

THE ROLE OF JUNCTIONS IN NANOMATERIAL NETWORKS

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A THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNDER THE SUPERVISION OF
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SCHOOL OF PHYSICS
TRINITY COLLEGE DUBLIN, THE UNIVERSITY OF DUBLIN

MARCH 2026

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ABSTRACT

Printed nanomaterial networks promise scalable routes to revolutionary flexible, transparent and high-performance electronic systems, yet device characteristics are routinely throttled by inter-particle junctions. Conventional electrical characterisations, such as sheet resistance, conductivity and mobility measurements, collapse all physics into a single effective value, obscuring the complex interplay between the inter-particle and intra-particle transport. This thesis reframes electrical characterisation around the two elemental contributions that govern conduction in nanomaterial networks: the nanoparticle (intra-particle) resistance, R_{NP} , and the junction (inter-particle) resistance, R_J . We develop a simplistic, geometry-independent resistor-chain model that relates network resistivity to the resistance of an average nanoparticle-junction (NP-J) pair and show how it yields two complementary, practical and quantitative routes to decouple and extract both terms. First, DC nanomaterial size-dependent studies (nanowire length for 1D, nanosheet thickness for 2D) enable extraction of nanoparticle resistivity, ρ_{NP} and junction resistance, R_J . Second, AC impedance spectroscopy is used by converting the network impedance spectra into the impedance of an average NP-J pair allowing extraction of R_{NP} and R_J .

Using the DC route, we validate the scaling predictions on silver nanowire (AgNW) networks and liquid-phase-exfoliated (LPE) graphene nanosheet networks. For AgNWs, network resistivity scales with the inverse nanowire length, as predicted by our model, yielding nanowire resistivities $\sim 10^{-8} \Omega m$ (close to bulk Ag) and typical junction resistances $\sim 200 \Omega$, with $R_{NW}/R_J \approx 0.03 - 0.7$, confirming predominantly junction-limited transport. For graphene, network resistivity scales with nanosheet thickness, providing values of $\rho_{NS} = (3.5 \pm 0.6) \times 10^{-5} \Omega m$ and $R_J = 7.8 \pm 0.5 k\Omega$. R_J/R_{NS} rises from 0.56 to 6.11 across size fractions, indicating a transition from mixed to strongly junction-limited regimes as the nanosheets get thicker. These measurements establish a broadly applicable DC methodology for separating intra- from inter-particle contributions.

To overcome the extensive sample preparation demands using DC size-dependent studies, we establish a rapid, single-sample AC impedance-spectroscopy route. Our model enables the conversion of network impedance spectra into a single average NP-J pair representation. Fitting a modified Randles circuit (R_{NS} in series with R_J , CPE pair) to the NP-J impedance spectra permits extraction of R_{NS} , R_J and C_J rapidly. Applied to liquid-liquid-interface-deposited (LLID) networks of electrochemically exfoliated (EE) MoS_2 , this method yields $R_J = 2.9 \pm 0.1 M\Omega$, $R_{NS} = 0.67 \pm 0.07 M\Omega$, $C_J = 8.4 \pm 0.4 fF$ and $n = 0.985$. The extracted $R_J/R_{NS} = 4.4 \pm 0.2$ indicates these dense, aligned EE networks are not strongly junction limited. Independent verifications (field-effect and THz mobilities and in-operando KPFM mapping) are consistent with the impedance-extracted

parameters. We also determine the practical window for this technique, bounded at high frequency by analyser bandwidth and at large impedances by IDE parasitic capacitance.

We extend both approaches to temperature-dependent studies, enabling mechanistic transport assignments to R_{NS} and R_J , separately. In AgNW networks, plotting ρ_{Net} versus $1/l_{NW}$ at each T isolates $\rho_{NW}(T)$ and $R_J(T)$. ρ_{NW} follows Bloch–Grüneisen behaviour while $R_J(T)$ confirms metallic silver junctions expected after annealing, with consistent Debye temperatures, residual resistivities and electron–phonon coupling constants for both the junctions and the nanowires; evidence that junctions are effectively sintered metallic contacts rather than tunnelling barriers. In LPE-graphene networks, the extracted $\rho_{NS}(T)$ is weakly thermally activated and is well captured by two parallel semiconducting channels associated with Bernal (2H) and rhombohedral (3R) stacking in graphite. Fitting yields $E_g \approx 42$ meV (Bernal) and ≈ 195 meV (3R), consistent with graphite literature. Junction transport shows a distinct power-law behaviour with an exponent $\alpha = 0.1866 \pm 0.0005$, consistent with hopping just above a mobility edge in partially disordered systems.

Temperature-dependent impedance reveals band-like nanosheet transport with an exponent $\alpha \approx 1.1$, characteristic of phonon-limited conduction at elevated carrier densities, while junctions exhibit a 3D-VRH to thermally activated crossover with $E_a = 55 \pm 2$ meV and $T_0 = (471 \pm 37) \times 10^3$ K. A $C_J/A_J \approx 2$ $\mu\text{F cm}^{-2}$ matches geometric capacitance estimates with ~ 0.6 nm inter-sheet spacing. Together these results separate intra- from inter-flake transport behaviour, replacing previous network-only analyses that conflate the two.

Overall, this work turns network optimisation from intuition into measurement-driven design. The DC methodology is simple and universal but sample-intensive while the AC route is rapid and information-rich, but instrument and device limited. Together, they provide complementary methods to quantify R_J and R_{NS} across materials systems and temperatures, to pinpoint the true rate-limiting element, and to prescribe targeted improvements. Because the underlying model is independent of particle and network geometry, these strategies are transferable across printed conductors and semiconductors, offering a general framework for rationally engineering the electrical properties of nanomaterial networks.

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1. **Coleman, E.**, Kelly, A.G., Gabbett, C., Doolan, L., Liu, S., Yadav, N., Vij, J.K., Coleman, J.N. (2025). Extracting the Temperature Dependence of Both Nanowire Resistivity and Junction Resistance from Electrical Measurements on Printed Silver Nanowire Networks. *ACS APPLIED ELECTRONIC MATERIALS*, 7, (2), 806-815,
2. Gabbett, C., Kelly, A.G., **Coleman, E.**, Doolan, L., Carey, T., Synnatschke, K., Liu, S., Dawson, A., O'Suilleabhain, D., Munuera, J., Caffrey, E., Boland, J.B., Sofer, Z., Ghosh, G., Kinge, S., Siebbeles, L.D.A., Yadav, N., Vij, J.K., Aslam, M.A., Matkovic, M., Coleman, J.N. (2024) Understanding how junction resistances impact the conduction mechanism in nano-networks. *NATURE COMMUNICATIONS*, 15, 4517.
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ACKNOWLEDGMENTS

Firstly, I would like to thank Johnny for providing me with such an amazing opportunity. Being able to work with such a great group of people for four years has greatly lightened the PhD load. Our many questionable “group hikes” or “Christmas seminars” fostered many fantastic “networking” opportunities. Although, perhaps *telling* the new students we’re going on a group hike only to end up in the pub may be a better tradition than *actually doing* a group hike... However, despite these questionable networking events, Johnny does always find a way to provide the help, direction and clarity for our work, no matter how busy things get.

I would like to thank Adam for mentoring me when I first joined the group and teaching me how the world of academia *really* works. Thanks to Cian for imprinting a memory I’d rather not have every time I hear a Robbie Williams song. Of course, thanks to the inseparable Eoin and Luke for always providing the best advice on how to consume as much free alcohol as possible at conferences and seminars. To Dom, James, Sean, Rebecca and Yumei for sharing an office with me, both past and present, that is somehow simultaneously freezing and boiling. To the rest of the group Tian, Joe, Shixin, Bharathi, Jack Maughan, Weimao, Finn, Jack Doran, Laila, Oran C., Oran B., Yash and Domhnall, thanks for enduring the past four years with me.

To Mammy and Daddy, I cannot thank you enough for all the support, belief and encouragement you have offered. I always knew you would help me no matter what I wanted to do. I hope you understand how much I appreciate you. I could not have done this without you.

And finally, to Aoife, thanks for putting up with me for almost my entire academic career. I think you are the only one who really understands how much work I have put into this over the last four years. You were always there to hear stories of how my days went and enthusiastic to let me explain everything and anything I could at you. You truly are the light of my life.

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*"There is nothing impossible to him who will
try"*

Alexander the Great

CHAPTER 1

INTRODUCTION

The field of nanomaterials has exploded in the 21st century, promising to revolutionise every aspect of our lives, akin to the discovery fire by the caveman. It is increasingly common for new products to include the term "nano" as a facade to appear on the cutting-edge. Everything from Samsung's "Silver Nano" branding to nano-ceramic paint and window coatings to graphene drivers in headphones and Apple's "nano-texture" glass are marketed with the "nano" buzzword, to appeal to the masses. It is no wonder then that nanoscience publications make up ~8% of all scientific publications today. However, despite all the hype and aggressive marketing, scientists have struggled to pivot nanomaterials from the lab into industry. Some recent progress has led to niche industrial deployments, but the broader promise is not yet fully realised.

Over the past few decades, advances in liquid-phase synthesis, exfoliation and processing have made it possible to produce conductors, semiconductors and insulators as solution-processable 0D nanoparticles, 1D nanowires and nanotubes and 2D nanosheets. These nanomaterial building blocks combine exceptional intrinsic properties (high conductivity and mobility,^{21, 22} large specific surface area,²³ tuneable band structures²⁴ and excellent mechanical properties²⁵) with the long-established practicality of solution processing.²⁶⁻²⁸ As a result, they are

increasingly being explored in applications spanning transparent conductors,^{29, 30} flexible electronics,³¹ energy storage^{23, 32} and other emerging platforms.³³

A defining feature of this landscape is printed networks; percolating films formed by the deposition of nanomaterial inks using established printing techniques. Printed networks were targeted because they offer the path of least resistance for industry adoption of nanomaterial networks, providing scalability and compatibility with established manufacturing processes. But printed networks expose a fundamental challenge with nanomaterial-based electronics: particle-particle junctions. No matter how remarkable the properties of a single nanowire, nanotube or nanosheet might be, device-level performance emerges from a series of inter-particle and intra-particle transport events repeated thousands or even millions of times across each percolating conduction pathway.

That repetition ultimately creates a persistent limitation. In all but the highest-performance networks today, junctions dominate electronic charge transport. Imperfect nanoparticle overlap, tunnelling gaps, adsorbates or residual stabilisers are some of the factors causing junctions to be the bottleneck in charge transport. But how do we quantitatively measure the role of junctions in nanomaterial networks? Standard electrical measurements such as sheet resistance or temperature-dependent mobility or conductivity, tend to collapse the physics into a single effective curve. This overall picture obscures the individual contributions from the nanomaterials and the junctions, making network optimisation guesswork: should time be invested in improving the junctions or are the nanomaterials themselves the problem?

To make this a rational decision, the two contributions must be decoupled and separately assessed. The need to extract the inter-particle junction resistance, R_J , and the intra-particle nanomaterial resistance, R_{NP} , is clear. With R_J and R_{NP} in hand, the element limiting transport can be determined and quantified. This thesis aims to develop a general framework to do just that.

We begin by developing a model governing conduction in nanomaterial networks, which is the basis of [Chapter 3](#). Taking a minimal physical picture, each percolating path can be represented by a series chain of particles and junctions. From this, we can quickly see that the unit of resistance associated with a network is $R_J + R_{NP}$. Averaging over the many parallel paths in a network, an overall expression for the resistivity (or conductivity or mobility) can be obtained. This model and expression lead to two practical outcomes. First, it connects the DC network resistivity to the physical and geometrical properties of the network, allowing key parameters to be extracted. Second, it provides a means to directly convert the network impedance spectrum to that of an average nanoparticle-junction pair, enabling the use of impedance spectroscopy to quantitatively examine the electrical properties of nanomaterial networks, a technique novel to the field. Building on this framework, we implement two complementary techniques to extract R_J and R_{NS} .

[Chapter 4](#) of this thesis discusses the use of simple DC measurements to extract R_J and ρ_{NP} in silver nanowire (AgNW) and liquid-phase exfoliated (LPE) graphene nanosheet networks. The model predicts that for 1D nanowires/nanotubes the network resistivity scales with the inverse of nanowire length, $1/l_{NW}$, while in 2D nanosheet systems it scales with nanosheet thickness, t_{NS} . Both trends were confirmed using a AgNW length-dependence study and a graphene nanosheet thickness-dependence study. Fitting these data allows for the extraction of R_J and ρ_{NP} from the slope and intercept, respectively. In both cases we find the junctions to be the primary bottleneck for conduction. This technique is broadly applicable, where nanomaterial size-dependent studies are feasible.

We then use AC impedance spectroscopy to probe the junctions and nanosheets. Junctions act as barriers to charge transport meaning charge can accumulate at either side of them under an applied bias. This induced a junction capacitance, C_J , allowing us to directly probe the network junctions by measuring the complex network resistivity across a range of frequencies. Due to the arrangement of many

nanoparticle-junction pairs in series and parallel throughout the network, fitting this data alone can only provide qualitative estimates for R_J and R_{NP} . However, using our previous model, we can convert the measured network impedance to that of an average nanoparticle-junction pair, enabling the extraction of quantitative values. In [Chapter 5](#) we use impedance spectroscopy to extract R_{NS} , R_J and C_J for a liquid-liquid interface deposited (LLID) network of electrochemically exfoliated (EE) MoS₂ nanosheets. We then discuss the difficulties with using this technique, such as the interdigitated electrode design and the frequency range of the measuring instrument.

These two methods, DC and AC, provide complementary techniques for the separation and extraction of R_J and R_{NP} in nanomaterial networks. The DC approach is simple and universally applicable but suffers from low throughput due to the laborious task of performing nanoparticle size-dependent studies. The AC approach trades rapid measurements and richer physics per device for complexity and limited applicability.

We expand on both of these approaches in [Chapter 6](#). By performing temperature-dependent studies on nanomaterial size-dependent networks, R_J and ρ_{NP} can be extracted as a function of temperature. This enables the assessment of the transport mechanisms in the nanoparticles and the junctions separately. We show this for AgNWs and for LPE graphene networks and attribute distinct mechanisms to the junctions and nanomaterials. Similarly, by carrying out temperature-dependent impedance measurements, R_{NP} , R_J and C_J can be extracted as a function of temperature as we show for a network of EE MoS₂.

The significance of this thesis is twofold. First, the electrical characterisation of nanomaterial networks is reframed from “what is the overall temperature-dependence and transport mechanism?” to “which elements limit transport and how do they evolve?”. Second, it provides guidance for engineering the electrical properties of networks. If R_J dominates, prioritise network morphology and

deposition. If R_{NS} dominates, improve nanoparticle properties or substitute the nanomaterial for a more suitable candidate. Because the model is initially defined independent of particle or network geometry, it should be transferable across a wide class of printed electronic materials and device geometries.

In summary, this thesis develops a model for electrical conduction in printed nanomaterial networks and uses it to deliver two techniques that decouple and extract the two quantities that matter most: R_J at particle-particle junctions and R_{NS} within the particles themselves. This separation turns the electrical optimisation of networks from intuition into measurement-driven design.

*"If I have seen further, it is by standing on
the shoulders of Giants"*

Isaac Newton

CHAPTER 2

LOW-DIMENSIONAL NANOSTRUCTURES

Nanomaterials occupy a unique corner of the materials landscape, where the macroscopic everyday rules of matter begin to bend and the extraordinary takes shape. At the nanoscale (typically below 100 nm), materials display behaviours that defy classical expectations, unlocking a rich palette of electronic, optical and chemical properties. These length scales permit quantum phenomena to reign, enabling properties that are inaccessible in bulk materials. From the remarkable to the ordinary, from the distant promise of revolutionising science and technology to marginal gains in elasticity of tennis rackets, nanomaterials sit at the heart of 21st century innovation.

Nanomaterials are often classified by their dimensionality. 0D nanomaterials, such as quantum dots and nanoparticles, are defined by nanoscale sizes (< 100 nm) in all spatial directions and exhibit discrete electronic states. 1D nanomaterials, like nanowires and nanotubes, are nanoscale in two spatial directions and extend in the third, enabling anisotropic charge transport along their length and affording mechanical flexibility. 2D nanomaterials, like nanosheets, are confined to a nanoscale thickness while remaining laterally extended, opening an entirely new *plane* of opportunity. Each class exhibits unique properties and challenges across synthesis, stabilisation and size control, issues that form the focus of this chapter.

2.1 Silver Nanowires

Silver Nanowires (AgNWs) represent a cornerstone material in the development of next generation printed electronics. AgNW networks are prized for their unique combination of high electrical conductivity, optical transparency and mechanical flexibility. AgNWs are one-dimensional (1D) nanostructures, typically with diameters ranging from 10 to 200 nm and lengths up to tens of micrometers. The most prevalent synthesis route for AgNWs is the polyol process, first reported in 2002, which involves the reduction of silver nitrate (AgNO_3) with ethylene glycol in the presence of seeds and polyvinylpyrrolidone (PVP) which acts as a capping agent.^{34, 35} This reliable, scalable and controllable technique enables the growth of high aspect ratio AgNWs, as shown by the TEM image in [Figure 2.1A](#). Nanowire lengths up to 300 μm can be achieved while this method simultaneously coats the AgNWs with a PVP layer, facilitating solution processing. The resulting AgNWs possess an intrinsic electrical conductivity nearly equivalent to that of bulk silver ($\sigma_{\text{Ag}} = 6.3 \times 10^7 \text{ S/m}$). This solution-processability while retaining the outstanding properties of silver transformed AgNWs from the realm of scientific curiosity into a viable material for industrial applications.

A primary utility of AgNWs arises from the production of percolating conductive networks, similar to that shown in [Figure 2.1B](#). These networks are typically fabricated by depositing dispersions of AgNWs onto a substrate using methods such as spray-coating (discussed in detail later), spin-coating and slot-die coating. While the metallic nature of individual nanowires provides a low-resistance channel for charge transport, the overall conductivity of the network is not governed by the AgNWs themselves. Instead, it is overwhelmingly dictated by the electrical transport across the multitude of junctions formed at the points where nanowires overlap and intersect.^{6, 36} Post-deposition treatments, such as thermal annealing,^{29, 37, 38} are commonly employed to sinter these junctions, thereby significantly enhancing the conductivity of AgNW networks.

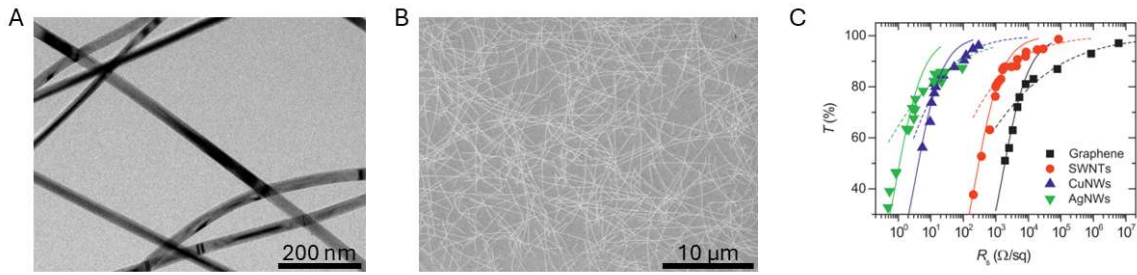


Figure 2.1: Silver Nanowires. **A)** TEM image of a AgNW produced using the polyol process. [Adapted from Ref. ¹²]. **B)** SEM image of a percolating low density AgNW network. **C)** Optical transmittance (at 550nm) versus sheet resistance for transparent conducting networks of nanomaterials. The solid line represents the percolating regime, and the dashed line represents the bulk regime. [Adapted from Ref. ¹⁹]

Networks of AgNWs are known for their excellent electrical conductivity,^{19, 30, 39} transparency⁴⁰ and flexibility⁴¹ making them attractive candidates for a variety of next generation technologies. AgNW networks are extensively used for transparent conductive electrodes (TCEs), offering a low-cost and flexible alternative to indium tin oxide (ITO). This enables their use in flexible touchscreens,⁴² organic light emitting diodes⁴² (OLEDs) and solar cells.⁴³ The high aspect ratio of AgNWs permits the formation of conductive networks at very low loading densities,¹⁹ preserving optical transparency. Figure 2.1C shows AgNW networks outperform competing nanomaterial networks for high conductivity electrodes at reasonable transparencies.⁴⁴ Moreover, their mechanical resilience makes them suitable for use in flexible⁴¹ and stretchable electronics while their sensitivity to strain and pressure allows integration into wearable sensors and electronic skin devices. Recent research highlights their versatility across emerging technologies, with AgNW networks being explored for electromagnetic shielding,⁴⁵ photonic devices,⁴⁶ and as substrates for surface-enhanced Raman spectroscopy (SERS).⁴⁷

2.2 Two-Dimensional Nanomaterials

Two-dimensional nanomaterials represent a class of crystalline solids consisting of a single layer of atoms. These are typically layered materials which exhibit strong in-plane bonding and weak out-of-plane van der Waals interactions between

layers. Since the discovery of graphene, interest in 2D nanomaterials has exploded, revealing a broad family of materials. These materials display a rich spectrum of optical, electronic and mechanical properties that are often drastically different than their bulk counterparts.

Graphene

The discovery of graphene nanosheets in 2004²¹ catalysed a wave of scientific research worldwide. However, the concept of a monolayer of graphene had piqued the interest of scientists for more than a century. Benjamin Brodie recognised the thin layered structure of thermally reduced graphite oxide as early as 1859.⁴⁸ X-ray diffraction was employed independently by Debye,⁴⁹ Hull⁵⁰ and Bernal⁵¹ to determine the crystallographic structure of graphite in the early 20th century. Wallace was the first to model the electronic band structure of graphite using a tight-binding approach,⁵² laying the theoretical foundation that would later be extended to monolayer graphene. He successfully predicted the linear dispersion relation and semimetallicity of graphene. Over the following decades, further advancements were made, including TEM imaging of few-layer graphite⁵³ and the growth of graphene monolayers on substrates.⁵⁴ However, theoretical and experimental observations suggested that perfectly flat, freestanding 2D monolayers should be thermodynamically unstable at finite temperatures.⁵⁵

These predictions, however, could not quench the indomitable human spirit: in 2004 Geim and Novoselov successfully exfoliated graphene monolayers from graphite using the now-famous scotch tape method.²¹ It was later discovered that the stability of monolayer graphene arises from intrinsic wrinkling of the nanosheets,⁵⁶ whereas previous experiments had assumed perfectly flat sheets. This breakthrough spurred a broader scientific interest in the discovery and characterisation of other 2D monolayered materials.

