in mu_3_list:
32.         for mu_2 in mu_2_list:
33.             for mu_1 in mu_1_list:
34.                 for sigma_3 in sigma_3_list:
35.                     for sigma_2 in sigma_2_list:
36.                         for sigma_1 in sigma_1_list:
37.                             popt_list = []
38.                             SE_profile_list = []
39.                             basal_pop_list = [0.999, 0.99, 0.775, 0.75, 0.725,
    0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1]
40.                             for basal_pop in basal_pop_list:
41.                                 Population_3 = round((split*(basal_pop**16))*b
    asal_pop,5) # Defect population
42.                                 Population_2 = basal_pop-
    Population_3 #Bulk Population
```

```

43.                                     Population_1 = 1 -
    basal_pop # Edge population
44.                                     Pop_list = []
45.                                     SE_list = []
46.                                     granularity = 1000
47.                                     final_cov = granularity-1
48.                                     inject_size = float(1)/granularity
49.
50.                                     #Defect #####
    #####
51.                                     #sigma_3 = 0.0175
52.                                     #mu_3 = 0.04
53.                                     step_3 = 0.005
54.
55.                                     SE_array_3 = np.arange(mu_3-
    (5*sigma_3),5*sigma_3 + mu_3+step_3,step_3)
56.                                     for s in SE_array_3:
57.                                         if s < 0:
58.                                             SE_array_3 = np.delete(SE_array_3,0)
59.
60.                                     for s in SE_array_3:
61.                                         s = round(s,4)
62.                                         SE_list.append(s)
63.
64.                                     Initial_Pop_list_3 = []
65.                                     for x in SE_array_3:
66.                                         k = scipy.stats.norm(mu_3, sigma_3).pdf(x)
67.
68.                                         Initial_Pop_list_3.append(k*step_3)
69.
70.                                         sum_pop = sum(Initial_Pop_list_3)
71.                                         for p in Initial_Pop_list_3:
72.                                             Pop_list.append(p*Population_3/sum_pop) #
remember to put*Population_3 back in
73.
74.                                     #Bulk #####
    #####
75.                                     #sigma_2 = 0.002
76.                                     #mu_2 = 0.042
77.                                     step_2 = 0.005
78.
79.                                     SE_array_2 = np.arange(mu_2-
    (5*sigma_2),5*sigma_2 + mu_2+step_2,step_2)
80.                                     for s in SE_array_2:
81.                                         if s < 0:
82.                                             SE_array_2 = np.delete(SE_array_2,0)
83.
84.                                     for s in SE_array_2:
85.                                         s = round(s,4)
86.                                         SE_list.append(s)
87.
88.                                     Initial_Pop_list_2 = []
89.                                     for x in SE_array_2:
90.                                         k = scipy.stats.norm(mu_2, sigma_2).pdf(x)
91.
92.                                         Initial_Pop_list_2.append(k*step_2)
93.
94.                                         sum_pop = sum(Initial_Pop_list_2)
95.                                         for p in Initial_Pop_list_2:
96.                                             Pop_list.append(p*Population_2/sum_pop)
97.
98.                                     #Edge #####
    #####
99.                                     #sigma_1 = 0.002
100.                                    #mu_1 = 0.039
101.                                    step_1 = 0.005

```