Graphene is an allotrope of carbon, possessing exceptional physical properties due to its two-dimensional nature and sp^2 -hybridised hexagonal lattice. [Figure](#)

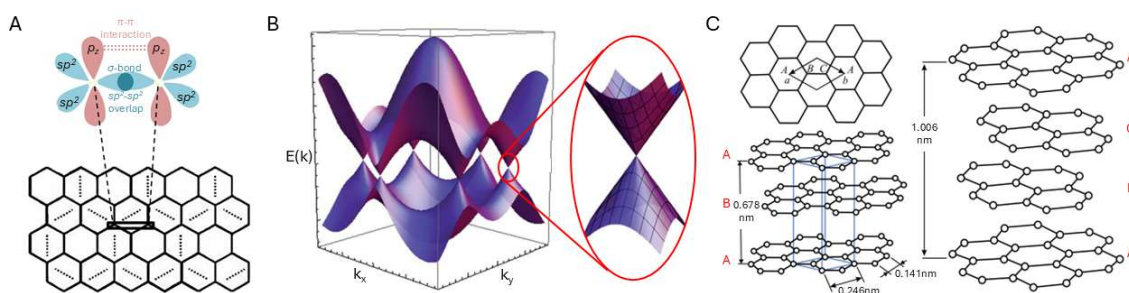


Figure 2.2: Graphene. A) The structure and bonding present within graphene layers.

[Adapted from Ref. ⁷] B) The dispersion relation of graphene. The zoomed inset shows the linearity at the Dirac points. [Adapted from Ref. ¹⁵] C) Crystal structure of graphite showing the 2H (ABAB) and 3R (ABCABC) stacking of graphene layers.

2.2A shows a schematic representation of this structure, where each carbon atom forms three strong in-plane σ -bonds with neighbouring atoms at a distance of 1.42 Å.⁵¹ These σ -bonds are responsible for graphene's extraordinary in-plane mechanical properties and resistance to crystallographic defects and dislocations.⁵⁷ The out of plane p_z -orbitals form π -bonds and π^* -bonds with neighbouring atoms, which combine to create a delocalised valence and conduction band that extends across the entire sheet, giving rise to graphene's remarkable electronic properties.⁵²

Graphene exhibits unusual electronic properties as a zero-gap semiconductor, often referred to as a semimetal in this context. This behaviour arises due to the conduction and valence bands meeting at discrete points in momentum space, known as Dirac points, located at the K and K' points of the Brillouin zone, as shown in Figure 2.2B. Near these points, the energy-momentum relationship is linear, meaning charge carriers behave as massless Dirac fermions.⁵⁸ This leads to an exceptionally high in-plane carrier mobility (up to 275,000 cm² V⁻¹ s⁻¹ at 4.2 K²²) and ballistic transport over submicron distances. The semimetallic nature of graphene arises because the density of states at the Dirac point is zero and the Fermi level lies exactly at this point. This unique band structure enables ambipolar electric field-effect behaviour⁵⁹ and makes graphene extremely sensitive to external perturbations such as gating,⁶⁰ doping²⁴ or contact with other materials.⁶¹

In addition to its remarkable electronic properties, graphene also demonstrates outstanding thermal and mechanical properties. It has an intrinsically high thermal conductivity, often exceeding $2000 \text{ W m}^{-1} \text{ K}^{-1}$, due to the efficient in-plane phonon transport.⁶² Graphene is also one of the strongest known materials, with a tensile strength of around 130 GPa and a Young's modulus of 1 TPa,²⁵ stemming from the strong in plane σ -bonds. Furthermore, it exhibits high flexibility,⁶³ large surface area and chemical tunability.⁶⁴ This collection of outstanding properties is enough to explain why graphene triggered the so-called 2D materials "gold rush".

In few-layer graphene and bulk graphite, individual layers are stacked together via van der Waals (vdW) interactions. This stacking is most commonly in the 2H (hexagonal or Bernal) and 3R (rhombohedral) phases,⁶⁵ as shown in [Figure 2.2C](#). 2H stacking follows an ABAB stacking sequence, where every other layer is aligned, being the most stable and prevalent arrangement. This structure can preserve some features of monolayer graphene but introduces interlayer coupling that can alter the band structure. In contrast, 3R stacking forms an ABCABC stacking sequence, resulting in distinct interlayer interactions that can lead to a tuneable bandgap under certain conditions.⁶⁶ Both stacking orders are typically present in nano-graphite or graphene samples, as we will show for LPE graphene in [Chapter 6](#). These different stacking domains introduce three parallel contributions to charge transport in graphite samples: two semiconducting pathways corresponding to the Bernal and rhombohedral stacking and a metallic-like conducting channel at the interfaces between the crystalline regions.⁶⁵

Transition Metal Dichalcogenides

The isolation of a stable monolayer of graphene opened the door to a new era of condensed matter physics. Now that it was possible to isolate monolayers of layered materials, a hunt was on to identify and characterise other monolayer materials. Among some of the most obvious candidates were transition metal dichalcogenides⁶⁷ (TMDs). TMDs are a class of layered materials composed of

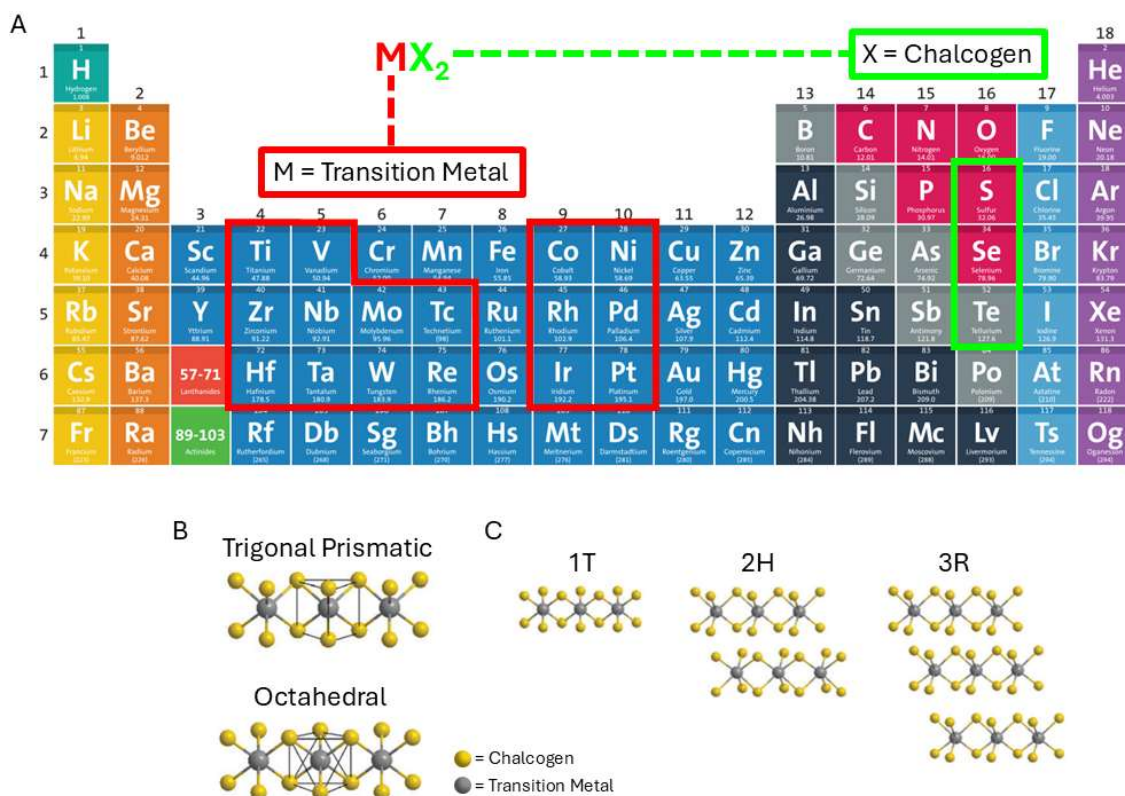


Figure 2.3: Transition Metal Dichalcogenides. A) Periodic table of elements showing the suitable elements for TMDs. **B)** Trigonal prismatic and octahedral polymorphs of TMDs. **C)** The 1T, 2H and 3R polytypes of TMDs. [Adapted from Ref. 9]

strong covalently bonded hexagonal layers which are held together by weak van der Waals interactions, similar to graphite.⁶⁸ TMDs take on an MX_2 stoichiometry, where M refers to a transition metal and X refers to a chalcogen atom, which can be sulphur, selenium or tellurium.

Up to forty combinations of metals and chalcogens highlighted in Figure 2.3A can form layered crystal structures, each with unique chemistry and band structure. These include a broad electronic range, with semiconductors such as MoS_2 and WS_2 , semimetals such as WTe_2 and $PtSe_2$ and metals such as NbS_2 and VSe_2 ⁶⁹. A TMD monolayer consists of a plane of hexagonally orientated transition metal atoms sandwiched between two offset planes of hexagonally oriented chalcogen atoms, as shown in Figure 2.3B. This creates an X-M-X monolayer configuration with thicknesses in the range 6-7 Å (6.5Å for MoS_2 for example).⁷⁰

Although all TMD monolayers are composed of hexagonally arranged atomic planes, the specific structure of the X-M-X layers varies depending on the transition metals and chalcogens involved. This gives rise to distinct polymorphs,⁷¹ different intralayer metal-chalcogen coordinations, stabilised by the most energetically favourable bonding configuration. Monolayers can be found in either a trigonal-prismatic or octahedral configuration, as shown in [Figure 2.3B](#). The manner in which these layers stack can also vary, leading to the existence of polytypes.⁷¹ The most common polytypes, shown in [Figure 2.3C](#), are the 1T (trigonal), 2H (Hexagonal) and 3R (Rhombohedral) phases, where the integer refers to the number of layers per unit cell. In MoS₂, for example, the semiconducting 2H phase of is the most stable form, although a metallic 1T phase can be stabilised under specific pressure and temperature conditions.⁷²

As the transition metal progresses from Group IV to Group X elements across the periodic table, the d-orbitals become increasingly filled. This d-electron configuration plays a central role in the electronic diversity of TMDs. Strong covalent bonding between the metal d-orbitals and the chalcogen s- and p-orbitals create bonding (σ) and antibonding (σ^*) bands, between which lie the d-bands,¹³ as shown in [Figure 2.4A](#). The occupancy of these bands determines the materials electronic properties.⁶⁹ When the d-bands are only partially filled the material displays metallic behaviour, such as in 1T-ReS₂. In contrast, the 2H phase of MoS₂ and WS₂ have a completely filled d_z -band, placing the Fermi level between the energy bands, which leads to semiconducting properties.¹³

Additionally, the number of d-electrons in the transition metal centre strongly influences the preferred structural phase of a TMD. Group IV TMDs, which possess d^0 electron configurations, typically adopt an octahedral coordination environment. In contrast, Group VI TMDs with d^2 configurations are generally found in the trigonal prismatic 2H phase. This phase preference can be altered by modifying the d-electron count through alkali metal intercalation. For example, the intercalation of alkali metals into MoS₂ leads to the donation of electrons to

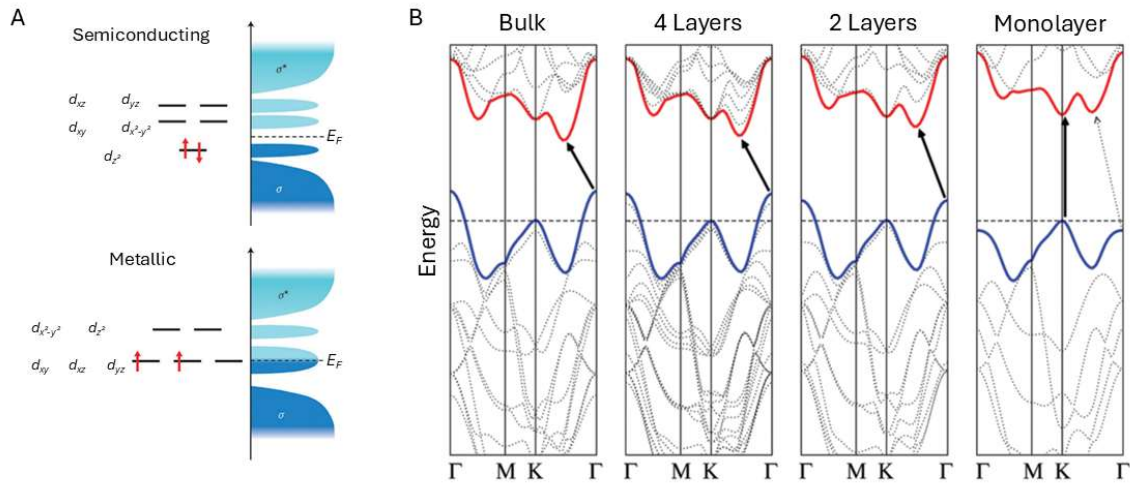


Figure 2.4: TMD Band Structures. **A)** Filling of the non-bonding d-orbitals for a typical d^2 TMD along with the band structure and the representative position of the Fermi level for the 2H phase (semiconducting) and 1T phase (metallic). [Adapted from Ref. ¹³] **B)** Calculated band structures for different thickness MoS_2 showing a transition from an indirect gap to a direct gap band structure. [Adapted from Ref. ¹⁷]

the Mo d -bands, destabilising the 2H phase and inducing a phase transition to the 1T phase.^{73, 74} Experiments indicate that this transition is not strictly binary but can proceed through the formation of intermediate polymorphic states combining features of both 2H and 1T phases.⁷⁵ Chalcogen atoms also play a role in shaping the band structure of TMDs by influencing orbital overlap. As the atomic number of the chalcogen atom increases, the d -band broadens and the bandgap narrows.⁷⁶ For example, in moving from MoS_2 to MoTe_2 , the bandgap reduces from 1.3eV to 1.0eV.⁶⁸

As TMDs are thinned to the monolayer limit, changes in symmetry, interlayer coupling, and quantum confinement significantly alter their properties.⁷⁷ For example, as shown in Figure 2.4B, bulk MoS_2 is an indirect bandgap semiconductor, with its valence band maximum (VBM) at the Γ -point and conduction band minimum (CBM) between the Γ and K. In contrast, monolayer MoS_2 becomes a direct-gap semiconductor with both VBM and CBM at the K-point.⁷⁵ This shift arises from modified hybridisation between sulphur p_z - and molybdenum d -orbitals due to confinement effects. The resulting direct bandgap

leads to a four-order-of-magnitude increase in photoluminescence and a 50% increase in the bandgap energy compared to the bulk.⁷⁸ This tuneable 1-2 eV bandgap range makes group VI TMDs promising for optoelectronic applications compatible with silicon technology.

2.3 Synthesis of Nanomaterial Dispersions

The synthesis of nanomaterials can be broadly categorised into two paradigms, bottom-up and top-down. Bottom-up methods involve constructing nanostructures atom-by-atom, typically through tightly controlled chemical or physical processes.⁷⁹ Chemical Vapour Deposition (CVD) is a prime example of a bottom-up approach, enabling the synthesis of high-quality films of materials such as graphene or transition metal dichalcogenides (TMDs).⁸⁰ CVD offers excellent control over thickness, crystallinity and uniformity making it ideal for fundamental studies and device fabrication, however, it suffers from operational complexity and exorbitant costs. Other bottom-up routes include wet chemical syntheses, such as the polyol process, which remains the predominant method to produce silver nanowires with high aspect ratios and excellent electrical properties.³⁵

In contrast, top-down approaches produce nanostructures from bulk precursors by physical or chemical disintegration.⁷⁹ A notable example is micromechanical exfoliation, which gained fame following the isolation of monolayer graphene via the infamous "scotch tape method".²¹ While this method does yield high quality flakes, its lack of scalability limits its practical applicability. Liquid-phase exfoliation and electrochemical exfoliation have since emerged as the dominant scalable alternatives for the production of 2D nanomaterials.^{81, 82} These methods harness physical or chemical forces to overcome the van der Waals interactions within layered crystals, resulting in the cleaving of nanosheets into liquid suspensions. LPE and EE are valued for their versatility and simplicity.

The ability to produce liquid dispersed nanomaterials has made solution processing a highly attractive approach for their synthesis, manipulation and characterisation. Liquid-based nanomaterial inks allow for extensive processing and high-throughput analysis, enabling techniques such as optical spectroscopy to extract statistically meaningful insights from dispersions containing vast ensembles of nanomaterials.⁸³ Dispersed nanomaterials can be readily sorted by size or thickness,¹⁴ facilitating precise control over material properties. Moreover, liquid dispersions are compatible with a range of long-established scalable deposition techniques, including inkjet printing,⁸⁴ aerosol jet printing,^{85, 86} spray coating,^{87, 88} spin coating^{89, 90} and screen printing.⁹¹ In the case of layered crystals, such as graphene and TMDs, the liquid phase delamination process can typically be categorised into two approaches: intercalation-based and exfoliation-based processing.

Liquid-Phase Exfoliation

Liquid-phase exfoliation (LPE) emerged rapidly following the isolation of graphene, with its development occurring just four short years after the breakthrough of mechanical exfoliation.⁸¹ Building on a long history of research into chemical exfoliation methods, LPE provided a straightforward and scalable route to isolating mono- and few-layer nanosheets from layered crystals. Unlike earlier methods that were laborious and typically produced only nanoscale quantities of nanomaterials, LPE enables production of gram to kilogram scale quantities of high quality nanosheets^{28, 81} that are largely defect free and preserve the basal plane;²⁸ characteristics that are desirable for electronic and optoelectronic applications.

The process involves dispersing layered crystal powders in a liquid medium and applying an energy (typically, shear force mixing or ultrasonication) which is sufficient to overcome the van der Waals interactions holding the layered crystals together. [Figure 2.5A](#) illustrates this process: a bulk layered material is introduced into a stabilising environment, typically organic solvents or aqueous solutions

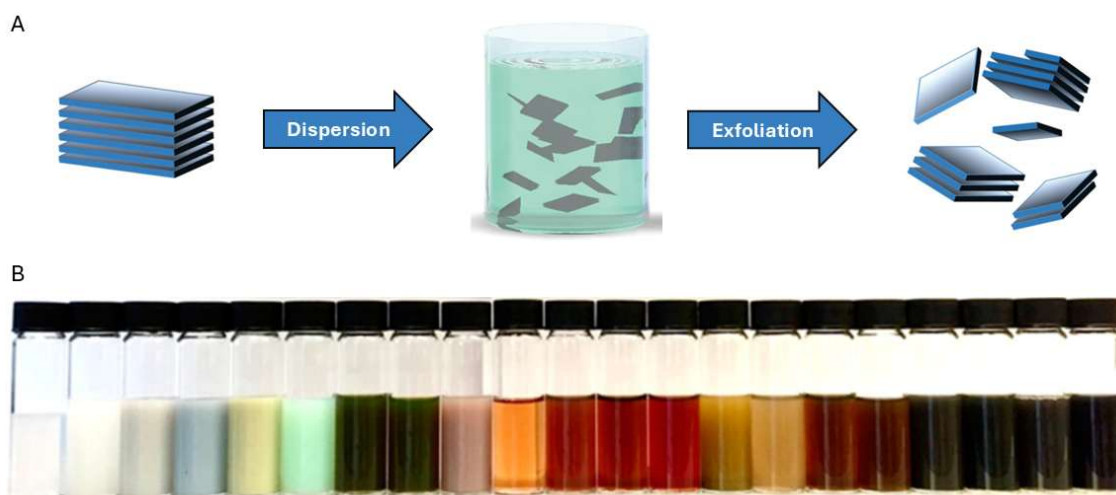


Figure 2.5: Liquid-Phase Exfoliation. **A)** Schematic of the LPE process. [Adapted from Ref. ¹] **B)** A range of nanomaterial dispersions produced using LPE. [Adapted from Ref. ³]

containing surfactants or polymers. These stabilisers not only aid in the exfoliation process but also prevent reaggregation of the exfoliated material (discussed in detail later),³ highlighting the importance of solvent selection or stabiliser selection. Then the dispersion is subjected to a suitable form of energy, such as ultrasonication or equipment which produce large shear forces. This energy cleaves the layers from their parent material to produce a dispersion of nanomaterials. One of LPE's greatest strengths is its versatility. Virtually every member of the layered material family including graphene, TMDs and hexagonal boron nitride has been successfully exfoliated using this technique (Figure 2.5B).⁹² Furthermore, LPE produced dispersions can be readily formulated into inks,⁹³ pastes⁹⁴ and composites,⁹⁵ or can be easily post-processed using established techniques, enabling scalable integration into devices via printing and coating technologies.

Ultrasonication

Ultrasonication is the most widely used method for lab-scale LPE. Originally developed for submarine detection during World War 1,⁹⁶ the field of ultrasonics has since expanded into a diverse range of applications, from medicine⁹⁷ and communications⁹⁸ to cheap ultrasonic jewellery and glassware cleaners.

Ultrasonication involves using a transducer to generate high frequency mechanical vibrations. When employed for LPE these vibrations are directed into metal probes at frequencies of ~20 kHz with amplitudes of ~100 μm . These oscillations produce intense ultrasonic waves at the probe tip, which propagate through the liquid medium causing the surrounding molecules in the liquid to oscillate about their equilibrium positions.⁹⁹ When local pressure drops below a critical threshold, transient cavities (referred to as cavitations) form in the liquid. These cavitations collapse violently, producing high energy microjets and shockwaves,¹⁰⁰ which create a highly energetic local environment. The resulting shear and tensile stresses act on the dispersed material and facilitates exfoliation and fragmentation of the layered crystals,^{28,81} as displayed by [Figure 2.6](#).

Ultrasonication reliably produces mono- and few-layer nanosheets from a wide variety of layered materials,^{92, 101} cementing its status as the ubiquitous lab-scale exfoliation technique. Tip sonication generally produces higher concentrations of 2D nanomaterials, however, the rapid decay of acoustic intensity away from the probe tip imposes some limitations on the scalability of the method. Bath sonication is a promising alternative but suffers from spatial inhomogeneity due to standing wave interference patterns of ultrasonic waves within the bath, which can affect reproducibility.¹⁰² These limitations are often mitigated through post processing and characterisation techniques such as centrifugation,¹⁴ which allows isolation of desired nanosheet sizes.

There has been some speculation that high intensity ultrasonication may induce basal plane defects and scission.¹⁰² However, extensive studies suggest that the resulting nanosheets broadly retain a pristine basal plane,²⁶ with many basal plane defects often attributed to the quality of the starting material rather than the exfoliation technique itself.¹ This places ultrasonic LPE at the forefront of solution-based methods for 2D material processing. Despite its widespread use, further optimisation of the technique is still possible due to the broad range of operational parameters. For instance, recent work has shown the ability to control graphene

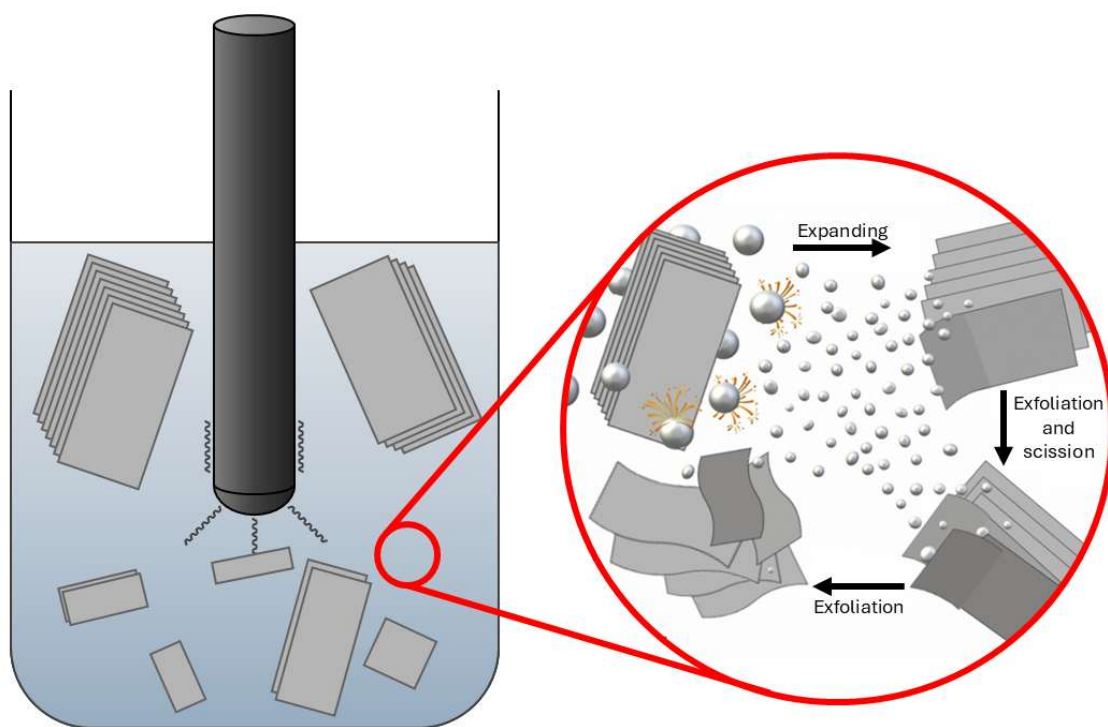


Figure 2.6: Ultrasonic LPE. Schematic illustration of the ultrasonication process for LPE.

flake size by tuning sonication parameters, achieving yields of ~20% few-layer graphene after just 3 hours of processing time.¹⁰⁰ While many optimisations can be made to ultrasonic LPE, it is a reliable technique for the production of many 2D materials, including some presented later in this thesis.

Beyond Ultrasonication

Several alternative LPE strategies exist beyond ultrasonication, offering improved scalability and compatibility with industry. Among these, shear-based exfoliation has emerged as a particularly promising route for the large-scale production of 2D materials.^{103, 104} By applying high shear forces on liquid dispersed layered crystals, the van der Waals interactions between layers can be overcome, allowing for exfoliation to proceed. Devices such as rotor-stator mixers, high-shear homogenisers or even the humble kitchen blender can achieve this effect.¹⁰⁵ These methods are particularly appealing to industry due to their simplicity, scalability and low cost, however, they often yield broader nanosheet thickness distributions and generally suffer from low mono- or few-layer yields.¹⁰⁴

More recently, other LPE techniques have gained traction, including microfluidisation and high-pressure homogenisation. In microfluidisation, the liquid dispersed layered crystals are driven through narrow microchannels at extremely high pressures, creating strong shear gradients and turbulence that facilitates exfoliation. This method has been shown to offer good size control with narrow polydispersity in many cases.¹⁰⁶ High pressure homogenisation employs repeated cycles of pressure-driven fluid acceleration through narrow valves, inducing cavitation, shear and impact forces which exfoliate the parent crystal.¹⁰⁷

Each of these techniques present distinct advantages in terms of throughput, nanosheet quality, simplicity and integration. While ultrasonication remains the dominant lab-scale technique due to its simplicity and versatility, shear and pressure driven methods represent critical steps toward the scalable production of 2D materials in industry.

Electrochemical Exfoliation

The very human desire for ever increasing performance has led to the search for methods to produce larger and thinner nanosheets. The energies required in LPE to exfoliate 2D nanomaterials from their parent crystal in a reasonable timeframe are also typically large enough to induce scission in the basal plane of the nanomaterials.¹⁰² This means that finding large, thin nanosheets using LPE is like searching for a black cat in a coal cellar. This is the greatest limitation faced by LPE. The rise to prominence of electrochemical exfoliation (EE) seeks to overcome this limitation. EE promises to produce large and thin nanosheets for use in high performance printed electronic devices.¹⁰⁸

Electrochemical exfoliation is an exfoliation method in which large intercalating ions are introduced between the layers of vdW crystals, typically by means of applying a bias across the parent crystal.¹⁰⁹ The introduction of intercalants between the layers increases the interlayer spacing which in turn reduces the van der Waals binding energy between the layers.¹¹⁰ Some light exfoliation techniques

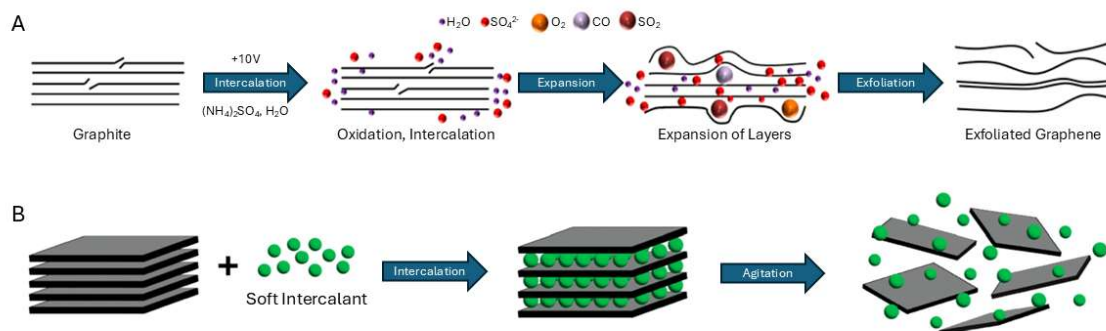


Figure 2.7: Electrochemical Exfoliation. A) Process of EE for graphene nanosheets.

[Adapted from Ref. ¹¹] **B)** Process of intercalation using soft intercalants for TMD nanosheets. [Adapted from Ref. ¹⁶]

(even vigorous shaking by hand) can then be used to cleave single layers of nanomaterials from the parent crystal. The lack of harsh ultrasonication or shear forces preserves the lateral size of the nanosheets and can result in much larger mono- or few-layer 2D nanomaterials.

Exfoliation by intercalation has been around for over a century. In 1859, graphite oxide was synthesised through the intercalation of graphite with concentrated acids followed by exfoliation with strong oxidisers.⁴⁸ The form that intercalation exfoliation takes today is seen by many to have much *less fatal* side effects. Modern electrochemical exfoliation strategies have evolved beyond the conventional oxidative or reductive protocols by leveraging softer, non-destructive intercalants such as quaternary ammonium salts^{108, 110} (e.g. TPA⁺ or THA⁺) and inorganic salts (e.g. (NH₄)₂SO₄).¹¹¹ These intercalants enable more gentle exfoliation pathways to reduce damage to the basal plane of the layered crystals. A promising attribute of these soft intercalants is their ability to avoid excessive oxidation or structural damage to the layered crystals, while still facilitating expansion of crystal which enables this “gentle” exfoliation. However, intercalants can also be selected to engineer the resultant nanosheets. For example, MoS₂ can be intercalated with BuLi to induce the 1T phase,¹¹² while quaternary ammonium salts achieve a the 2H phase^{20, 82} in the MoS₂ nanosheets.

Figure 2.7A shows the electrochemical exfoliation of graphene using ammonium sulphate ((NH₄)₂SO₄).^{111, 113, 114} In this process, a graphite crystal serves as the working electrode. Sulphate anions SO₄²⁻ intercalate between the layers of graphite under an applied bias, expanding the interlayer spacing and weakening the vdW interactions. It is believed that electrochemical generation of oxygen and hydroxyl radicals at the anode attacks the graphite edges and grain boundaries via oxidative cleavage.¹¹⁵ These radicals promote intercalation of sulphate anions but may also introduce defects in the graphene nanosheets, an effect not seen in LPE. Once intercalated, the decomposition of sulphate ions and electrochemical oxidation of water lead to the evolution of SO₂ and O₂ gases, which further expand the graphite structure.¹¹ The expanded graphite is then gently sonicated to exfoliate graphene nanosheets.

Another common EE pathway is the intercalation of layered materials with quaternary ammonium salts,^{20, 31, 110, 116} which is displayed in Figure 2.7B. These bulky organic cations wedge between layers, and, due to their large size steric repulsion is enough to expand the interlayer spacing and reduce the vdW interactions in the crystal.¹¹⁷ The use of quaternary ammonium salts has the huge benefit of preserving the basal plane without causing significant oxidation or defects.¹¹⁶ The expanded layered crystal can then be gently sonicated to exfoliate large area, clean and electronically intact nanosheets, perfectly suited to high-performance electronic devices.

These soft intercalants are compatible with a broad range of materials, including TMDs, h-BN and many other layered materials.^{82, 108} For example, exfoliation of MoS₂ using THA⁺ or TPA⁺ can produce thin (often monolayer) nanosheets with lateral sizes up to 10 µm and defect free basal planes.³¹ Most of the residual intercalants can often be removed through washing steps, further enhancing this method for use in high-performance electronic devices.

Electrochemical exfoliation using soft intercalants offers several key advantages such as high aspect ratio nanosheets, relatively pristine basal planes and tunability while also avoiding the use of harsh chemicals, high temperatures or pressures. However, despite these benefits, EE faces some notable challenges. Throughput is typically low due to the limited exfoliation rates and batch-based processing, making scalability a concern for industry.¹¹⁸ The prohibitively high cost of high purity starting crystals can also drive-up costs, further alienating this technique from industry. Balancing the superior nanosheet quality with the practical limits imposed by this technique remains a critical challenge for current day research.

2.4 Stabilisation of Nanomaterial Dispersions

Successful exfoliation of layered crystals into dispersion is one thing but keeping them stable in dispersion is a whole other challenge. The same vdW forces that once held the layers together in the bulk crystal will now act to pull the individual exfoliated nanosheets back towards each other and reunite them into large aggregates. Stabilisers can be introduced to prevent this phenomenon from occurring while also having the added benefit of reducing the energetic barrier to exfoliation through favourable interactions with nanosheet surfaces.¹ This is most commonly achieved through the clever selection of solvents¹¹⁹ or incorporating surfactants¹²⁰ or polymers^{121, 122} into the dispersion.

Solvent Stabilisation

Efficient stabilisation in dispersions occurs when the energetic cost of mixing is minimised by matching the parameters which govern the solubility of the solvent and solute. Early work with carbon nanotubes (CNTs) showed that stable dispersions could be achieved by matching surface energies.¹²³ This concept was later extended to 2D nanosheets where further studies showed that better surface energy matching between the nanosheets and the solvent could significantly improve dispersion concentration, though often at the cost of using hazardous

solvents like NMP and DMF.¹²⁴ While this principle holds broadly, a full understanding of stabilisation requires considering all intermolecular interactions,¹²⁵ best described by the system's Gibbs free energy, ΔG_{Mix} :

$$\Delta G_{\text{Mix}} = \Delta H_{\text{Mix}} - T\Delta S_{\text{Mix}} \quad [2.1]$$

where T is the temperature, ΔH_{Mix} is the enthalpy of mixing and ΔS_{Mix} is the entropy of mixing. Given their size, the entropy component for nanomaterials is assumed to be negligible,²⁷ so to minimise the Gibbs free energy of the system, the enthalpy of mixing must be minimised. This is governed by the Flory-Huggins interaction parameter, χ , where $\chi < 0$ indicated favourable solvent-solute interactions and $\chi > 0$ leads to aggregation.¹²⁶ For nanosheets, a relevant form of χ is:

$$\chi = \frac{v_0}{k_B T} (\delta_A - \delta_B)^2 \quad [2.2]$$

Here, v_0 is the molecular volume, T is the temperature and δ_i are what's known as the Hildebrand solubility parameters of the solvent and solute.¹²⁷ The Hildebrand solubility parameter is a commonly used form of the cohesive energy density which can be divided into three components:

$$\frac{E_{C,T}}{V} = \frac{E_{C,D}}{V} + \frac{E_{C,P}}{V} + \frac{E_{C,H}}{V} \quad [2.3]$$

where $E_{C,T}$ is the total molar cohesive energy, V is the molar volume of the solvent and $E_{C,D}$, $E_{C,P}$, $E_{C,H}$ is the molar cohesive energy of the dispersive, polar and hydrogen-bonding components. The square root of each component is the so-called Hansen solubility parameter:

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad [2.4]$$

In polar solutes, it is necessary to match each of the Hansen solubility parameters to achieve a stable dispersion, while non-polar solutes only need to match the Hildebrand solubility parameters. We can arrive at a general expression for the

Flory-Huggins interaction parameter by inserting the Hansen solubility parameters in place of the Hildebrand parameters in Equation 2.2, giving

$$\chi = \frac{v_0}{k_B T} \left[\left(\delta_{D,A} - \delta_{D,B} \right)^2 + \left(\delta_{P,A} - \delta_{P,B} \right)^2 + \left(\delta_{H,A} - \delta_{H,B} \right)^2 \right] \quad [2.5]$$

Through the reduction of χ the free energy of a dispersion can be minimised resulting in more stable dispersions of nanomaterials and more efficient exfoliation.¹²⁸

Surfactant Stabilisation

To avoid the many drawbacks of high-boiling point, often toxic solvents, exfoliated nanosheets can instead be stabilised in aqueous dispersions using surfactants as stabilisers.¹²⁰ This strategy, which is rooted in early work on CNTs,¹²⁹ relies on amphiphilic molecules that adsorb non-covalently onto nanosheets. The hydrophobic tail interacts with the basal plane of the nanosheets via London dispersion forces. The hydrophilic head interacts with the polar aqueous environment, promoting dispersion.¹³⁰ Common surfactants like dodecylbenzene sulfonate (SDBS) and sodium cholate (SC) have been successfully employed to exfoliate and disperse various 2D nanomaterials.^{83, 131-133}

Surfactants stabilise dispersions by forming an electrical double layer (EDL) around each nanosheet, generating electrostatic repulsion that prevents reaggregation.¹²⁹ This interaction can be described by DLVO theory,¹³⁴⁻¹³⁶ where the balance between vdW attraction and electrostatic repulsion is modelled. By considering the attractive and repulsive energies of spherical particles of radius, r , and separation, D , the following equation for the potential energy of the system, V , can be obtained:¹³⁷

$$V = \frac{\epsilon_0 \epsilon_r r^2 \zeta^2}{D} e^{-\kappa D} - \frac{Ar}{12D} \quad [2.6]$$

Where ζ is the zeta potential of the dispersion, A is the Hamaker constant, ϵ is the permittivity and κ^{-1} is the Debye screening length. Long-term stability typically requires ζ exceeding ± 30 mV or can be enhanced by increasing the Debye screening length through higher surfactant concentrations, approaching the critical micelle concentration.

Despite the promise of non-toxic, scalable and cheap aqueous surfactant systems, they present challenges for practical use. Surfactants can cause interfaces between junctions in networks which can significantly impair device performance (discussed in detail later). Moreover, the relatively high viscosity of water also poses challenges for well-established printing methods, like inkjet or AJP, where low-viscosity, volatile solvents are generally preferred.

2.5 Size Selection

Exfoliation methods such as LPE and EE delaminate layered crystals into nanosheet dispersions. However, this process introduces a significant amount of polydispersity in both lateral size and thickness.^{1, 138} Commercially available bulk powders already possess a broad distribution of flake sizes, and exfoliation processes introduce additional fragmentation across the basal plane, further broadening lateral dimension distributions. Moreover, incomplete exfoliation leaves a wide range of thicknesses, particularly with LPE based methods. This polydispersity poses challenges for applications: thin monolayers are needed for optoelectronics and high-performance electronic devices,³¹ while mechanical reinforcement may benefit from larger flakes.¹³⁹

Liquid Cascade Centrifugation

To address this, centrifugation has become the primary technique for size and thickness sorting of 2D nanomaterials. Two strategies have been widely employed; density gradient ultracentrifugation (DGU) and liquid cascade centrifugation (LCC). DGU separates materials based on their buoyant density within a medium

of graded density. This technique has been employed, to great success, for sorting carbon nanotubes,^{140, 141} however extremely low yields and contamination from residual density media ultimately confine the technique to the realm of the laboratory. Moreover, the near-identical density of mono- and many-layer nanosheets limits its use for the separation of 2D nanosheets.

A more widely adopted technique is sedimentation-based separation, where nanosheets are sorted by their sedimentation under centrifugal forces. The Svedberg equation¹⁴² states

$$s = \frac{m(1 - PV)}{f} \quad [2.7]$$

The sedimentation coefficient, s , depends on the mass, m , solvent density, ρ , partial specific volume, V , and the frictional coefficient, f . Larger and thicker nanosheets, having greater mass, sediment rapidly, while thinner flakes remain suspended for longer.

Building upon this principle, liquid cascade centrifugation (LCC) was developed to fractionate nanosheet dispersions by incrementally increasing the centrifugal force (centrifugation speed) and sequentially removing the sediment from each fraction.^{3, 14} A typical LCC workflow is shown in [Figure 2.8](#) and consists of the following: The as-liquid-phase-exfoliated dispersion is first subjected to a centrifugation at $28 \times g$. The sediment from this first fraction is discarded as it contains any unexfoliated or extremely large particles. The supernatant is then centrifuged at sequentially higher speeds ($112 \times g$, $252 \times g$, $447 \times g$, $699 \times g$, $1006 \times g$, $1789 \times g$, $4025 \times g$). After each stage, the sediment is collected and can be readily redispersed by gentle sonication,¹⁴³ yielding dispersions with progressively smaller (in lateral size) and thinner nanosheets. This cascade-like process allows for fine-tuning or selectivity in nanosheet dimensions. Furthermore, since all material is recovered after each step (i.e. both the sediment and the supernatant), LCC offers very low wastage.

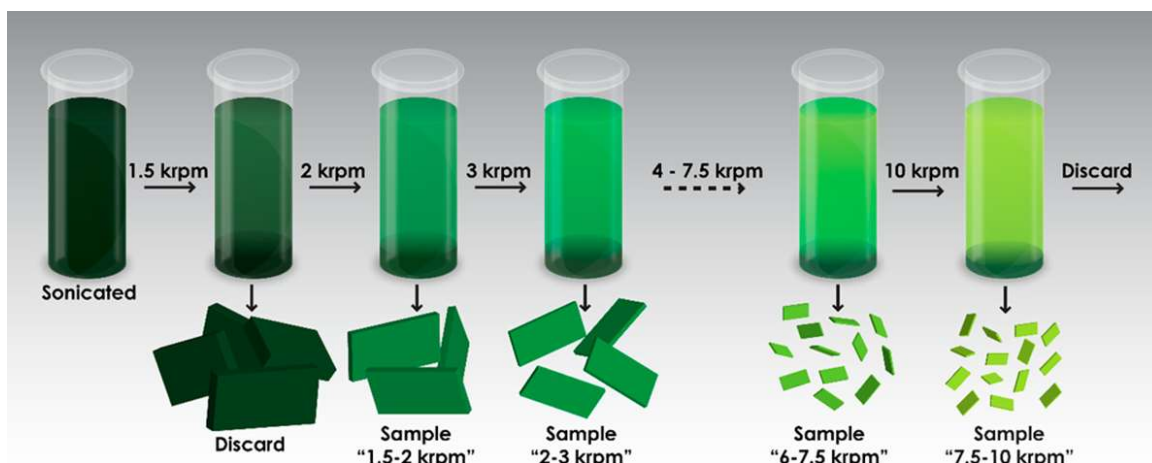


Figure 2.8: Liquid Cascade Centrifugation. The workflow followed during an LCC process to size select nanosheet dispersions. [Adapted from Ref. ¹⁴]

It is worth noting that LCC cannot select nanosheet aspect ratio. Each fraction tends to have similar mean aspect ratios, as large, thin nanosheets sediment alongside small, thick ones due to their similar mass. It has recently been shown that the lateral length, l_{NS} , and thickness, t_{NS} , of nanosheets in fractions produced by LCC are intrinsically linked by $\langle l_{NS} t_{NS} \rangle \propto \omega^{-2}$ where ω is the angular frequency of the centrifugation step.¹⁴⁴ While LCC is a powerful tool due to its simplicity, accessibility and compatibility with high-throughput processing, it is limited by distribution of aspect ratios of the starting dispersion. Nonetheless, its ability to trap specific nanosheet populations make it an ideal tool for applications such as nanomaterial size-dependent studies.

Sonication-Induced Scission

Previously, we discussed how basal plane fragmentation presents a major limitation to the LPE processes, restricting the lateral size of monolayers produced. However, sonication-induced scission can also serve as a powerful post-synthetic tool to size-select nanomaterials such as 1D nanowires¹⁴⁵ or nanotubes¹⁴⁶ or even 2D materials¹⁴⁷ close to the monolayer limit. As previously stated, when a dispersion of nanomaterials is subjected to ultrasonic agitation, acoustic cavitation leads to the formation, growth and collapse of microscopic gas bubbles. The rapid

implosion of these bubbles generates intense local shear forces, high temperatures and pressure gradients, which are sufficient to induce scission in 1D nanostructures and within the basal plane of 2D nanosheets. In 1D nanowires (NWs) and nanotube (NTs), this fragmentation occurs almost exclusively in the axial direction, thereby shortening the NWs or NTs over time.¹⁴⁸

The degree of scission depends on both the properties of the material and the sonication parameters. Higher aspect ratio and longer nanomaterials, such as long AgNWs or CNTs, are more susceptible to fragmentation due to the larger drag forces they experience in the collapsing cavitation field.¹⁴⁸ Intrinsic bonding characteristics of nanomaterials also plays a role in the scission process.¹⁴⁹ For example, CNTs display exceptional mechanical strength and Young's modulus in the axial direction due to strong sp^2 carbon bonding, whereas AgNWs are held together by weaker metallic bonds. As a result, CNTs typically require longer sonication durations or higher sonication powers to achieve a comparable degree of shortening.¹⁵⁰

The evolution of mean nanowire or nanotube length under scission follows a power law relationship with time.¹⁴⁹ This behaviour arises because the scission process is most efficient at fragmenting longer, higher aspect ratio material. As the structures shorten, the probability of scission reduces and the required force to induce scission increases, resulting in a decelerating rate of length reduction. This behaviour follows

$$\langle l_{NW} \rangle \propto t^\alpha \quad [2.8]$$

Where l_{NW} is the length of the NW or NT after a time, t . α is typically in the range 0.2 to 0.5,^{40, 146, 148, 149} depending on material, bonding strength, solvent and energy input. This power law decay reflects an asymptotic behaviour in which the length of the nanomaterial population approaches a steady-state length distribution at which further scission is no longer possible or favourable.