```

98.
99.             SE_array_1 = np.arange(mu_1 -
100. (5*sigma_1), 5*sigma_1 + mu_1 + step_1, step_1)
101.             for s in SE_array_1:
102.                 if s < 0:
103.                     SE_array_1 = np.delete(SE_array_1,0)
104.             for s in SE_array_1:
105.                 s = round(s,4)
106.                 SE_list.append(s)
107.             Initial_Pop_list_1 = []
108.             for x in SE_array_1:
109.                 k = scipy.stats.norm(mu_1, sigma_1)
110.                 Initial_Pop_list_1.append(k*step_1*
111. Population_1)
112.                 sum_pop = sum(Initial_Pop_list_1)
113.                 for p in Initial_Pop_list_1:
114.                     Pop_list.append(p*Population_1/sum_
115. pop)
116.                 dsfg = tuple(Pop_list)
117.                 D_Pop_list = list(dsfg)
118.                 Hept_Pop_list = list(tuple(Pop_list))
119.                 Oct_Pop_list = list(tuple(Pop_list))
120.                 Non_Pop_list = list(tuple(Pop_list))
121.                 #Hexane #####
122. #####
123.                 SE_Hexane = 0.0184
124.                 area_Hexane = 5.15E-19
125.                 TinC = 25 #Temp in Celsius
126.                 kT = 1.38e-23*(273.15 + TinC)
127.
128.                 Hexane_P_list = []
129.                 for SE in SE_list:
130.                     free_energy_absorption = -
131. 2 * area_Hexane * math.sqrt(SE * SE_Hexane)
132.                     Hexane_P = math.exp(-
133. (free_energy_absorption/kT))
134.                     Hexane_P_list.append(Hexane_P)
135.                 Hexane_no_duplicates = list(unique_ever
136. seen(Hexane_P_list))
137.                 Hexane_Ptotal = sum(Hexane_no_duplicate
138. s)
139.                 Hexane_Energy_prob_list = []
140.                 for Hexane_P in Hexane_P_list:
141.                     Hexane_Energy_prob_list.append(Hexa
142. ne_P/Hexane_Ptotal)
143. #####
144. #####
145.                 coverage = []
146.                 Hexane_SE_measured_list = []
147.                 Hexane_SE_actual_list = []
148.                 injected_amount = 0
149.                 for i in range(granularity-1):
150.                     H_PreNorm_probs = [a*b for a,b in z
151. ip(Pop_list,Hexane_Energy_prob_list)]

```

```

150.                                     norm_const = 1/sum(H_PreNorm_probs)
151.
152.                                     Postnorm_prob_list = []
153.                                     for j in H_PreNorm_probs:
154.                                         postnorm_prob = norm_const*j
155.                                         Postnorm_prob_list.append(postn
orm_prob)
156.
157.                                     Probe_SE_list = [c*d for c,d in zip
(Postnorm_prob_list,SE_list)]
158.                                     SE_meas = sum(Probe_SE_list)
159.                                     Hexane_SE_measured_list.append(SE_m
eas)
160.                                     SE_actual = np.mean(Hexane_SE_measu
red_list)
161.                                     Hexane_SE_actual_list.append(SE_act
ual)
162.
163.
164.                                     for Pop_prob, post_norm_prob in zip
(Pop_list, Postnorm_prob_list):
165.                                         Pop_prob = ((Pop_prob * (float(
1) - injected_amount)) - (inject_size * post_norm_prob)) / (float(1)-
(injected_amount+inject_size))
166.                                         Pop_list.pop(0)
167.                                         if Pop_prob < 0:
168.                                             Pop_prob = 0
169.                                         Pop_list.append(Pop_prob)
170.
171.                                     injected_amount += inject_size
172.                                     injected_amount = round(injected_am
ount,5)
173.                                     coverage.append((float(i)+1)/granul
arity)
174.                                     print(sum(Pop_list))
175.
176.
177.                                     #Decane #####
#####
178.
179.                                     SE_Decane = 0.0234
180.                                     area_Decane = 7.5E-19
181.
182.                                     Decane_P_list = []
183.                                     for SE in SE_list:
184.                                         D_free_energy_absorption = -
2 * area_Decane * math.sqrt(SE * SE_Decane)
185.                                         Decane_P = math.exp(-
(D_free_energy_absorption/kT))
186.                                         Decane_P_list.append(Decane_P)
187.
188.                                     Decane_no_duplicates = list(unique_ever
seen(Decane_P_list))
189.                                     Decane_Ptotal = sum(Decane_no_duplicate
s)
190.
191.                                     Decane_Energy_prob_list = []
192.                                     for Decane_P in Decane_P_list:
193.                                         Decane_Energy_prob_list.append(Deca
ne_P/Decane_Ptotal)
194.
195.                                     #####
#####
196.
197.                                     D_coverage = []

```