*"If a man knows not which port he sails,
how can he know which winds are
favourable?"*

Seneca

CHAPTER 3

DEPOSITION AND CHARACTERISATION OF NANOMATERIAL NETWORKS

Nanomaterials promised to revolutionise everything from electronics to energy, medicine to manufacturing. Decades later, the only thing they've truly revolutionised is the buzzwords used in scientific funding applications. The great nanomaterial revolution is being held back in two key areas: nanomaterial synthesis and deposition. The ability to harness the exceptional properties of nanomaterials, such as high conductivity, mechanical flexibility, and chemical tunability, relies not only on the synthesis of high-quality nanostructures, but critically the ability to incorporate them into functional macroscopic devices. One of the most versatile approaches is the formation of ensembles of 0D, 1D, or 2D nanostructures forming a complex network. Networks of nanomaterials, such as those shown in [Figure 3.1A-C](#), are percolating films made from many discrete nanomaterial building blocks (such as AgNWs, graphene nanosheets and MoS₂ nanosheets) whose macroscopic properties arise from the numerous interactions between individual nanoparticles.

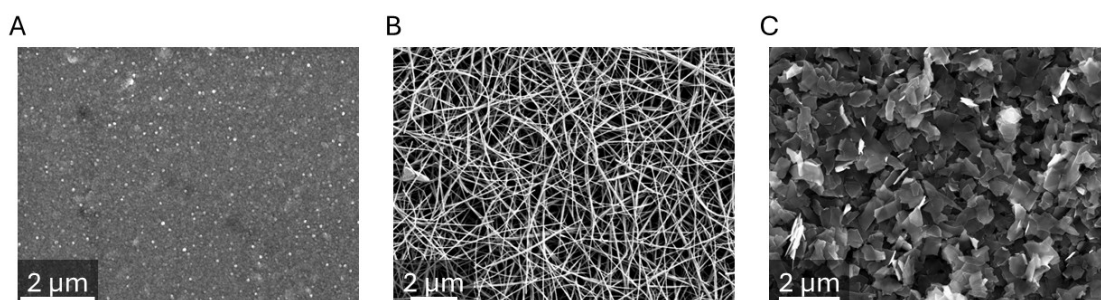


Figure 3.1: Nanomaterial Networks. SEM images of networks of **A)** 0D AlO nanoparticles, **B)** 1D AgNWs and **C)** 2D LPE Graphene Nanosheets

Nanomaterial networks underpin a growing range of emerging technologies including printed electronics,¹⁵¹ wearable sensors,^{152, 153} flexible devices,^{154, 155} and neuromorphic devices.³³ Their electrical performance is dictated by both the intrinsic properties of the constituent nanomaterials, and by the structure, morphology, and especially the electrical properties of the inter-particle junctions that dominate charge transport through the network.

This chapter covers the deposition techniques and characterisation methods required to understand and control the performance of nanomaterial networks with a focus on the enhancement of their electrical properties. Following deposition, a range of structural and electrical characterisation methods, including spectroscopic measurements, microscopy, DC resistance measurements, and impedance spectroscopy, are employed to interrogate both the network and the individual junctions that make up the network. By decoupling nanomaterial and junction resistance contributions, this chapter lays a basis for the understanding of charge transport mechanisms in nanomaterial networks.

3.1 Network Deposition

Deposition of nanomaterial networks range from precise printing methods, such as inkjet and aerosol jet printing (AJP), which allow controlled deposition and high-resolution patterning, to rapid but inaccurate techniques like spin-coating and screen printing, known for creating large-area uniform films. These methods all

come with their own benefits and downfalls, and each are well suited to their own niche applications.

Spray-coating and liquid-liquid interface deposition (LLID) offer versatility and suitability to creating large-area nanomaterial networks; hence they are the primary deposition techniques used in this work. Spray-coating provides a straightforward, scalable, broadly compatible approach, efficiently accommodating various solvents and substrates with minimal ink formulation constraints. LLID complements spray coating by providing exceptional control over nanosheet alignment and network morphology, facilitating the production of high quality, densely packed networks that significantly enhance (opto)electronic performance.

Spray Coating

The pop-culture term “airbrush” – often associated with smoothing away minute imperfections in celebrities’ photos – has its roots in a much more literal process: spray-coating.¹⁵⁶ Long before it became shorthand for digital vanity, airbrushing referred to the controlled deposition of materials using pressurised gas. Spray coating can be traced back to the late 19th century when it was patented for fine artistic work.¹⁵⁷ A simple, versatile and scalable method, spray coating found use across a wide range of industries from cosmetics¹⁵⁸ and art to industrial coatings and manufacturing.¹⁵⁹ Spray-coating first found its way into nanomaterials research when it was explored as a technique to deposit carbon nanotubes, creating transparent conductors as alternatives to ITO.¹⁶⁰ It quickly caught on as a rapid prototyping technique within the lab and has since been used to deposit all kinds of nanomaterials and functional inks.^{87, 88, 161-164}

The spray coating process involves atomising an ink into a fine aerosol and directing it towards a substrate using a carrier gas, often nitrogen gas (N₂). [Figure 3.2B](#) shows a schematic of a laboratory spray coating setup, where the ink is typically gravity fed from a reservoir into the nozzle assembly. The trigger of the

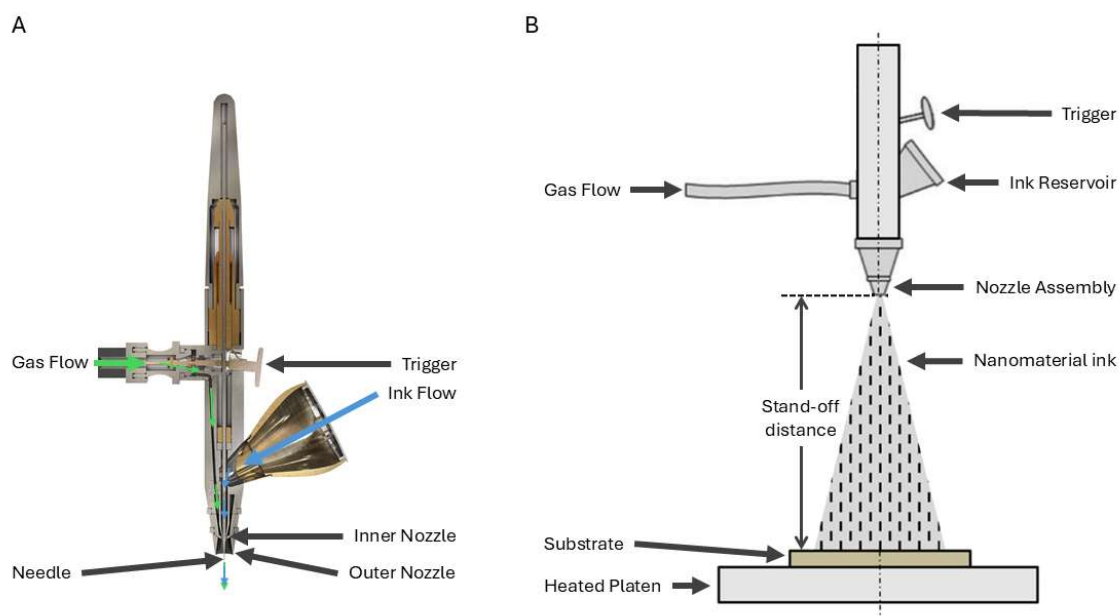


Figure 3.2: Spray-Coating. **A)** Cross-sectional image of an airbrush used for spray-coating. **B)** Schematic illustration of the spray-coating process for the production of nanomaterial networks. [Adapted from Ref. 8]

spray gun directly controls the position of the needle shown in Figure 3.2A. Once the trigger is operated, the needle retracts from the nozzle to create an opening, allowing a controlled flow of pressurised N_2 to escape. Ink is fed toward the nozzle assembly where the high velocity gas shears small droplets, typically tens of microns in diameter, from the ink supply and directs them towards a heated substrate. Some of the ink solvent is evaporated during this travel time and once the droplet lands on the substrate, any remaining solvent rapidly evaporates, leaving behind a dry, uniform layer of material.

The versatility of spray coating stems from its generation of a fine aerosol through gas assisted atomisation. Spray coating inherently decouples solvent and substrate constraints by avoiding strict ink viscosities or surface tension requirements, unlike droplet-on-demand methods such as inkjet printing.¹⁵⁴ This permits the use of a broad range of solvents, without additives, such as water, alcohols and even high boiling point organics (when done in a safe and controlled manner). It also enables deposition onto various substrates such as silicon wafers, glass, PET, textiles and paper.¹⁶⁵ This flexibility allows spray coating be compatible

with a diverse range of nanomaterials such as nanoparticles,¹⁶⁶ nanowires,¹⁶² CNTs,¹⁶⁷ graphene²⁶ and TMDs;⁸⁸ making it a powerful tool in the field of flexible and printed electronics.

Despite its simplicity, spray coating offers a high degree of parameter tunability, enabling optimisation of film formation and reproducibility. The key variables in spray coating, some of which are illustrated in [Figure 3.2A,B](#), include stand-off distance, gas flow rate, backpressure, nozzle diameter, ink flow rate, rastering speed and substrate temperature. The footprint of the spray plume and hence the density of deposited material is influenced by the stand-off distance. Smaller distances can increase the flux of material landing on the substrate but may risk splashing or substrate wetting. Larger stand-off distances broaden the deposition area at the cost of reduced material flux.¹⁶⁸

The gas backpressure regulates the ink's exit velocity, which plays the dominant role in controlling droplet size and can affect the plume size.¹⁶² Higher backpressures will increase shear forces acting on the ink at the nozzle tip, creating smaller droplets with a narrow size distribution. A narrower size distribution will result in more uniform, homogeneous films while the smaller droplet size expedites solvent drying and evaporation, also reducing solvent coalescence and preventing the occurrence of the "coffee ring" effect (material accumulation at droplet edges due to capillary flows during solvent evaporation). Previous studies performed on AgNWs¹⁶² demonstrated that increasing the N₂ backpressure from 15 to 30 psi significantly reduced droplet size and improved film homogeneity. Similar improvements in film uniformity have been observed in other nanomaterial systems, especially when combined with elevated substrate temperature.

Substrate heating also plays a vital role in controlling solvent evaporation. Heating the substrate to elevated temperatures accelerates solvent evaporation upon droplet impact. This can reduce wetting, spreading and coalescence, leading to improved film uniformity. However, if the substrate temperature is too hot, the

solvent can violently boil off causing splashing and film damage. Moreover, some substrates such as polymers and textiles are not compatible with elevated temperatures. The interplay between these factors – droplet size, substrate temperature and solvent volatility – all collectively determine the drying dynamics of the droplet and, ultimately, the film morphology.

Spray coating presents many advantages for nanomaterial network production. It is well suited to controllable, large area, homogeneous deposition of films but may suffer from its inability to directly pattern. Where selective area coverage is required, spray coating must be combined with masks or stencils to define features. While this approach is suitable for a vast range of applications such as displays, solar cells and electrochromic devices, it can fall short in applications demanding high resolution features.

Liquid-Liquid Interface Deposition

A critical aspect in determining the electrical, optoelectronic and chemical performance of nanomaterial networks is their morphology.¹⁸ Non-contact deposition techniques, such as spray coating or AJP often produce poorly aligned, highly porous and randomly oriented networks. While such structures may be beneficial for catalysis and sensing, they typically hamper charge transport in electronic applications.⁶ In 2D systems, improved basal plane alignment and overlap are known to significantly improve electrical performance.^{20, 151} Liquid-liquid interface assembly techniques aim to achieve this by physically confining nanosheets into ordered, dense films at the boundary between immiscible liquids.

The concept of interface assembly has historical roots. In 1835, Justus von Liebig developed the silver mirror reaction by reducing silver nitrate to metallic silver directly on glass.¹⁶⁹ In the late 1800s the Schotten-Baumann reaction mediated chemical synthesis using biphasic organic-aqueous systems.^{170, 171} These early examples demonstrated the ability of fluid interfaces to control material deposition. A major leap came in 1917, when Langmuir developed the concept

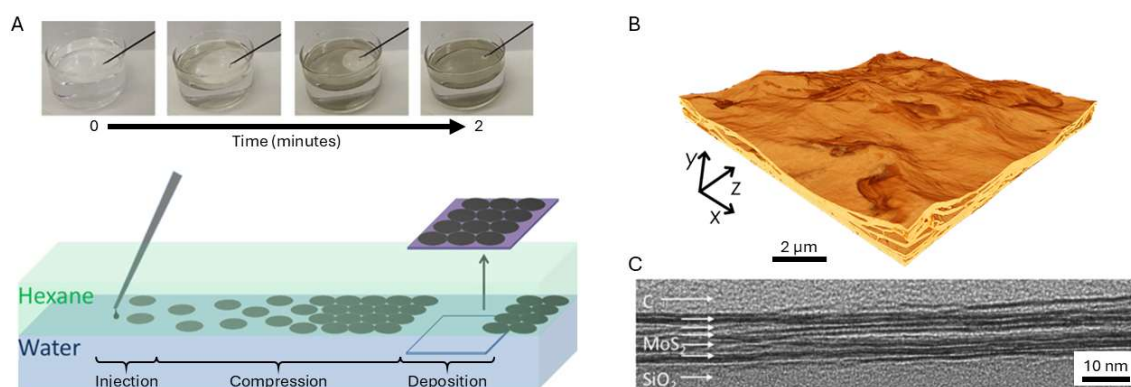


Figure 3.3: Liquid-Liquid Interface Deposition. **A)** Schematic illustration of the LLID process for the production of nanomaterial networks. [Adapted from Ref. ¹⁰] **B)** 3D-FIBSEM nanotomography image of a representative LLID graphene nanosheet network. [Adapted from Ref. ¹⁸] **C)** Cross-sectional SEM image of a MoS₂ nanosheet LLID network. [Adapted from Ref. ²⁰]

of monolayers assembling on air-water interfaces.¹⁷² Katherine Blodgett later developed a method to transfer these monolayers onto substrates by vertically extruding the substrate perpendicular to the interface,¹⁷³ now known as Langmuir-Blodgett deposition. In 1938 Schaefer showed the devil really is in the details by introducing a technique involving the withdrawal of a substrate in the *horizontal* position through the interface, now known as the Langmuir-Schaeffer method.¹⁷⁴ The transition from molecular monolayers to nanostructures began in 1980, when Pieranski showed that nanoparticles could self-assemble into dense films at liquid-liquid interfaces.¹⁷⁵ Furthermore, shortly after the isolation of graphene monolayers the deposition of graphene films using liquid interfaces quickly followed when in 2009, Biswas employed liquid-liquid interface assembly to create a thin film of graphene.¹⁷⁶

At its core, liquid-liquid interface deposition (LLID) relies on the thermodynamically driven assembly of nanosheets at the boundary between two immiscible liquid phases, typically, water and an organic solvent. When a dispersion of nanosheets is introduced to one of the phases, the nanosheets spontaneously align on the liquid-liquid interface due to surface tension gradients and differences in polarity. The amphiphilic nature of nanosheets means they will experience an energetic

penalty when fully immersed in either the polar (aqueous) or non-polar (organic) phase. Their hydrophobic basal planes and hydrophilic edges minimise interfacial energy by straddling the two environments, forcing them to align parallel to the interface. Once aligned at the interface, lateral diffusion drives the nanosheets to arrange into dense, ordered, close packed films.¹⁰

Early work with 2D material LLID involved dispersing the nanosheets in one of the liquid phases. A second immiscible liquid was then introduced, and through gentle agitation, the nanosheets would align at the interface.¹⁷⁶ More recent work has refined the LLID approach by controlled injection of a small amount of dispersion directly between the interface of two immiscible liquids. This strategy facilitates the rapid growth of large area uniform films, with extremely low material requirements.¹⁰ Figure 3.3A shows an illustration of this technique. Subsequent layers can then be deposited, enabling thickness control. Crucially, each subsequent layer lies flat atop the last, promoting a high degree of basal plane overlap. This results in improved transport across nanosheet-nanosheet junctions (a concept which will be discussed in the next section).

LLID can be used in combination with electrochemically exfoliated nanosheets to produce networks with near theoretical electrical performance. The high degree of basal plane alignment in LLID networks, in conjunction with the highly conformable and large area nanosheets produced by EE, results in a network morphology consisting of well aligned nanosheets, with large overlap areas at junctions and low porosity,¹⁷⁷ as shown in Figure 3.3B,C. These techniques have been employed to produce flexible transistors of MoS₂ and WS₂, which achieve outstanding mobilities of up to 11 cm² V⁻¹ s⁻¹ and on/off ratios of up to 2.6×10^3 .^{31, 116} Additionally, it has been shown that EE graphene films as thin as 11 nm can reach near theoretical conductivities of up to 1.3×10^5 S m⁻¹.¹¹⁴ LLID also shows great versatility, having been successfully employed to produce high quality, ultrathin networks of TMDs, graphene and low-aspect ratio silver nanosheets.²⁰

The highly aligned and low porosity nature of LLID networks of 2D nanosheets results in minimal pinholes, even at low thicknesses, enabling the production of ultrathin, solution deposited, pinhole free dielectrics. This opens the door to the production of heterostructures and stacked 2D material systems for next generation electronic devices. Despite its many advantages, LLID remains largely constrained to laboratory settings, being difficult to scale and often exhibiting poor reproducibility for thinner films. Expanding this process toward industry scalability remains a key challenge in nanomaterial research.

3.2 The Role of Junctions in Nanomaterial Networks

Whether composed of 0D nanoparticles, 1D nanowires/tubes, or 2D nanosheets, a defining characteristic of nanomaterial networks is the presence of inter-particle junctions. These junctions serve as critical bottlenecks to electrical conduction, forming where two nanoparticles come into contact and charge carrier exchange is permitted. From here on, "nanoparticles" refers to a nanostructure without defining any geometry, unless otherwise stated. So, for example, these could be 2D nanosheets, 1D nanowires/tube or 0D nanodots. The intrinsic conductivity of individual nanoparticles is typically much higher than that of the resulting networks, a discrepancy which is primarily attributed to these junctions. Accordingly, the overall network conductivity is largely governed by the nature of these junctions. Thus, in the context of charge transport, the junction resistance (R_j) emerges as a key determinant of network performance.

At its core, a junction is the physical interface where a charge carrier must transit from one discrete nanoparticle to another. The nature of this interface, and the energetic barrier it presents, is fundamentally dictated by the geometry and electrical properties of the constituent nanoparticles. Whether a network is composed of 0D, 1D or 2D nanoparticles, the geometry, surface chemistry and

resultant electronic properties of these junctions define the limits of charge transport in the network.

In systems of 0D nanoparticles, junctions are effectively point contacts. Furthermore, due to their extreme surface area to volume ratio, 0D nanoparticles are heavily reliant on capping agents and bulky stabilising ligands to prevent agglomeration. As a result, the conductivity of as produced networks of 0D nanoparticles is often very poor relative to their constituent nanoparticles due to the electronic transport being overwhelmingly dominated by quantum tunnelling across the junctions. As a result, 0D networks often require post-processing techniques such as thermal annealing or chemical treatment to form intimate contact at the junction interface. In 1D nanoparticle networks, such as silver nanowires or carbon nanotubes, junctions typically form as crossed overlapping line contacts. While the physical contact area of 1D networks is only marginally larger than that found in 0D networks, the junction density per nanoparticle (i.e. the number of junctions formed with a single nanoparticle) has the potential to be much larger in 1D networks. As with 0D nanoparticles, 1D nanoparticles also regularly rely on capping agents during synthesis and hence networks of 1D nanoparticles also typically require some post-processing steps to reduce the junction resistance and increase the overall conductivity. In networks of silver nanowires, for example, where polyvinylpyrrolidone (PVP) is used as a capping agent, thermal annealing initiates sintering of the junction interface, converting an insulating tunnelling barrier into a continuous metallic weld.³⁰

2D nanomaterials present a distinct geometry advantage in the potential for large basal plane overlap. Structurally, when two nanosheets stack on top of each other, the junction can come close to mimicking the van der Waals interactions of the bulk material, offering a huge contact area for charge transport. In solution-processed networks, these junctions are rarely pristine, with residual solvent and/or stabilisers typically present at the nanosheet basal planes. Electronically, charge carriers must transition from highly efficient in-plane transport to restricted out-of-

plane transport. Consequently, the junction resistance is highly sensitive to the basal plane alignment and conformity and the chemical purity of the interface.^{6,18}

Across all dimensionalities, the physical geometry and local chemistry of these interfaces collapse into a single macroscopic parameter, the inter-particle junction resistance. Nanoparticle networks inherently consist of thousands or millions of such imperfect contacts repeated across each percolating pathway. Isolating their electronic contribution from the intrinsic properties of the nanoparticles themselves is paramount to optimising network performance.

Conductive nanoparticles have recently seen some success in approaching the intrinsic conductivity of their constituent nanomaterial with graphene networks reaching $\sim 10^5 \text{ S m}^{-1}$,¹⁵¹ MXenes reaching $\sim 10^6 \text{ S m}^{-1}$,¹⁷⁸ AgNWs reaching $>10^6 \text{ S m}^{-1}$ ^{30, 179} and AgNSs reaching $>10^7 \text{ S m}^{-1}$.¹⁸⁰ While conductive networks are nearing the performance of their constituent nanoparticles, semiconducting networks continue to lag. Semiconducting single-walled carbon nanotube (s-SWCNT) networks typically display mobilities $<100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ^{90, 181} compared to $>10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ achievable for individual nanotubes.¹⁸² Similarly, networks of TMDs such as MoS₂ achieve $<20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ^{31, 116} compared to $>100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ achievable for individual nanosheets.^{183, 184} In such systems, even when the nanoparticles themselves possess excellent intrinsic properties, resistance at the junctions can drastically degrade the electronic performance of the overall network.

The conformity and morphology of the network play a strong role in determining the degree of junction limitation. Conformal, large-area junctions facilitate efficient charge transfer, reducing R_j and enhancing network conductivity. For example, when EE nanosheets are spray-coated they exhibit conductivities up to $4 \times 10^4 \text{ S m}^{-1}$,^{18, 177} whereas LLID networks have shown conductivities up to $1.3 \times 10^5 \text{ S m}^{-1}$.¹¹⁴ This improvement is attributed to better alignment and nanosheet overlap in LLID networks. Similarly, the conformity or flexibility of nanomaterials can also affect the junction resistance. So thinner, higher aspect ratio nanosheets will

produce better junctions. Spray-coated networks of EE graphene show conductivities reaching $\sim 10^5 \text{ S m}^{-1}$, significantly higher than spray-coated LPE graphene networks reaching $4 \times 10^4 \text{ S m}^{-1}$.¹⁸ Such observations make it clear that there are many factors affecting junction resistance; therefore, understanding the impact of synthesis and deposition on junction morphology is critical to evaluating and improving network transport.

Studying charge transport across *both* the junctions and the nanoparticles themselves is essential for a comprehensive understanding of network transport behaviour. Although many examples of charge transport studies in nanomaterial networks in the literature are junction-limited, assuming this universally can be misleading. In high-performance systems where R_J is comparable to the nanoparticle resistance, R_{NP} , this assumption no longer holds and may lead to incorrect interpretations. Traditional methods for studying charge transport mechanisms, such as the measurement of conductivity and/or mobility as a function of temperature, do not fully capture the complexities of charge transport in these networks. This is because charge carriers traversing a nanonet must alternate between two modes of conduction; intra- and inter-particle charge transport.^{6, 181, 185}

Carriers must spend some time traversing the nanoparticles themselves (intra-particle transport), which may occur via bandlike conduction in crystalline materials¹⁸⁶ or hopping in disordered or defective ones.¹⁸⁷ However, after traveling through a nanoparticle, it will always be necessary for the carrier to transit to the next nanoparticle, i.e., to cross a particle–particle junction. We refer to this as inter-particle transport and, in most cases, it will occur via hopping or tunnelling.^{151, 181} Movement of carriers over long distances within networks will always involve alteration between intra- and inter-particle transport. As such, the basic unit of resistance associated with a nanomaterial network is $R_J + R_{NP}$, where R_{NP} is the resistance of the (average) nanoparticle and R_J is the resistance of the (average) junction.⁶ Consequently, measurements of temperature-dependent network

resistivity probe only $R_J + R_{NP}$, making it difficult to separate the effects of intra- and inter-particle charge transport.

To properly study the charge transport mechanism in nanomaterial networks, it is necessary to independently characterise both intra-particle and inter-particle charge transport mechanisms. Put simply, both R_J and R_{NP} must be measured as a function of temperature (or magnetic field or gate voltage etc.). Only through decoupling these contributions can one truly assess and improve the electrical performance of nanomaterial networks.

Current Literature Knowledge on Junction Resistances in Networks

Currently, data from the literature on values of R_J are hard to come by. Extracting values for R_J can typically only be achieved by measuring single junctions,¹⁸⁸ computational analysis² or by employing convoluted models. Metallic nanowires are the most studied system in the literature, likely due to the ease of working with them. Various studies exist for AgNWs, from which R_J can be found to lie in the range $1 - 10^4 \Omega$. These results are extracted from a mixture of single junction measurements¹⁸⁸⁻¹⁹² and fitting simulation to experiment.^{2, 193, 194} The vast range in R_J can be attributed to differing junction morphologies which can be present at AgNW-AgNW junctions.¹⁸⁸ For CuNW networks, Manning et al.¹⁹⁵ found R_J to be $205 \pm 58 \Omega$ from single junction measurements.

Few similar studies have been carried out for CNT systems. Fuhrer et al.¹⁹⁶ used direct 4-terminal measurements on SWCNTs to extract a junction resistance of $90 - 360 \text{ k}\Omega$. Using a similar method, Postma et al.¹⁹⁷ found R_J on the order $1 - 10 \text{ M}\Omega$ for SWCNT buckles and junctions. Nirmalraj et al.¹⁹⁸ used conductive AFM (cAFM) on SWCNT networks and found R_J roughly in the range $0.1 - 10 \text{ M}\Omega$, depending on how the networks were treated (annealing, acid-treated or pristine) and the nanotube diameter. Nirmalraj et al.¹⁹⁹ also carried out cAFM on junctions of graphene strips to find that the junction resistance scales linearly with flake thickness from $0.1 - 10 \text{ k}\Omega$. Similarly, Clifford et al.²⁰⁰ found the junction resistance in

graphene networks to scale with nanosheet length using a size-dependent model, similar to that which we propose later in this chapter. They found R_J to range from 0.1 – 10 k Ω for LPE graphene.

Despite the scarcity of studies on the junction resistance in nanomaterial networks, we can still come to some conclusions. It is clear, that for all systems, there is a large distribution in junction resistances. This is likely due to the large amount of variability in junction morphologies that can exist in these networks, especially when random deposition techniques such as spray-coating or drop-casting are used. It is also clear that, currently, the junction resistance is difficult to measure, often requiring the use of specialised techniques, such as conductive AFM or the deposition of micro-electrodes. A model which could account for junction variability and could be used with simple, existing characterisation techniques would be an extremely valuable tool for network optimisation.

Modelling the Junction Resistance

A primary focus of this work was to develop a model relating the conductivity of a nanomaterial network to both the junction resistance and nanomaterial resistance. To achieve this, we considered a completely general case of a network of nanoparticles. By examining a single conducting path through the network (as shown in [Figure 3.4A,B](#)), we can quickly see that it is equivalent to a chain of resistors. As described previously, carriers must spend time traversing the nanoparticles themselves, then cross a junction to reach the next nanoparticle, and so on. This suggests that our resistor chain consists of alternating nanoparticle resistors (R_{NP}) and junction resistors (R_J). Therefore, the basic unit of resistance associated with a network is $R_J + R_{NP}$.

Note: A complete derivation of the model⁶ is available in the [Appendix A.4](#) of this text. For the sake of everyone's sanity, a very brief overview of the derivation is provided here. When we consider a voltage, V , that is applied to the network, we can calculate the voltage drop across the junctions and nanoparticles

individually. From this, we can determine the time it takes for a carrier to traverse the entire network and, once again, reduce this the time associated with individual junctions and nanoparticles. With the time, voltage drop, and resistance associated with carriers transiting the junctions, the nanoparticles and the network, we can derive an equation for the mobility, μ_{Net} , of a network

$$\mu_{Net} = \frac{(d_{NP} + d_J) / d_{NP}^2}{\left[1 + \frac{R_J}{R_{NP}}\right]} \frac{\mu_{NP} / \kappa_{Net}}{\left[1 + \frac{\mu_{NP} e R_{NP}}{d_{NP}^2}\right]} \quad [3.1]$$

where d_{NP} and d_J represent the average distances a carrier travels through a nanoparticle and junction, μ_{NP} is the nanoparticle mobility and κ_{Net} is the tortuosity of the network, indicating the deviation of conducting pathways from a straight line (a measure of how convoluted the charge transport pathways are). Typically, $d_J \gg d_{NP}$, therefore

$$\mu_{Net} \approx \frac{\mu_{NP} / \kappa_{Net}}{\left[1 + \frac{R_J}{R_{NP}}\right] \left[1 + \frac{d_{NP} / A_{NP}}{n_{NP} d_{NP}^2}\right]} \quad [3.2]$$

where A_{NP} is the effective nanoparticle cross-sectional area, with $R_{NP} = d_{NP} / \sigma_{NP} A_{NP}$ and $\sigma_{NP} = n_{NP} e \mu_{NP}$. Here, μ_{NP} , σ_{NP} and n_{NP} are the nanoparticle mobility, conductivity and carrier density, respectively. While an equation for the network mobility is very useful, it would be even more valuable to have an expression for the resistivity or conductivity of a network. Two methods to achieve this are detailed in [Appendix A.4](#). One approach involves making the reasonable assumption that $n_{Net} = n_{NP}(1 - P_{Net})$, where P_{Net} is the network porosity, yielding

$$\sigma_{Net} \approx \frac{\sigma_{NP}(1 - P_{Net}) / \kappa_{Net}}{\left[1 + \frac{R_J}{R_{NP}}\right] \left[1 + \frac{d_{NP} / A_{NP}}{n_{NP} d_{NP}^2}\right]} \quad [3.3]$$

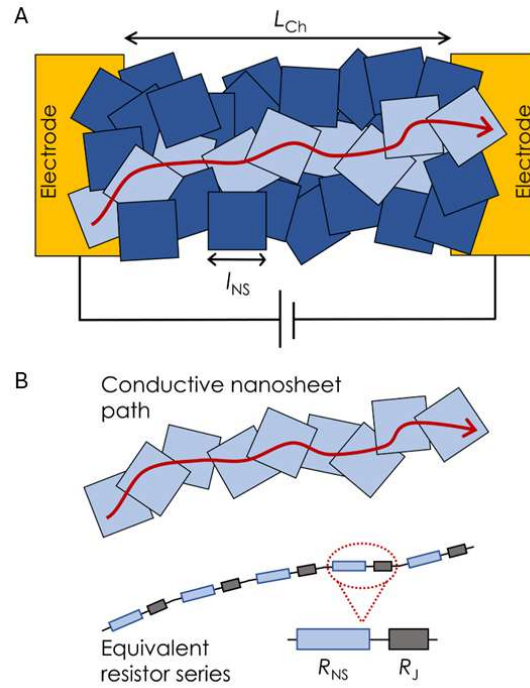


Figure 3.4: Model Schematic for Nanosheet Network. **A)** Schematic illustrating a nanosheet network connected to two electrodes with a channel length, L_{Ch} , under an applied voltage. A single conducting path consisting of a linear array of nanosheets is shown spanning the channel length (red arrow). The nanosheet lateral size is l_{NS} . While the schematic depicts a nanosheet network, a similar diagram could easily be produced to represent networks of other nanostructures. **B)** This conducting path can be considered as a chain of resistor pairs, with each pair consisting of a resistance representing a nanosheet, R_{NS} , and the inter-sheet junction, R_J . [Adapted from Ref. ⁶]

It is important to note that this equation is completely general and does not define any specific geometry. The geometric parameters d_{NP} and A_{NP} are written in a completely geometry-independent form. Therefore Equation 3.3 can be applied to any relevant system of conducting particles, whether they are 0D, 1D or 2D, by defining appropriate values of d_{NP} and A_{NP} .

3.3 Nanomaterial and Network Characterisation

Now that we have a model to describe the conductivity of a network, we need to characterise it. Numerous characterisation techniques exist to extract useful information from both networks and nanomaterials; far too many to

comprehensively cover here. A brief discussion on some of the relevant techniques is provided, followed by a deeper exploration of some of the electrical characterisation techniques which are fundamental to this work.

UV/Vis spectroscopy is a widely used technique for characterising nanomaterial dispersions. This technique functions by passing light at various wavelengths through a sample and measuring the transmitted light, as displayed by [Figure 3.5A](#). The absorption of light occurs when the energy of the photons matches the energy required for electronic transitions in the nanomaterial. In semiconductors, this transition is typically from valence to conduction band, while in molecular systems it can be from bonding to antibonding orbitals. The resulting absorption spectrum is displayed as a function of wavelength, with peaks corresponding to these specific electronic transitions. For nanomaterial dispersions, UV/Vis spectroscopy can provide information about electronic structure, size, shape and concentration.^{3, 83, 201, 202} In this work, UV/Vis is used to confirm the presence of graphene nanosheets in dispersion and validate our use of LCC for size-selection.

Raman spectroscopy is a powerful tool for characterising nanomaterial dispersions and networks. [Figure 3.5B](#) shows the technique works by inelastically scattering monochromatic light off a sample, causing shifts in the scattered light's frequency that correspond to the vibrational modes of the material. The resulting Raman spectrum provides information about vibrational, rotational, and other low-frequency modes of the material. Raman spectroscopy is especially useful for studying the structural properties of individual nanostructures, such as defect density, crystallinity and functionalisation. For example, as shown in the experimental chapters of this work, in graphene nanosheets the intensity ratio of the D to G bands can indicate the relative defects in the system.^{83, 203}

Scanning and transmission electron microscopy (SEM and TEM) are both powerful electron-based imaging techniques widely used for characterising nanomaterials and networks, providing complementary insights into the material's

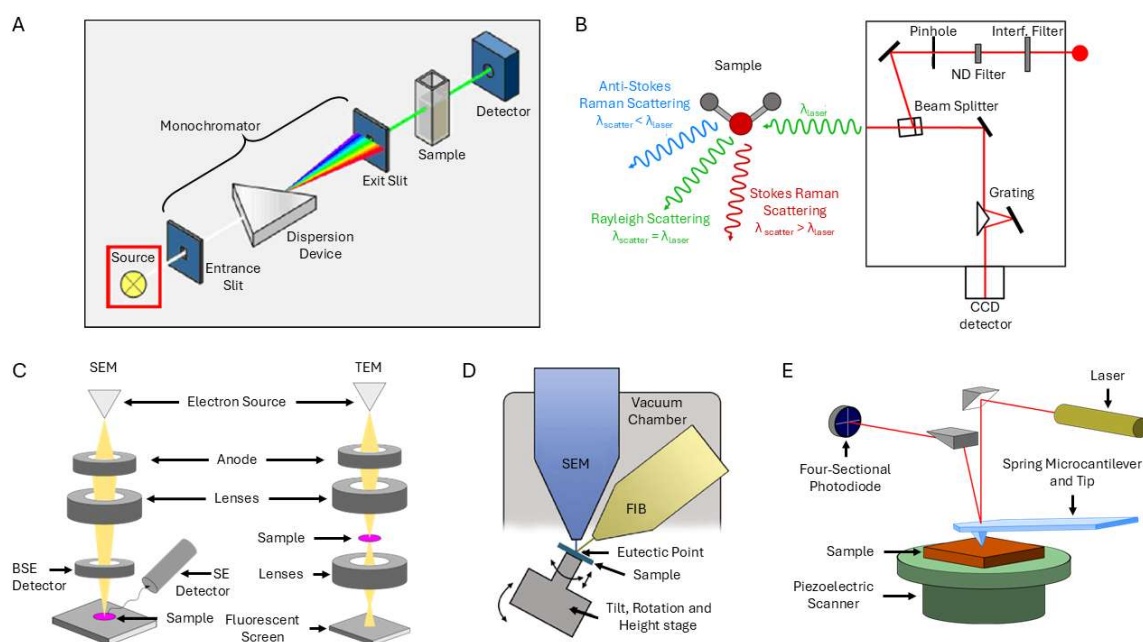


Figure 3.5: Characterisation Techniques. **A)** Schematic illustrating UV/Vis Spectroscopy. **B)** Schematic illustrating Raman Spectroscopy. **C)** Schematic illustrating both SEM and TEM. **D)** Schematic illustrating FIB-SEM nanotomography. **E)** Schematic illustrating AFM.

structure, morphology and composition and are displayed in Figure 3.5C. SEM scans the surface of a sample with a focused electron beam and measures the backscattered and secondary electrons to produce an image. It is useful for observing the shape and size of nanomaterials as well as the formation and morphology of networks. In contrast, TEM passes a beam of electrons through a thin sample and measures the transmitted electrons to produce an image. TEM offers extremely high resolution, and can be used for investigating the internal structure of nanomaterials, such as lattice structure, defects and atomic arrangement.⁶⁷ Together, TEM and SEM supply a comprehensive imaging system for nanomaterials and networks. Our work uses the techniques to analyse the shape and size of both nanowires and nanosheets.

Focused ion beam-scanning electron microscopy (FIB-SEM) combines the capabilities of both FIB and SEM, offering high-resolution imaging with the ability to modify the sample at the nanoscale. FIB uses a focused beam of ions to mill or etch the sample, which can allow for sample alterations or cross-section cutting.

Once a cross-section has been cut, it can be imaged with SEM, as shown in [Figure 3.5D](#). By using FIB to take small slices off the face of the sample, repeated imaging and milling can be used to produce a range of cross-section images of a network. After appropriate image segmentation, a large set of 2D images can be produced, with each pixel labelled by its material composition. These images can then be combined to generate a 3D image where each voxel represents (in our case) either free space (part of a pore) or the nanomaterial. Typically, such 3D images have resolution of 5 nm in the image plane and 15 nm out of plane, i.e., the voxel size is $5 \times 5 \times 15 \text{ nm}^3$. In principle, such images contain all structural and morphological information relating to the network which is available at the resolution of the image, such as network porosity, nanomaterial orientation and pore shape and size.

[Atomic force microscopy \(AFM\)](#) is a versatile technique used to characterise the surface properties of nanomaterials with high spatial resolution. AFM operates by scanning a sharp tip, mounted on a flexible cantilever, across the surface of a sample, as displayed in [Figure 3.5E](#). The tip interacts with the sample surface, inducing forces that create deflections in the cantilever, which are subsequently measured and converted in topographical images. AFM can provide details about surface roughness, morphology and some mechanical properties. In nanomaterial systems and in our case, AFM is particularly useful for measuring nanosheet thickness to create a thickness distribution of dispersions, making it an essential tool for nanomaterial characterisation.

DC Electrical Characterisation

Measuring the electrical resistance of a specimen is central to this work and essential for industrial applications of nanomaterial networks. To achieve this, the network's DC resistance, R_{Net} , must be measured. This is typically done by applying a voltage between two contacts across the sample and measuring the resulting current. Using Ohm's law, $R = V / I$, the resistance can then be calculated. In some

cases, it may be more suitable to run a voltage sweep across the sample and measure the output current as a function of voltage. A plot of voltage vs. current will display any non-linear behaviour, and the resistance can be extracted from the slope in the linear region.

Measuring resistance in this way introduces a significant challenge: contact resistance. Contact resistance refers to an additional resistance which arises between the sample and the electrodes. Many factors contribute to contact resistance, including imperfect electrical contact between the sample and the electrodes, mismatched work functions, poor Fermi level alignment between nanomaterials and electrodes, electron scattering at the interface and poor contact geometry. A four-terminal measurement configuration is often employed to exclude any contributions from contact resistance. This method involves contacting the sample in four locations. While various contact geometries exist, the most common and simplest configuration involves spacing the electrodes equally in a straight line, as demonstrated by [Figure 3.6](#). The two outer contact electrodes drive a constant current through the sample, and the two inner sense electrodes measure the potential difference between them. The sense electrodes, connected to a voltmeter, have a very high input impedance, meaning essentially no current flows through them. This results in the voltage measurement being

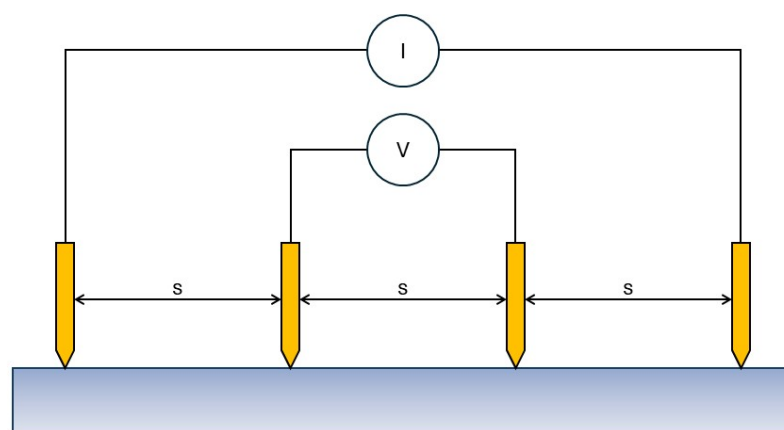


Figure 3.6: 4-probe Resistance Measurement. Diagram representing the electrode setup for a typical 4-probe resistance measurement. Each of the probes are placed an equal distance, s , apart.

uninfluenced by any current-induced voltage drop across the contact resistances at the sample-electrode interface.

Once the resistance of the sample is measured, the network conductivity, σ_{Net} , or resistivity, ρ_{Net} , can be extracted using

$$\sigma_{\text{Net}} = \frac{L_{\text{Ch}}}{R_{\text{Net}} t_{\text{Net}} W_{\text{Net}}}, \quad \rho_{\text{Net}} = \frac{1}{\sigma_{\text{Net}}} \quad [3.4]$$

where L_{Ch} is the channel length and t_{Net} and W_{Net} are the network thickness and width. It is important to note that t_{Net} can occasionally be measured using simple techniques such as a stylus profiler system, but where networks are thin or not mechanically robust other, more complex methods need to be employed. These methods can include cross-sectional imaging, phase shift interferometry or AFM measurements.

Relating the DC Electrical Properties to R_{J}

The network conductivity or resistivity can be related back to junction and nanomaterial resistance using our previous model. Recall [Equation 3.3](#), where the network conductivity was defined generally, without reference to nanomaterial geometry. By defining nanomaterial geometry, we can extract useful parameters from network resistivity measurements.

First, let's consider the case of 1D nanowires/tubes. Take R_{NS} as the resistance (on average) of the portion of the nanowire the electron passes through between junctions (length, d_{NW}). Assuming each nanowire has many junctions with other nanowires, this distance could vary from close to zero (junctions where electrons entered and left the nanowire very close together) to close to the nanowire length, l_{NW} , (junctions where electrons entered and left the nanowire very close to each end). The average distance travelled through the nanowire is roughly half the nanowire length, so d_{NW} can be replaced with $l_{\text{NW}}/2$. Then R_{NW} is given by

$$R_{NW} = \frac{l_{NW}}{2} \left/ \frac{\sigma_{NW} \pi D_{NW}^2}{4} \right. = \frac{2l_{NW}}{\sigma_{NW} \pi D_{NW}^2} \quad [3.5]$$

where $A_{NP} = \pi D_{NW}^2 / 4$. Then

$$\sigma_{Net} \approx \frac{\sigma_{NW} (1 - P_{Net}) / \kappa_{Net}}{\left[1 + \frac{R_J \sigma_{NW} \pi D_{NW}^2}{2l_{NW}} \right] \left[1 + \frac{8}{n_{NW} l_{NW} \pi D_{NW}^2} \right]} \quad [3.6]$$

This can be written in terms of ρ_{Net} and simplified to give

$$\rho_{Net} = \frac{\kappa_{Net}}{(1 - P_{Net})} \left[\rho_{NW} + \frac{\pi D_{NW}^2 R_J}{2l_{NW}} \right] \left[1 + \frac{8}{n_{NW} l_{NW} \pi D_{NW}^2} \right] \quad [3.7]$$

If we assume $\kappa_{Net} \approx 1$ and n_{NW} is very large (as is typically the case for conductors) then

$$\rho_{Net} = \frac{1}{(1 - P_{Net})} \left[\rho_{NW} + \frac{\pi D_{NW}^2 R_J}{2l_{NW}} \right] \quad [3.8]$$

From this equation we can see that $\rho_{Net} \propto 1/l_{NW}$, suggesting that measuring the network resistivity as a function of nanowire/tube length should yield a linear trend, with R_J and ρ_{NW} related to the slope and intercept, respectively.

Now, consider the case of 2D nanosheets. Assuming the nanosheets are square, the cross-sectional area can be written as $A_{NP} = l_{NS} t_{NS}$, where t_{NS} and l_{NS} are the mean nanosheet thickness and length. As with the 1D case, d_{NP} can roughly be equated to half the nanosheet length, resulting in $d_{NP} = l_{NS} / 2$, which gives

$$\frac{d_{NS}}{A_{NS}} = \frac{1}{2t_{NS}} \quad [3.9]$$

Therefore, an equation for the conductivity of a nanosheet network is given by

$$\sigma_{Net} \approx \frac{\sigma_{NS} (1 - P_{Net}) / \kappa_{Net}}{\left[1 + \frac{R_J}{R_{NS}}\right] \left[1 + \frac{2}{n_{NS} t_{NS} l_{NS}^2}\right]} \quad [3.10]$$

Once again, for conductors, n_{NS} is typically very large so the final term goes to 1. Assuming $\kappa_{Net} \approx 1$ then

$$\rho_{Net} = \frac{\rho_{NS} + 2t_{NS}R_J}{(1 - P_{Net})} \quad [3.11]$$

This equation predicts that the ρ_{Net} is proportional to t_{NS} , suggesting that measuring the network resistivity as a function of nanosheet thickness should yield a linear trend, and once again with R_J related to the slope and ρ_{NS} related to the intercept.