```

198. Decane_SE_measured_list = []
199. Decane_SE_actual_list = []
200. D_injected_amount = 0
201.
202. for i in range(granularity-1):
203.     D_Prenorm_probs = [a*b for a,b in zip
ip(D_Pop_list,Decane_Energy_prob_list)]
204.     D_norm_const = 1/sum(D_Prenorm_probs)
205.
206.     D_Postnorm_prob_list = []
207.     for j in D_Prenorm_probs:
208.         D_postnorm_prob = D_norm_const*
j
209.         D_Postnorm_prob_list.append(D_postnorm_prob)
210.
211.     D_Probe_SE_list = [c*d for c,d in zip
ip(D_Postnorm_prob_list,SE_list)]
212.     D_SE_meas = sum(D_Probe_SE_list)
213.     Decane_SE_measured_list.append(D_SE
_meas)
214.     D_SE_actual = np.mean(Decane_SE_measured_list)
215.     Decane_SE_actual_list.append(D_SE_actual)
216.
217.
218. for D_Pop_prob, D_post_norm_prob in zip(D_Pop_list, D_Postnorm_prob_list):
219.     D_Pop_prob = ((D_Pop_prob * (float(1) - D_injected_amount)) - (inject_size * D_post_norm_prob)) / (float(1)-(D_injected_amount+inject_size))
220.     D_Pop_list.pop(0)
221.     if D_Pop_prob < 0:
222.         D_Pop_prob = 0
223.     D_Pop_list.append(D_Pop_prob)
224.
225.     D_injected_amount += inject_size
226.     D_injected_amount = round(D_injected_amount,5)
227.     D_coverage.append((float(i)+1)/granularity)
228.     print(sum(D_Pop_list))
229.
230. #####
#####
231. SE_profile = []
232. RTlnVn_hex = []
233. RTlnVn_hept = []
234. RTlnVn_oct = []
235. RTlnVn_non = []
236. RTlnVn_dec = []
237.
238. for hex_experienced_nraj in Hexane_SE_actual_list:
239.     hex_rtlnvn = 84136*(np.sqrt(hex_experienced_nraj))
240.     RTlnVn_hex.append(hex_rtlnvn)
241.
242. for hept_experienced_nraj in Heptane_SE_actual_list:
243.     hept_rtlnvn = 97812*(np.sqrt(hept_experienced_nraj))
244.     RTlnVn_hept.append(hept_rtlnvn)

```

```

245.
246.                                     for oct_experienced_nroj in Octane_SE_ac
tual_list:
247.                                     oct_rtlnv = 110739*(np.sqrt(oct_ex
perienced_nroj))
248.                                     RTlnVn_oct.append(oct_rtlnv)
249.
250.                                     for non_experienced_nroj in Nonane_SE_ac
tual_list:
251.                                     non_rtlnv = 125208*(np.sqrt(non_ex
perienced_nroj))
252.                                     RTlnVn_non.append(non_rtlnv)
253.
254.                                     for dec_experienced_nroj in Decane_SE_ac
tual_list:
255.                                     dec_rtlnv = 138978*(np.sqrt(dec_ex
perienced_nroj))
256.                                     RTlnVn_dec.append(dec_rtlnv)
257.
258.                                     y2_y1 = [f-
g for f,g in zip(RTlnVn_dec,RTlnVn_hex)]
259.                                     x2_x1 = 4#4.48e-20
260.                                     for p in y2_y1:
261.                                         m = p/x2_x1
262.                                         n = (m*m)/(4*6.022*6.022*6*6e6*(0.0
359 + (0.000058*(20-TinC))))
263.                                         SE_profile.append(n)
264.                                         SE_profile_list.append(Hexane_SE_actual
_list)
265.
266.                                     try:
267.                                         popt = curve_fit(func,coverage,Hexa
ne_SE_actual_list)
268.                                         decay_const = 1/popt[0][2]
269.                                         popt_temp = popt[0][0], popt[0][1],
1/popt[0][2], Hexane_SE_actual_list[0]*1000, Hexane_SE_actual_list[-1]*1000
270.                                         popt_list.append(popt_temp)
271.                                     except:
272.                                         popt_list.append(["na","na","na",SE
_profile[0]*1000, SE_profile[-1]*1000])
273.
274.
275.                                     l = zip(*popt_list)
276.                                     with open("Params " + "N_" + str(split) + "
cDef_" + str(mu_3) + " cBulk_" + str(mu_2) + " cEdge_" + str(mu_1) + " wDef_"
+ str(sigma_3) + " wBulk_" + str(sigma_2) + " wEdge_" + str(sigma_1) + ".csv"
,"wb") as g:
277.                                         writer = csv.writer(g)
278.                                         writer.writerows(l)
279.
280.
281.
282.                                     r = zip(*SE_profile_list)
283.                                     with open("Profile " + "N_" + str(split) +
" cDef_" + str(mu_3) + " cBulk_" + str(mu_2) + " cEdge_" + str(mu_1) + " wDef_"
+ str(sigma_3) + " wBulk_" + str(sigma_2) + " wEdge_" + str(sigma_1) + ".csv"
,"wb") as g:
284.                                         writer = csv.writer(g)
285.                                         writer.writerows(r)
286.
287.
288.                                     duration = 1000
289.                                     freq = 220
290.                                     winsound.Beep(freq, duration)

```

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