AC Electrical Characterisation – Impedance Spectroscopy

Impedance spectroscopy (or electrochemical impedance spectroscopy, EIS) originated in the early 20th century with the development of impedance measurements in AC circuits and has continued to perplex many poor PhD

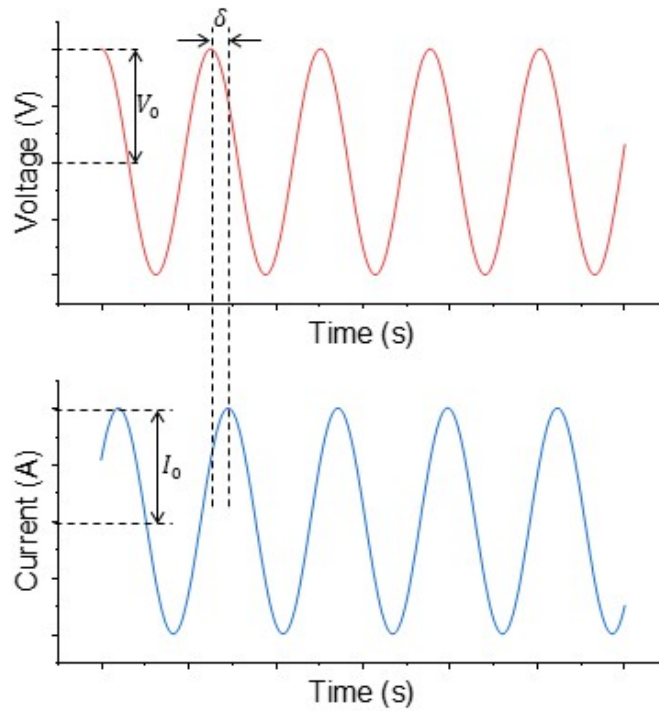


Figure 3.7: Impedance Spectroscopy. A graph of the applied voltage and resultant current during EIS. The current has a phase shift, δ , to the voltage.

students since. It gained wider use in the 60s and 70s with improved instrumentation, initially focusing on applications such as battery analysis^{204, 205} and corrosion studies.²⁰⁶ The technique quickly expanded its reach into materials science, particularly for characterising the electrical properties of thin films and semiconductors.²⁰⁷ While EIS has previously been used for the qualitative analysis of nanomaterial networks, such as CNT networks^{208, 209}, it has never been employed for the quantitative extraction of junction and nanomaterial resistances within such networks.

EIS operates by applying a small alternating sinusoidal voltage (or current) to a sample with an amplitude, V_0 , and frequency, ω , as shown in Figure 3.7, such that

$$V(\omega) = V_0 e^{i\omega t} \quad [3.12]$$

The resulting current alternates at the same frequency but may be phase shifted by an amount, δ , depending on the circuit elements under measurement

$$I(\omega) = I_0 e^{i(\omega t - \delta)} \quad [3.13]$$

The impedance, Z , is defined by Ohm's law

$$Z = \frac{V}{I} = \frac{V_0 e^{i\omega t}}{I_0 e^{i(\omega t - \delta)}} = \frac{V_0}{I_0} e^{i\delta} \quad [3.14]$$

The real, Z' , and imaginary, Z'' , components of impedance are given by de Moivre's theorem

$$Z' = \frac{V_0}{I_0} \cos(\delta), \quad Z'' = \frac{V_0}{I_0} \sin(\delta) \quad [3.15]$$

Typically expressed in terms of the modulus of impedance, $|Z|$, as

$$Z = |Z| \cos(\delta) + i |Z| \sin(\delta) = Z' + iZ'' \quad [3.16]$$

An impedance analyser typically measures $|Z|$ and δ across a range of frequencies, from which Z' , $-Z''$ and any other variables of interest can be calculated, and an impedance spectrum can be produced. The phase shift reveals reactance characteristics of the measured sample. Different circuit elements will induce a differing phase shift.

A resistor has purely real impedance, with a phase shift of 0°

$$Z_{\text{Res}} = R, \quad \delta = 0^\circ \quad [3.17]$$

A capacitor has purely imaginary impedance, with a phase shift of -90°

$$Z_{\text{Cap}} = -\frac{i}{\omega C}, \quad \delta = -90^\circ \quad [3.18]$$

Finally, an inductor has purely imaginary impedance, with a phase shift of 90°

$$Z_{\text{Ind}} = i\omega L, \quad \delta = 90^\circ \quad [3.19]$$

In practice, impedance spectroscopy involves measuring Z' and $-Z''$ as a function of frequency and fitting this data to an appropriate equivalent circuit model. As such, we must define an equivalent circuit for the analysis of nanomaterial networks. Previously, we said that there will be a resistance associated with the junctions and that carriers typically traverse junctions via hopping or tunnelling. Because of this resistance, when a potential is applied, there will be an accumulation of charge on either side of the junction, inducing a capacitance. This capacitance can be measured by impedance spectroscopy. We propose modelling these junctions with a Randles circuit, where the series resistance represents the nanomaterials and the parallel resistance and capacitance represents the junctions, as shown in [Figure 3.8A,B](#).

Direct measurement of a network's impedance yields a complex combination of many Randles circuits in series and parallel, offering only qualitative insights on the junctions and nanomaterials. This combination of Randles circuits is also equivalent

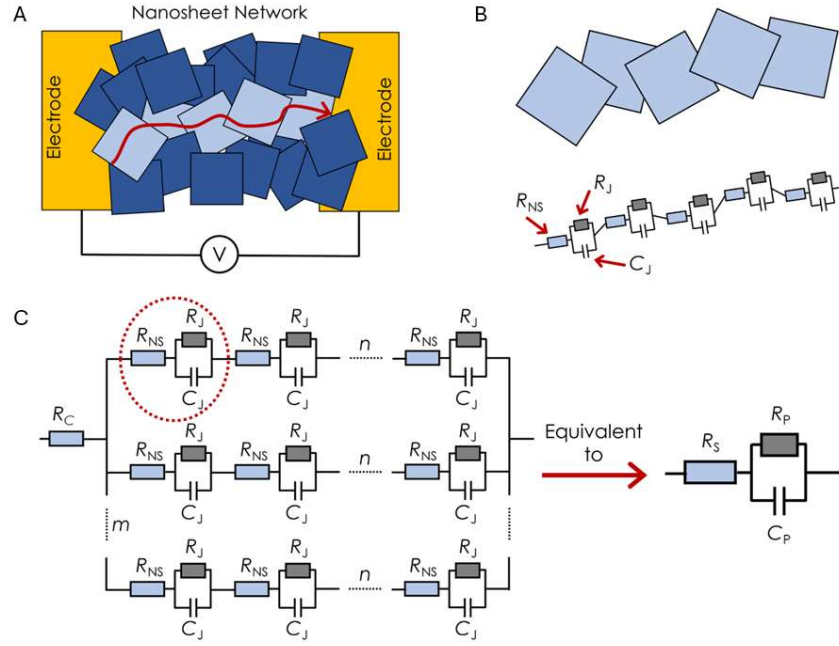


Figure 3.8: Equivalent Circuit Representing a Nanoparticle Network. **A)** Schematic of a nanosheet network between two electrodes under an applied voltage, V . Current flows through many parallel current paths (red arrow). **B)** Such a path is a linear chain of nanosheet-junction pairs. Each nanosheet-junction pair in the chain can be thought of a combination of a resistor representing the nanosheet (R_{NS} , blue) and a parallel combination of resistor (R_J , grey) and capacitor (C_J) representing the junction. **C)** Schematic showing a nanosheet network to consist of an array of circuit elements, each representing individual nanosheet-junction pairs (red dashed circle). In this representation, there are m parallel current paths, each containing n NS-J elements in series. The overall electrode-network contact resistance, R_C , is also shown. This is equivalent to the Randles circuit on the right, which comprises a series resistor, R_S , and a parallel combination of a resistor, R_P , and a capacitor, C_P .

to a single Randles circuit, as shown in Figure 3.8C, however, to obtain quantitative results, the overall network impedance must be converted into that of an average nanoparticle-junction pair using our previous model (Equation 3.3). For instance, in the 2D nanosheet network case; the network resistivity is related to R_{NS} and R_J via

$$\rho_{Net} = \frac{2t_{NS}}{(1 - P_{Net})} [R_{NS} + R_J] \left[1 + \frac{2}{n_{NS} t_{NS} l_{NS}^2} \right] \quad [3.20]$$

Here, all parameters are averages across the network. The mean resistance of a nanosheet-junction pair ($R_{NS} + R_J$) can be more generally represented by the

impedance of the nanosheet-junction pair, Z_{NS-J} . In addition, the network impedance is related to the network resistivity via $Z_{Net} = \rho_{Net} L_{Ch} / A_{Net}$, where L_{Ch} is the channel length and A_{Net} is the cross-sectional area of the network. In the case of a 2D network, this becomes

$$Z_{Net} \approx \frac{L_{Ch}}{A_{Net}} \frac{2t_{NS}\kappa_{Net}}{(1-P_{Net})} Z_{NS-J} \left[1 + \frac{2}{n_{NS}t_{NS}l_{NS}^2} \right] \quad [3.21]$$

This can be solved in terms of Z_{NS-J} to produce an equation which can convert the real and imaginary components of network impedance to that of a single average nanosheet-junction pair

$$Z_{NS-J} = Z_{Net} \frac{A_{Net}}{L_{Ch}} \frac{(1-P_{Net})}{2t_{NS}\kappa_{Net}} \left[1 + \frac{2}{n_{NS}t_{NS}l_{NS}^2} \right]^{-1} \quad [3.22]$$

A similar procedure can be followed for the 0D and 1D cases, as shown in [Appendix A.4](#). Therefore, the impedance of a network can be measured, converted into the impedance of an average nanosheet-junction pair and the mean junction resistance and nanoparticle resistance can be extracted.

A critical consideration is the inherent distribution of junction resistances and capacitances within a network, arising from local variations in geometry and morphology. In [Figure 3.8C](#), if all R_JC_J components are not identical, the combined impedance of the junctions and nanoparticles in series and parallel will not be equivalent to that of a pure Randles circuit. To account for this variability, a constant phase element (CPE), commonly used in electrochemistry to model imperfect capacitors is employed.^{210, 211} The impedance of a CPE is given by

$$Z_{CPE} = \frac{1}{Y_0(i\omega)^n} \quad [3.23]$$

where Y_0 and n are constants. The impedance of a Randles' circuit with a CPE is then given by²¹¹

$$Z = R_{NS} + \frac{R_J}{1 + (i\omega R_J C_J)^n} \quad [3.24]$$

with real and imaginary components given by

$$Z'(\omega) = R_{NS} + \frac{R_J \left[1 + (\omega R_J C_J)^n \cos\left(\frac{n\pi}{2}\right) \right]}{1 + 2(\omega R_J C_J)^n \cos\left(\frac{n\pi}{2}\right) + (\omega R_J C_J)^{2n}}$$

[3.25]

$$-Z''(\omega) = \frac{R_J (\omega R_J C_J)^n \sin\left(\frac{n\pi}{2}\right)}{1 + 2(\omega R_J C_J)^n \cos\left(\frac{n\pi}{2}\right) + (\omega R_J C_J)^{2n}} \quad [3.26]$$

The exponent, n , provides insight into the degree of heterogeneity within the junctions: $n = 1$ signifies uniform junctions (equivalent to the ideal Randles circuit), while smaller values of n indicate a broader distribution in $R_J C_J$ due to network variability.

3.4 Temperature-Dependent Transport Measurements

Temperature dependent resistivity measurements provide invaluable insight into identifying and understanding charge transport mechanisms within materials, including nanomaterials and networks.^{36, 212, 213} By measuring the resistivity (or conductivity) over a range of temperatures, insights into the underlying physical processes governing electrical conduction can be obtained. The observed temperature-dependence typically follows distinct functional forms depending on the dominant charge transport mechanism. Fitting this data enables the identification of these regimes such as band-like, thermally activated, variable range hopping (VRH), nearest neighbour hopping (NNH) and tunnelling.

In metallic systems, band-like transport occurs where resistivity increases linearly with temperature due to enhanced electron scattering from phonons.²¹⁴ This metallic regime can crudely be described by

$$\rho(T) = \rho_0 + \alpha T \quad [3.27]$$

where ρ_0 is the residual resistivity due to defects or impurities and α is the temperature coefficient of resistivity. Materials exhibiting metallic conduction include bulk metals, metallic nanowires and high quality metallic CNTs, where charge carriers propagate freely through delocalised states.²¹⁵ In AgNWs the transport can more accurately be described by the Bloch-Gruneisen equation^{4, 5,}

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$$\rho(T) = \rho_0 + \rho_{e-ph}(T),$$

$$\rho_{e-ph}(T) = \alpha_{e-ph} \left(\frac{T}{\Theta_D} \right)^5 \times \int_0^{\Theta_D/T} \frac{x^5}{(e^x - 1)(1 - e^{-x})} dx \quad [3.28]$$

where ρ_0 is the residual resistivity due to defect scattering, ρ_{e-ph} is the resistivity arising from electron-phonon (e-ph) interactions, α_{e-ph} is a constant characterizing e-ph coupling and Θ_D is the Debye temperature. This model assumes that the dominant source of temperature-dependence is the scattering of electrons by phonons. As the temperature increases, the increased thermal energy permits the phonons to more efficiently scatter electrons, reducing their mean free path and causing the resistivity to increase.

Semiconducting materials, by contrast, often display a characteristic decrease in resistivity with increasing temperature, arising from the thermal excitation of carriers across the bandgap (E_g). In an intrinsic semiconductor, each excitation produces both an electron and a hole leading to a carrier density of

$$n(T) \propto \exp\left(-\frac{E_g}{2k_B T}\right) \quad [3.29]$$

and hence a resistivity of

$$\rho(T) = \rho_0 \exp\left(\frac{E_g}{2k_B T}\right) \quad [3.30]$$

where ρ_0 is a pre-factor and k_B is Boltzmann's constant. However, this is only the case if the mobility is assumed to be weakly temperature dependent and the temperature dependence of the carrier density dominates. In practice, many semiconductors deviate from simple Arrhenius behaviour. Doping, traps or disorder can shift the dominant transport mechanism from the carriers to the mobility, or a mixture of both. TMDs such as MoS₂ typically exhibit this non-ideal behaviour. This. While the Arrhenius form provides a useful framework for describing the ideal case, real semiconducting systems frequently display a more complex temperature dependence.^{65, 217}

Networks of nanomaterials are far more disordered than nanomaterials themselves, so transport is dominated by hopping or tunnelling between localised states.^{6, 213, 217} Variable range hopping typically emerges at lower temperatures and can be described by

$$\rho(T) = \rho_0 \exp\left(\frac{T_0}{T}\right)^{\frac{1}{d+1}} \quad [3.31]$$

where T_0 is a characteristic temperature related to the density of localised states and their spatial distribution and d represents the dimensionality. VRH is commonly observed in networks of graphene nanosheets,²¹³ TMDs^{6, 212, 213} and CNTs,²¹⁸ where charge carriers hop between spatially localised energy states. It is very common for VRH to be the dominant transport mechanism at lower temperatures, which transitions into activated hopping at higher temperatures, due to the availability of additional charge carriers.

Finally, tunnelling transport occurs when electrons pass through insulating barriers between conductive elements. Tunnelling resistivity often follows a stretched exponential dependence given by

$$\rho(T) = \rho_0 \exp\left(\frac{T_0}{T}\right)^n \quad [3.32]$$

where T_0 and n are parameters influenced by barrier height and geometry. Networks of high purity CNTs or high-quality graphene regularly display this behaviour.^{89, 181, 219} However, tunnelling transport can also display power-law behaviour given by

$$\rho(T) \propto T^{-\alpha} \quad [3.33]$$

This typically occurs in cases such as near a mobility edge or in granular metals.

Temperature-dependent resistivity measurements provide a critical tool for identifying distinct charge transport mechanisms within nanomaterials and nanomaterial networks. Traditionally, measurements done on networks are assumed to be junction limited, and the dominant charge transport mechanisms are attributed to the junctions. However, this may lead to misinterpretations as R_J is improved toward R_{NP} . Therefore, it is critical to measure the transport of both the nanomaterials and the junctions to achieve a comprehensive understanding of transport in nanomaterial networks.

“Emboldened by the flame of ambition”

Margit

CHAPTER 4

DECOUPLING JUNCTION AND NANOMATERIAL RESISTANCE IN NANOMATERIAL NETWORKS USING SIMPLE DC MEASUREMENTS

4.1 Introduction

Electrical transport in nanomaterial networks is governed by two competing resistive contributions: the intrinsic resistivity of the nanoparticle (intra-particle) and the resistance of the particle-particle junctions (inter-particle). Intra-particle transport typically occurs via bandlike transport in ordered systems or hopping in disordered or defective ones.^{6, 151, 181} When charge travels from one nanoparticle to the next it must traverse a nanoparticle-nanoparticle junction, known as inter-particle transport. This typically occurs via hopping or tunnelling.^{6, 213} Conventional methods for characterising the electrical conductivity or transport mechanisms in these networks can only reflect the dominant transport bottleneck and cannot give a complete picture of the electrical conduction in these systems.

Building on the work in [Chapter 3](#), this chapter presents a broadly applicable methodology for the separation and measurement of the nanoparticle resistivity and junction resistance in nanomaterial networks. This work relies on a nanoparticle size-dependent study of nanomaterial networks and presents both the 1D nanowire and 2D nanosheet cases; however, this procedure can be

applied to any nanomaterial and network geometry. Furthermore, the nanoparticle and junction resistance values can be compared to determine whether the electrical transport in a network is junction limited, nanoparticle limited, or both, providing a key insight into the electrical performance of the networks. This chapter paves the way to a comprehensive characterisation and optimisation of the electrical properties in nanomaterial networks.

4.2 Experimental Procedure

AgNW Network Preparation

Silver nanowire stock dispersions (A40 40 nm $\times$ 35 μ m in 2-propanol and A60 60 nm $\times$ 45 μ m in 2-propanol) were sourced from Novarials Corporation. The AgNWs were size-selected using sonication-induced scission in an ultrasonic bath (Fisherbrand 112xx series). In each case a stock AgNW dispersion was sonicated for a fixed duration at a concentration of 1 mg mL⁻¹ in IPA. Sonication times of 0.05, 0.25, 0.5, 1, 1.5, and 2 h were used to produce the size-selected AgNW inks. Spray coating was carried out at a AgNW concentration of 0.5 mg mL⁻¹ using a Harder and Steenbeck Infinity CRplus Airbrush attached to a computer-controlled Janome JR2300N mobile gantry. An N₂ back pressure of 45 psi, nozzle diameter of 400 μ m and stand-off distance of 100 mm between the nozzle and substrate were used.¹⁶² All deposited traces were defined using stainless steel shadow masks producing a serpentine-like pattern with a channel length of 97 mm and channel width of 500 μ m. Fused silica substrates (MicroChemicals, JGS2) were used due to their low surface roughness. The networks were then annealed at a temperature of 135 °C to reduce R_j by sintering the junctions.^{29, 220}

Graphene Network Preparation

Nanosheet inks were prepared using LPE.³ Graphite powder (Asbury, Grade 3763) was first sonicated in 80 mL of deionised (DI) water (18.2 M Ω cm) at a concentration of 35 mg mL⁻¹ for 1 h. A horn probe sonic tip (Sonics Vibra-cell VCX-

750 ultrasonic processor) at 55% amplitude, with a pulse rate of 6 s on and 2 s off was used. The resulting dispersion was centrifuged for 1 h at $2684 \times g$ (Hettich Mikro 220 R) to remove potential contaminants from the starting powder. The supernatant was decanted, and the sediment redispersed in 80 mL of DI water and sodium cholate at a concentration of 2 mg mL^{-1} (SC, Sigma Aldrich, >99%). This was sonicated for 8 h at an amplitude of 55% with a 4 s on 4 s off pulse rate. The resulting dispersion was separated into inks of different nanosheet sizes using liquid cascade centrifugation.¹⁴ An initial centrifugation step at $28 \times g$ for 2 h was used to isolate unexfoliated material in the sediment. The supernatant was then subjected to additional centrifugation steps at $112 \times g$, $252 \times g$, $447 \times g$, $699 \times g$, $1006 \times g$, $1789 \times g$, and $4025 \times g$, retaining the sediment at each interval to isolate nanosheet fractions of different sizes. In each case the sediment was redispersed in a 2 mg mL^{-1} DI:SC solution. The redispersed $112 \times g$ ink was subjected to a further centrifugation step at $28 \times g$ for 1 h to separate it into two size fractions. Each ink was then transferred to isopropanol (IPA, Sigma Aldrich, HPLC grade, 99.9%) for spray coating. To remove the sodium cholate, each dispersion was centrifuged for 2 h at $4052 \times g$. The supernatant was discarded, and the sediment redispersed in IPA. This step was repeated twice.

Graphene inks were spray coated using a Harder and Steenbeck Infinity airbrush attached to a computer-controlled Janome JR2300N mobile gantry. The inks were spray coated at a concentration of 0.02 mg mL^{-1} onto ultrasonically cleaned glass microscope slides with pre-patterned gold electrodes (Temescal FC2000 metal evaporation system) to facilitate electrical measurements. An N_2 back pressure of 45 psi, nozzle diameter of $400 \mu\text{m}$ and stand-off distance of 100 mm between the nozzle and substrate were used.¹⁶² All traces were patterned using stainless-steel masks while the substrate was heated to 80°C using a hotplate.

Graphene Nanosheet and Ink Characterisation

UV-Vis optical spectroscopy (Perkin Elmer 1050 spectrophotometer) was used to determine the concentration of the graphene inks using previously reported spectroscopic metrics.⁸³ Each ink was diluted to a suitable optical density and extinction spectra were recorded in 1 nm increments using a 4 mm quartz cuvette.

Atomic force microscopy was used to measure the nanosheet thickness and lateral dimensions in the size-selected graphene. A Bruker Multimode 8 scanning probe microscope was used in ScanAsyst mode (non-contact) in air under ambient conditions using aluminium coated silicon cantilevers (OLTESPA-R3). Substrates for AFM were coated with (3-Aminopropyl)triethoxysilane (APTES) by soaking them in a solution of APTES and deionized water for 15 minutes. Substrates were then removed and washed by rinsing with deionised water and pressurised nitrogen repeatedly. Inks as deposited for films were deposited on APTES coated SiO₂ wafers (5 × 5 mm²). A single drop of the dispersion (~10 µL) was dropped on the prepared substrate, held for 30 seconds, and then blown off with pressurised nitrogen. The sample was then rinsed with water followed by isopropanol which was then blown off with pressurised nitrogen. This prevents solvent airdrying on the substrate creating the coffee ring effect.²²¹ This process was then repeated with further drops until a dense coverage of nanosheets across the sample could be seen under an optical microscope. AFM scan sizes of between 10 × 10 and 20 × 20 µm² were used for shorter and longer nanosheet samples respectively. Scan rates between 0.35 – 0.7 Hz were used taking either 512 or 1024 lines per image for smaller or larger images respectively. Using step height analysis,^{3, 83} nanosheet apparent thickness was converted to layer number and then real thickness.

Network Characterisation

Scanning electron microscopy (SEM) of the printed nanosheet networks was performed using a Carl ZEISS Ultra Plus SEM. Samples were mounted on aluminium SEM stubs using conductive carbon tabs (Ted Pella) and grounded using

conductive silver paint (PELCO, Ted Pella). All images were captured at an accelerating voltage of 5 kV using a working distance of 5 mm and a 30 μm aperture. Both the In-lens and SE2 detectors were used for imaging.

An optical profilometer (Profilom3D, Filmetrics) operating in white-light interferometry mode with a 50 $\times$ objective lens was used for non-contact thickness measurements of the graphene nanosheet networks. The thickness of the AgNW networks was determined using SEM cross sections.

Bright-field transmission electron microscopy (TEM) was performed using a JEOL 2100 system operating at an accelerating voltage of 200 kV. AgNW dispersions were diluted and drop-cast onto holey carbon grids (Agar Scientific) for imaging. The grids were placed on filter membranes to wick away excess solvent and dried overnight at 120 $^{\circ}\text{C}$ in a vacuum oven.

Direct current (DC) electrical characterization of the printed networks was performed in ambient conditions using a Keithley 2612A source-meter connected to a probe station. Four-terminal measurements were used to determine the resistance of the printed AgNW networks. Two terminal measurements were used to measure the resistivity of the printed LPE graphene networks in the transmission line configuration.

A Renishaw Qontor Raman system, equipped with a 633 nm He/Ne laser was used to evaluate the defect density of graphene nanosheets collected at different rotate speeds. The spectra at 20 different spots were collected for each type of the sample and the data were fitted and averaged with a Lorentzian function.

FIB-SEM nanotomography (FIB-SEM NT) was performed using a ZEISS Auriga dual-beam system and ATLAS 5 software (Version 5.3.3.31, ZEISS) as described in Ref ¹⁸. All images were captured at a working distance of 5 mm using a 30 μm aperture and 2 kV accelerating voltage. Printed AgNW networks on fused silica substrates (MicroChemicals, JGS2) were directly mounted on aluminium stubs using

conductive carbon tabs (Ted Pella Inc.) and grounded using silver paint (Ted Pella Inc.). Network cross sections were milled using a 30 kV:600 pA gallium ion beam and imaged using both the In-lens and SE2 detectors. A slice thickness of 15 nm and in-plane pixel size of 5 nm were used to produce voxels 375 nm³ in size. The image stacks generated by the FIB-SEM NT run were aligned and interpolated using the sum of squared differences (SSD) matching algorithm in Dragonfly (Version 2022.2.0.1409, Object Research Systems). To enable quantitative analysis, the greyscale network cross sections (SE2 detector) were segmented into their nanowire/nanosheet and pore components using the trainable WEKA segmentation plugin²²² in FIJI.²²³ Prior to this the pixel intensity in each stack was normalized and the brightness and contrast were adjusted globally to maximise the difference between pore and nanowire/nanosheet pixels in FIJI. The two resulting image stacks contained only pore or AgNW/graphene nanosheet pixels, which were then converted to 3D images representing both phases using Dragonfly. Network porosity was determined from the 3D volumes using both Taufactor²²⁴ and FIJI.²²³

Note: The AFM presented in this chapter was carried out by Dr. Kevin Synnatschke and Anthony Dawson. The optical profilometry was carried out by Dr. Eoin Caffrey. The TEM was carried out by Dr. Danielle Douglas-Henry. The Raman spectroscopy was carried out by Dr. Weimiao Wang. The FIB-SEM NT was carried out by Dr. Luke Doolan and Dr. Cian Gabbett.

4.3 Results and Discussion: Silver Nanowires

Silver nanowire (AgNW) networks are some of the most studied and well understood systems in the field of printed nanomaterial networks. AgNW networks display extremely high conductivities,^{19, 30, 39} transparency⁴⁰ and good mechanical flexibility.^{42, 44} Perhaps then, it is no wonder they were one of the first nanomaterial networks to find their way out of the lab and into industrial use in flexible

transparent conductive electrodes (TCEs).^{42, 43, 225} AgNW networks offer a low cost, flexible alternative to indium tin oxide (ITO) and can currently be found in industrial use for bendable touchscreens and OLEDs in smartphone displays.⁴² Given their widespread use and well-studied properties, AgNW networks were used as a benchmark system to demonstrate the use of our model and to validate its predictions.

Control and Measurement of AgNW Length

A key aspect of this work will be to measure the dependence of network resistivity on nanowire length. To achieve this, batches of nanowires of two different diameters were purchased from Novarials Corporation. Scanning electron microscope (SEM) images of AgNWs deposited on substrates showed the nanowires to be long ($26.6\ \mu\text{m}$) and uniform as shown in [Figure 4.1A](#). Image analysis allowed the measurement of both the length and diameter of the nanowires, with both parameters showing reasonably narrow distribution as shown in [Figure 4.1B,C](#) (see [Appendix A.1](#) for all statistical data). The mean diameters, D_{NW} , of the two nanowire batches were 38 ± 1 and 57 ± 1 nm, while the corresponding mean nanowire lengths, l_{NW} , were found to be 26.6 ± 1 and $29.3 \pm 1\ \mu\text{m}$, respectively (errors are standard errors of the mean).

The AgNWs were size-selected by sonicating the dispersions for various timescales, a process known as sonication-induced scission.^{40, 226-228} SEM images such as that shown in [Figure 4.1D](#) confirmed that this process results in shortening of the nanowires. This produced a range of fractions, each with a different mean nanowire length. SEM measurements ([Figure 4.1E](#)) showed the length to decrease with sonication time, from 26.6 to $2.3\ \mu\text{m}$ for the 38 nm diameter AgNWs and 29.3 to $3.6\ \mu\text{m}$ for the 57 nm diameter AgNWs. This fall-off in length with sonication time followed a power law, consistent with previously observed behaviour.^{40, 226-228} The data in [Figure 4.1E](#) is replotted in [Figure 4.1F](#) as the nanowire aspect ratio, $l_{\text{NW}} / D_{\text{NW}}$, plotted versus sonication time, t . This graph clearly demonstrates that the

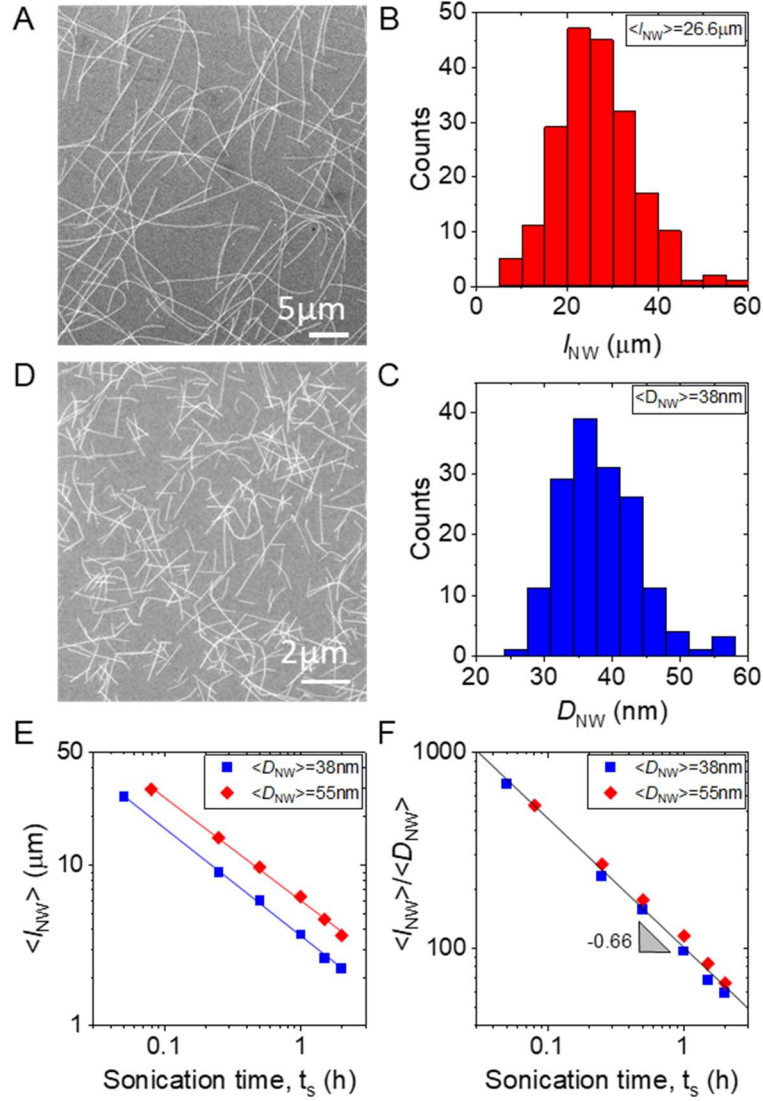


Figure 4.1: AgNW Characterisation. **A)** SEM image of as-purchased AgNWs ($D_{NW} = 38$ nm) deposited on Si/SiO₂. **B-C)** Example histograms showing the length (C) and diameter (D) distributions for the nanowires shown in A. **D)** SEM image of AgNWs ($D_{NW} = 38$ nm) deposited on Si/SiO₂ after sonication for 2 hours. **E)** Mean length of AgNWs within each size-selected fraction as a function of sonication time. Data is shown for both $D_{NW} = 38$ nm and $D_{NW} = 57$ nm nanowires. **F)** Plot of $\langle l_{NW} \rangle / \langle D_{NW} \rangle$ as a function of sonication time showing data for all fractions over both nanowire diameters falls on a master curve.

sonication data for both AgNW diameters converge onto a master curve consistent with $l_{NW} \propto D_{NW} \times t^n$, where $n = -0.66$. This exponent compares well to values of $n = -0.5$ obtained for single-walled carbon nanotubes (SWCNTs)¹⁴⁹ and graphene²²⁹ but differs somewhat from a previous report of $n = -0.34$ for AgNWs.⁴⁰

Sonication-induced scission recues the average length of the AgNWs, but we do not expect it to significantly alter their intrinsic conductivity, since bulk-like metallic conduction dominates and is largely insensitive to nanowire length. While extreme scission could introduce surface roughness, defects or oxidation at the fracture sites, these are localised and do not strongly impact the overall conductivity of the intact nanowire segments. Furthermore, the scission process in AgNWs proceeds very quickly (maximum 2 hours in our case), not allowing sufficient time for significant surface defects or roughness to form. Thus, scission mainly affects network conductivity rather than the intrinsic transport within each wire.

AgNW Network Characterisation

Nanowire networks were produced by spray-coating. Typically, networks were sprayed with an average thickness of $t_{\text{Net}} \sim 500$ nm; thick enough to avoid any percolative effects (i.e., thickness-dependent conductivity which occurs for network thicknesses below ~ 100 nm for AgNWs).³⁹ Spray coating produced disordered networks of randomly oriented nanowires as shown in Figure 4.2A,B.

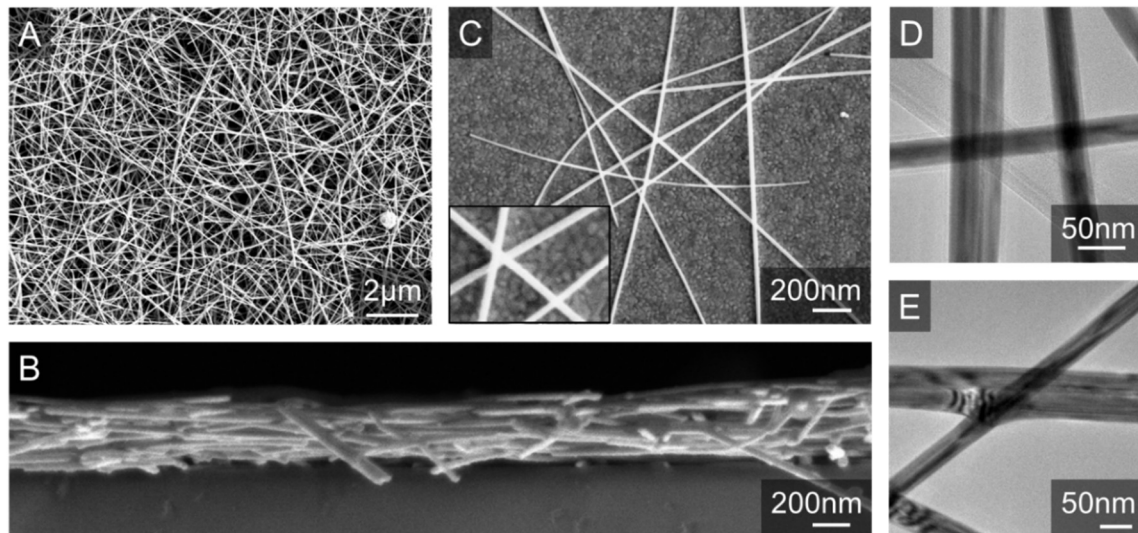


Figure 4.2: AgNW Network Characterisation. **A)** SEM image of the top surface of stock length AgNW network with $D_{\text{NW}} = 38$ nm nanowires. **B)** Typical cross-sectional SEM image of a AgNW network. **C)** High Magnification SEM image of typical junctions present within a AgNW network. **D)** TEM image of an unannealed AgNW-AgNW junction. **E)** TEM image of a completely annealed AgNW-AgNW junction showing sintering at the junction.

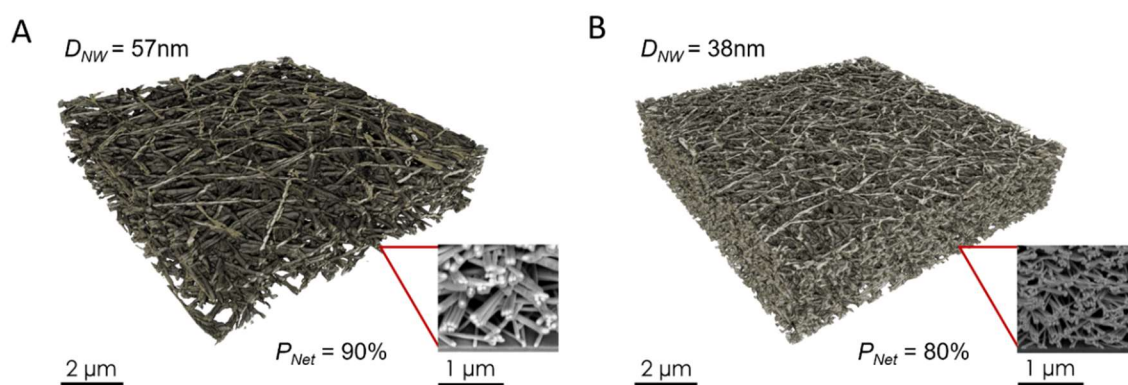


Figure 4.3: AgNW Network 3D Imaging. FIB-SEM tomography images of sections of networks spray cast from silver nanowires with diameters of $D_{NW} = 57$ nm (A) and $D_{NW} = 38$ nm (B). The insets at the bottom right of each panel show small sections of individual cross-sectional SEMs.

Such networks are also known to be highly porous with porosities of 80–90% typical.¹⁸

The inter-nanowire junctions can be seen more clearly by visualizing a sparse network using SEM (Figure 4.2C) or TEM (Figure 4.2D,E). These images show the junctions as consisting of nanowires in close contact. However, it is known that such as-produced nanowire junctions contain a layer of stabilizing poly(vinylpyrrolidone) (PVP) polymer, which acts as an insulating barrier between the AgNWs. This significantly hinders electron transport in as-produced AgNW networks, causing them to have a large network resistance. Thermal annealing has been shown to drastically reduce the network resistance by allowing the PVP layer to migrate from the junction contacts and allows sintering of the nanowires at the junctions.^{29, 37, 220} TEM images of individual junctions in AgNW networks after thermal annealing reveal dramatic changes in the junction morphology. In Figure 4.2E, post anneal, there is a clear welding at the junctions, suggesting displacement of the PVP layer and nanowire-nanowire sintering. Overall, the TEM images show that the annealing process enhances the intimacy of the contact between the AgNWs at the junctions, helping to drastically reduce junction resistance and improve inter-nanowire transport. It also implies that the junctions themselves are composed of metallic silver after annealing.

In order to quantify the morphology of these networks, we performed 3D imaging via nanotomography. As described by Gabbett and Doolan et al. ¹⁸, 3D imaging of nanomaterial networks can be achieved using a combination of repeated focused ion beam milling and scanning electron microscopy (FIB-SEM). After the appropriate image segmentation, this procedure yields a large set of 2D images where each pixel is labelled via its material composition. These images can then be combined to generate a 3D image where each voxel represents (in our case) either free space (part of a pore) or silver (part of a nanowire). Typically, such 3D images have resolution of 5 nm in the image plane and 15 nm out of plane, i.e., the voxel size is $5 \times 5 \times 15 \text{ nm}^3$.

Examples of 3D images collected for the nanowire networks under study here are shown in [Figure 4.3A,B](#). In principle, such images contain all structural and morphological information relating to the network which is available at the resolution of the image. This includes parameters relating to nanowire orientation as well as pore size and shape etc. However, for our purposes, the most important available information relates to the network porosity (P_{Net}) because of its effect on the network resistivity (as described in [Chapter 3](#)). Using the methods described in [Ref 18](#) we have calculated mean network porosities of $P_{\text{Net}} = 85 \pm 5 \%$ for networks of AgNWs with $D_{\text{NW}} = 38 \text{ nm}$ and $P_{\text{Net}} = 89 \pm 3 \%$ for networks of AgNWs with $D_{\text{NW}} = 57 \text{ nm}$.

Dependence of Electrical Properties on AgNW Length

In [Chapter 3](#) we demonstrated that the resistivity, ρ_{Net} , of a network of 1D nanowires (or nanotubes) is related to the resistivity of the nanowires themselves, ρ_{NW} , by

$$\rho_{\text{Net}} \approx \frac{\kappa_{\text{Net}}}{(1 - P_{\text{Net}})} \left[\rho_{\text{NW}} + \frac{\pi D_{\text{NW}}^2 R_{\text{I}}}{2l_{\text{NW}}} \right] \left[1 + \frac{8}{n_{\text{NW}} l_{\text{NW}} \pi D_{\text{NW}}^2} \right] \quad [4.1]$$

where κ_{Net} , P_{Net} , D_{NW} , l_{NW} and n_{NW} are mean values of network tortuosity, porosity, nanowire diameter, nanowire length and nanowire carrier concentration,

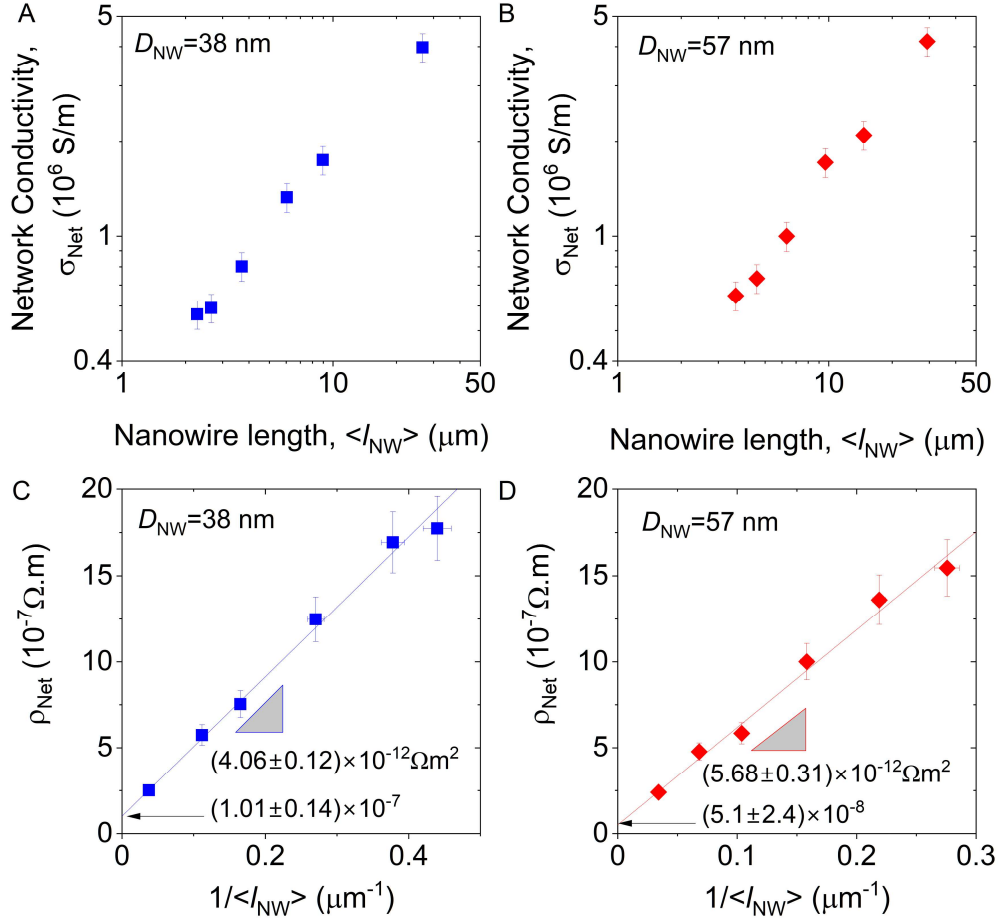


Figure 4.4: Dependence of AgNW Network Conductivity on AgNW Length. A-B)

Conductivity of spray-cast AgNW networks, σ_{Net} , versus mean nanowire length, l_{NW} , for AgNWs with $D_{NW} = 38$ and $D_{NW} = 57$ nm, respectively. **C-D)** Resistivity of spray-cast AgNW networks, ρ_{Net} , versus the inverse of the mean nanowire length for AgNWs of diameter 38 and 57 nm, respectively. The line is a fit to Equation 4.2 which allows for the extraction of ρ_{NW} and R_J from the intercept and slope, respectively.

respectively. For our purposes, we expect K_{Net} to be close to unity,¹⁸ so it is neglected from the following calculations. Additionally, in the case of conducting nanomaterials such as AgNWs, n_{NW} is very large, meaning the final term of this equation becomes negligible, giving

$$\rho_{Net} \approx \frac{1}{(1 - P_{Net})} \left[\rho_{NW} + \frac{\pi D_{NW}^2 R_J}{2l_{NW}} \right] \quad [4.2]$$

This equation predicts that measuring the network resistivity (ρ_{Net}) as a function of AgNW length (l_{NW}) will allow the extraction ρ_{NW} and R_J by fitting, once P_{Net} and D_{NW}

are known. The introduction of this equation serves as a foundational framework for our analyses, providing a quantitative basis for the determination of the role of junctions in AgNW networks.

To investigate the effect of nanowire length on the electrical properties of the network, we used the length-selected nanowire dispersions described above to fabricate a set of networks with various nanowire lengths. We then measured the network conductivity, σ_{Net} , using 4-probe techniques. Figure 4.4A,B shows σ_{Net} , measured for both nanowire diameters, as a function of the mean length of nanowires making up the network, l_{NW} . These graphs both appear to scale roughly linearly with AgNW length as previously observed by Sorel et al.⁴⁰ It is also worth noting that our most conductive networks display conductivities approaching 5×10^6 S/m, competitive with the best metallic nanowire networks,^{29, 30, 220} and, to our knowledge surpassed only by networks of silver nanosheets.¹⁸⁰

However, we note that Equation 4.2 predicts the network resistivity, ρ_{Net} , to scale linearly with the inverse of nanowire length. Plotting the data as ρ_{Net} versus $1/l_{\text{NW}}$ in Figure 4.4C,D shows straight lines for both nanowire diameters. Linear fitting allows us to extract values for ρ_{NW} and R_J for each nanowire type. We obtained values of $\rho_{\text{NW}} = 1.5 \pm 0.7 \times 10^{-8}$ Ωm and $\rho_{\text{NW}} = 0.6 \pm 0.3 \times 10^{-8}$ Ωm for the 38 and 57 nm AgNW networks, respectively. These values are broadly consistent with the resistivity of bulk silver ($\rho_{\text{Ag}} = 1.6 \times 10^{-8}$ Ωm), supporting the validity of our approach. The higher resistivity observed for the 38 nm nanowires is consistent with expected size-dependent surface scattering effects in smaller diameter nanowires.²³⁰

In addition, the junction resistances determined from our study are $R_J = 265 \pm 40$ and 124 ± 22 Ω for the 38 and 57 nm AgNW networks, respectively. The junction resistance increases for smaller diameter nanowires due to the reduced contact area at the junction interface. These data are consistent with a wide range of values of R_J reported by Forro et al.² for silver and copper nanowire networks which mostly cluster in the range $50 \text{ } \Omega < R_J < 2 \text{ k}\Omega$, as shown by Figure 4.5A. This range is

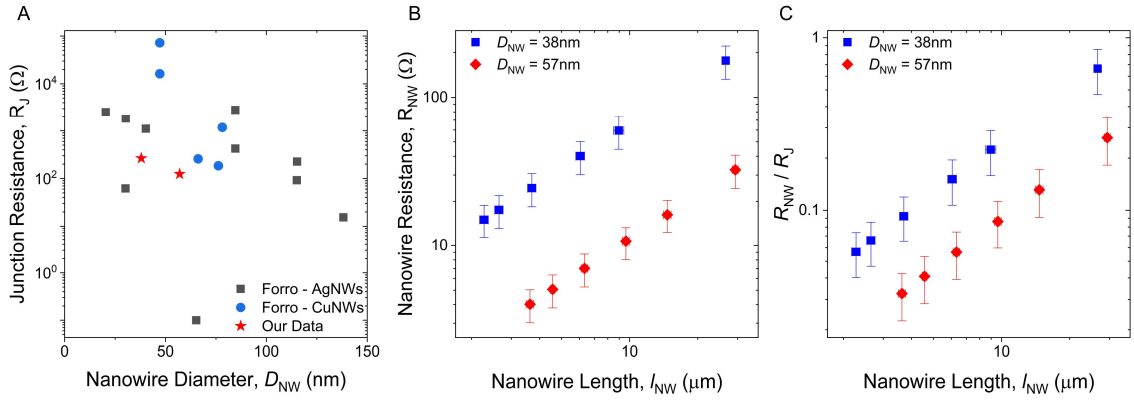


Figure 4.5: Junction and Nanowire Resistance. **A)** Junction resistance of various AgNW and CuNW networks as reported by Forro et al.² compared to our extracted junction resistances. **B)** Our extracted nanowire resistance plotted as a function of nanowire length. **C)** R_{NW}/R_J plotted as a function of nanowire length.

also consistent with a number of experimental studies which have reported R_J values from 11 Ω to 2 kΩ.¹⁸⁸⁻¹⁹² The wide range of reported R_J values may be attributed to the wide range of possible junction morphologies. Such a broad range of junction types is expected due to variations of nanowire diameter and, more importantly, annealing conditions.

We can use the known dimensions of our AgNWs, combined with the nanowire resistivities to estimate the nanowire resistances, R_{NW} . To do this, we assume that carriers travel, on average, through half the length of each nanowire, leading to $R_{NW} = \rho_{NW} (l_{NW} / 2) / (\pi D_{NW}^2 / 4)$. Figure 4.5B shows the calculated R_{NW} plotted as a function of nanowire length. Using these values allowed us to calculate R_{NW}/R_J , a parameter that determines how junction limited each network is, for each of our nanowire length fractions. We found values of R_{NW}/R_J ranging from 0.06 to 0.7 for the $D_{NW} = 38$ nm AgNW networks and from 0.03 to 0.26 for the $D_{NW} = 57$ nm AgNW networks, as shown by Figure 4.5C. We note that all networks studied here have $R_{NW}/R_J < 1$, showing them to be predominantly junction limited.

4.4 Results and Discussion: Graphene Nanosheets

Graphene nanosheets display a rich list of outstanding properties such as high electrical conductivity,²³¹ mobility,²³² exceptional mechanical properties,²⁵ excellent thermal conductivity,⁶² high optical transparency,²³³ high surface area²³⁴ and chemical tunability.²⁴ Despite these outstanding properties, graphene is yet to become widespread in industrial use due to difficulties with large scale synthesis and, importantly for us, deposition. Printed nanosheet networks provide one of the most promising routes for industrial adoption of graphene, however, incomplete electrical characterisation of these networks remains an issue. Here, we explore the use of our model to separate and extract the nanosheet resistivity and junction resistance in graphene nanosheet networks and provide a detailed analyses into their contribution to the network conduction.

Control and Measurement of Graphene Nanosheet Size

Fundamental to this study, was the production and isolation of graphene nanosheets with a range of thicknesses. Bulk graphite was exfoliated into graphite/graphene nanosheets by liquid phase exfoliation (LPE).^{3, 81} This process is known to result in a dispersion of graphene nanosheets with a vast range of both thicknesses and lateral sizes.^{3, 235} Liquid cascade centrifugation (LCC) is commonly employed to size select dispersions of nanosheets by sequentially centrifuging the dispersion at increasing centrifugal speeds/forces.¹⁴ After each centrifugation step, the largest and heaviest nanosheets in that fraction sediment and are collected. The resulting supernatant contains the smaller unsedimented nanosheets, which is then subjected to the next, higher-speed, centrifugation. This stepwise process produces a series of nanosheet fractions, each enriched with a distinct size range.^{6, 177, 236}

We performed AFM analysis on a subset of our size-selected fractions. AFM images, such as those shown in [Figure 4.5A,B](#), facilitate statistical analysis to measure the distribution of nanosheet lengths (l_{NS}) and thicknesses (t_{NS}) in each of the size-selected fractions (see [Figure 4.5C,D](#) for example histograms and [Appendix A.2](#) for

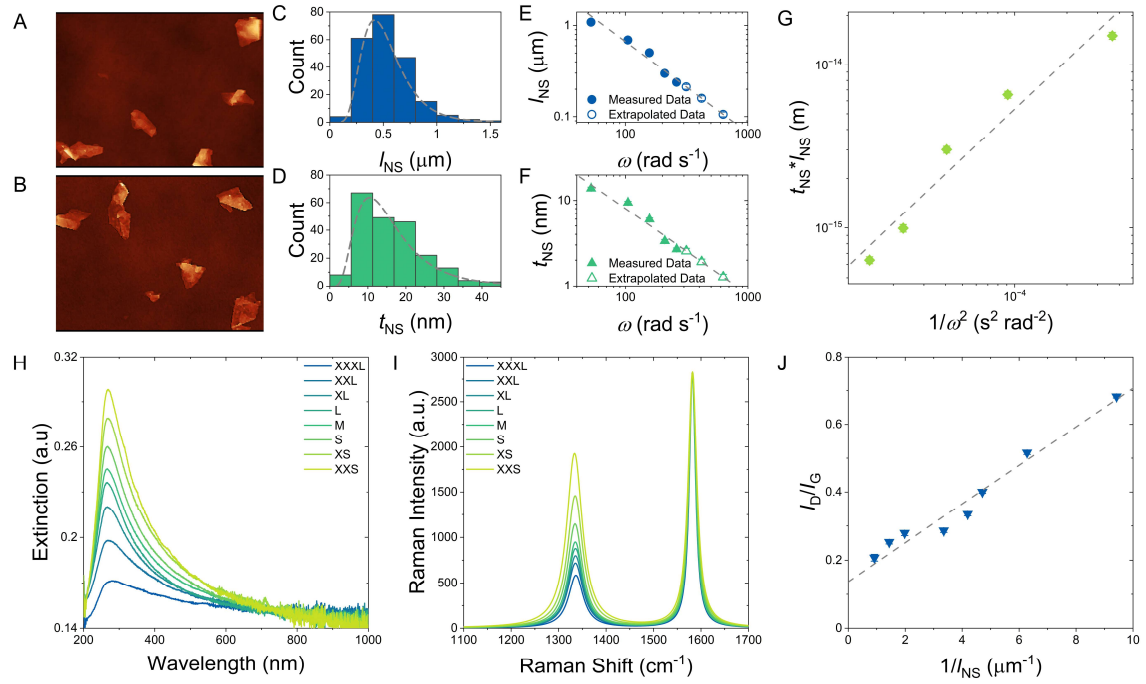


Figure 4.5: Graphene Nanosheet Characterisation. **A-B)** AFM images of the largest (A) and smallest (B) fractions. **C-D)** Example histograms displaying the measured nanosheet lengths (C) and nanosheet thicknesses (D) from AFM statistics for the $t_{NS} = 5.97$ nm sample. **E-F)** Graphs of the measured and extrapolated nanosheet lengths (E) and thicknesses (F) as a function of centrifugation speed. The lines are a linear fit with slope -1. **G)** A plot of $\langle t_{NS} \rangle \langle l_{NS} \rangle$ against ω^{-2} for the measured values showing a linear relationship **H)** UV/Vis spectra of the various size fractions. **I)** Raman spectra of the various size fractions showing the characteristic D and G peaks of graphene. **J)** A plot of I_D/I_G as a function of $1/l_{NS}$ displaying a linear relationship.

all statistical data). These histograms yield the mean values of l_{NS} and t_{NS} , which are plotted versus the (upper) centrifugation speed (ω) used in the cascade step to generate that fraction (Figure 4.5E,F). The dispersions subjected to the lower speed centrifugations contain large and thick nanosheets, closer to nanographite than graphene, while dispersions subjected to higher speed centrifugations contain much thinner and laterally smaller nanosheets, consistent with few-layer graphene.

Recently, Goldie et al.¹⁴⁴ applied centrifugation theory to dispersions of nanosheets size selected using LCC. They found that the product of mean nanosheet thickness and mean nanosheet length, is always inversely proportional

to the square of centrifugation speed: $\langle t_{NS} l_{NS} \rangle \propto \omega^{-2}$. Figure 4.5G confirms that our AFM data does indeed follow this trend. Furthermore, Ref. ¹⁴⁴ shows that, for systems where the mean nanosheet length scales linearly with the mean nanosheet thickness (as is usually approximately the case for LPE nanosheets),²³⁵ both mean nanosheet thickness and mean nanosheet length scale individually with inverse centrifugation speed: $\langle t_{NS} \rangle \propto \omega^{-1}$, $\langle l_{NS} \rangle \propto \omega^{-1}$. This behaviour is confirmed by the fit lines in Figure 4.5E,F. The confirmation of this trend allowed for the extrapolation and estimation of the nanosheet length (l_{NS}) and nanosheet thickness (t_{NS}) for the remaining, smaller fractions (as shown in Figure 4.5E,F).

UV/Vis spectroscopy of the dispersions displayed the characteristic graphene π - π^* transition peak at ~267 nm as well as the plateau at longer wavelengths,^{81, 237} as shown in Figure 4.5H. Previous observations have shown that the peak amplitude relative to the plateau increases with decreasing nanosheet thickness.⁸³ This trend was also observed in our UV/Vis spectra, further validating our use of the LCC process.

It is important to ensure that the defect content in the basal plane of the graphene nanosheets does not increase as the nanosheet size decreases. An increased basal plane defect density could reduce the intrinsic conductivity of the nanosheets, thereby affecting the overall conductivity of the network; a key parameter under investigation. To assess this, Raman spectroscopy was performed on the graphene nanosheets (post network deposition). Figure 4.5I shows the Raman spectra of the graphene nanosheets, with the characteristic D (~1330 cm^{-1}) and G (~1550 cm^{-1}) peaks clearly visible.^{238, 239} The G peak is known to arise from the in-plane stretching of the sp^2 carbon-carbon bonds, while the D peak originates from a breathing mode of sp^2 carbon rings and is activated by the presence of defects.²⁴⁰ The intensity ratio I_D/I_G is commonly used to estimate the level of disorder or defect density within graphene nanosheets. Figure 4.5J shows that I_D/I_G increases linearly with $1/l_{NS}$, indicating that the observed defects predominantly originate from the nanosheet edges rather than within the

nanosheet basal plane.^{83, 241} A slope of 56.9 ± 4.1 nm, which is related to the edge activated Raman process, and an intercept of 0.137, which is related to the defects present in the parent graphite, are consistent with previous reports.⁸³ This suggests that basal plane defects do not significantly contribute to variations in network conductivity with nanosheet size.

Graphene Nanosheet Network Characterisation

Networks of graphene nanosheets were produced via spray-coating.¹⁶² All networks were coated thicker than 1 μm to avoid percolative effects (i.e., the thickness-dependent conductivity observed in LPE graphene networks below $t_{\text{Net}} \sim 110$ nm).^{39, 242} Figure 4.6A,B shows SEM images of the network top surfaces for both larger and smaller nanosheets. In general, spray-coating resulted in disordered networks composed of randomly oriented nanosheets with point-like contacts at the nanosheet-nanosheet junctions.¹⁷⁷ Figure 4.6A,B displays this poor conformity at the junctions, particularly for the thicker nanosheets, with minimal overlap between flakes and predominantly point-like contacts. Figure 4.6C shows a cross-sectional image of a graphene network with the close-up in Figure 4.6D again displaying the point-like nature of the junction areas. Such morphology is consistent with LPE graphene nanosheets¹⁷⁷ and is expected to result in high junction resistances, as discussed later.

To characterize the morphology of the entire network, nanotomography based on focused ion beam-scanning electron microscopy (FIB-SEM) was used, following the method described in Ref. ¹⁷⁷. This approach involves sequential milling of the sample with a focused ion beam while imaging the exposed surfaces with SEM, producing a stack of 2D cross-sectional images. After segmenting these images to distinguish between different materials (i.e., pores and graphene nanosheets), the stack can be reconstructed into a 3D representation of the network, where each voxel corresponds to either a nanosheet or empty space (pore). The typical resolution achieved was 5 nm in-plane and 15 nm out-of-plane, giving a voxel size of $5 \times 5 \times 15$ nm³.

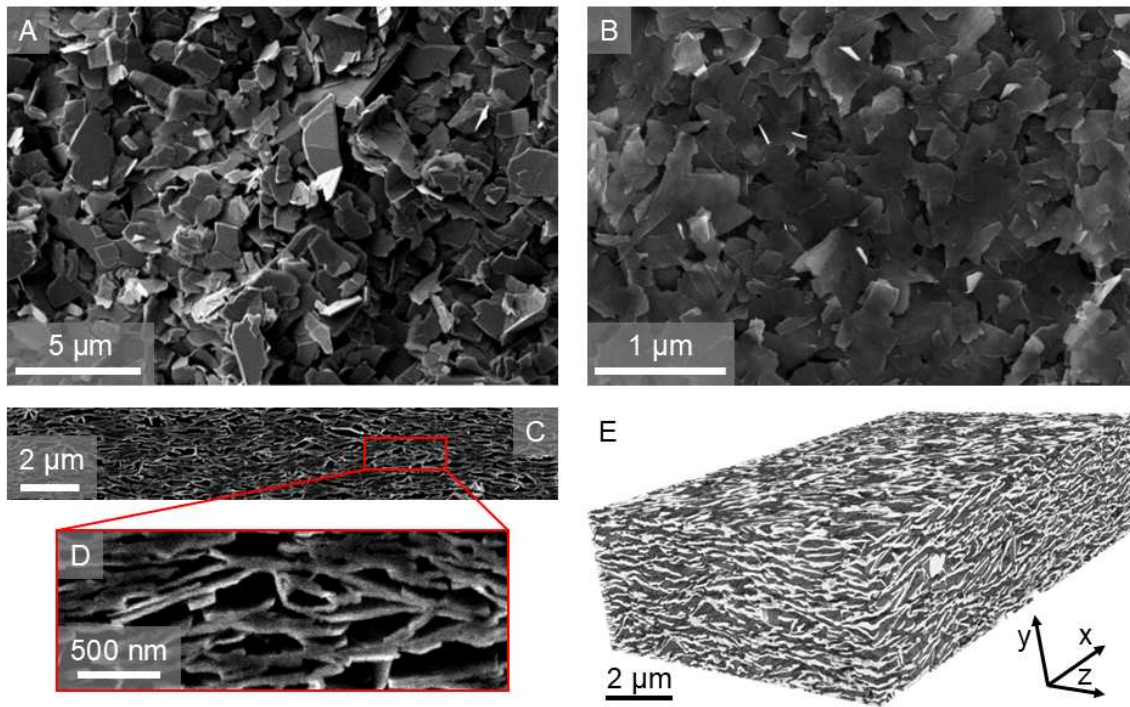


Figure 4.6: Graphene Network Characterisation. **A-B)** SEM images of the top surface of graphene nanosheet networks with nanosheet thicknesses of $t_{NS} = 6.0$ nm (A) and $t_{NS} = 1.3$ nm (B). **C)** Typical cross-sectional SEM image of a graphene nanosheet network. **D)** Close-up of the network cross-section showing the disordered nature of the nanosheet-nanosheet junctions **E)** FIB-SEM tomography image of a section of a network of spray coated graphene nanosheets with thicknesses of $t_{NS} = 3.3$ nm.

Figure 4.6E shows a representative 3D reconstruction of one of the graphene nanosheet networks ($t_{NS} = 3.3$ nm). In principle, such images should contain all morphological and structural data that is available at the imaging resolution ($5 \times 5 \times 15$ nm³). This includes details on nanosheet orientation, conduction path tortuosity, pore shape and size, etc. However, for the purposes of this study, we focus on the network porosity (P_{Net}) which directly relates to the network electrical resistivity (see Chapter 3 and Equation 4.4 below). Using the method described in Ref. ¹⁷⁷ the mean porosity of the produced networks was determined. Although the network porosity is known to vary slightly with nanosheet size,¹⁸ to simplify analysis we approximate the porosity as the mean porosity of all produced networks, which was found to be $P_{Net} = 45 \pm 1$ %, consistent with previous reports.⁶

¹⁷⁷

Dependence of Electrical Properties on Graphene Nanosheet Size

In [Chapter 3](#) we showed that for a network comprised of 2D nanosheets the network resistivity ρ_{Net} is given by

$$\rho_{\text{Net}} \approx \frac{[\rho_{\text{NS}} + 2t_{\text{NS}}R_{\text{J}}]}{(1 - P_{\text{Net}})} \left[1 + \frac{2}{n_{\text{NS}}t_{\text{NS}}l_{\text{NS}}^2} \right] \quad [4.3]$$

where ρ_{NS} , t_{NS} , R_{J} , and n_{NS} are the mean nanosheet resistivity, nanosheet thickness, inter-nanosheet junction resistance and nanosheet carrier concentration, respectively. Previously, this equation has been shown to predict trends in networks of graphene, WS_2 nanosheets, WSe_2 nanosheets AgNSs and AgNWs, and has been used to extract R_{J} and ρ_{NS} in each of these systems.^{6, 36} In the case of metallic or semimetallic nanosheets, such as graphene nanosheets, where n_{NS} is very large, the final term of the equation becomes negligible to get

$$\rho_{\text{Net}} = \frac{[\rho_{\text{NS}} + 2t_{\text{NS}}R_{\text{J}}]}{(1 - P_{\text{Net}})} \quad [4.4]$$

This equation predicts that the network resistivity is directly proportional to the nanosheet thickness. Furthermore, if ρ_{Net} is measured as a function of t_{NS} the extraction of both R_{J} and ρ_{NS} will be possible, once P_{Net} is known. This equation serves as the foundational framework for our analyses, providing a quantitative route to the determination of the role of junctions in LPE graphene networks.

To investigate the effect of nanosheet thickness on the electrical properties of LPE graphene networks, we used the size selected graphene nanosheet dispersions produced above to fabricate a set of networks with various nanosheet thicknesses. We then measured the channel length dependent resistance of the networks (see [Appendix A.3](#) for further details) to calculate the contact resistance (R_{C}) corrected conductivity of the networks. [Figure 4.7A](#) shows this conductivity to fall off with increasing nanosheet length. This behaviour, although slightly counter-intuitive, is a commonly observed phenomenon for networks comprised of conducting platelets.^{6, 177, 200, 236}

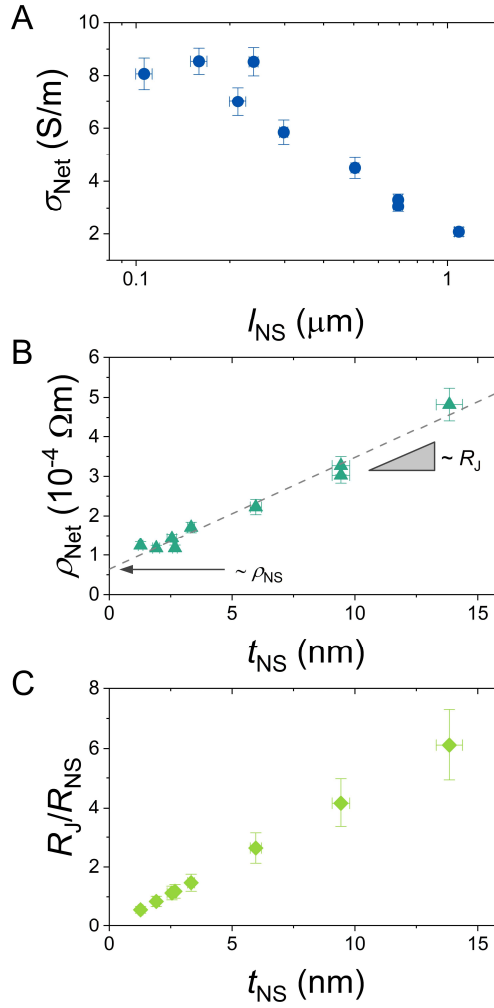


Figure 4.7: Dependence of Graphene Network Electrical Properties on Nanosheet Size.

A) Conductivity of spray-cast graphene nanosheet networks versus mean nanosheet length. **B)** Resistivity of spray-cast graphene nanosheet networks versus mean nanosheet thickness. The line is a fit to Equation 4.4 which allows for the extraction of ρ_{NS} and R_{J} from the intercept and slope, respectively. **C)** Ratio of junction to nanosheet resistance ($R_{\text{J}}/R_{\text{NS}}$) calculated from values of R_{J} and ρ_{NS} extracted from the fit in B.

As predicted by Equation 4.4, the network resistivity should scale linearly with nanosheet thickness. Figure 4.7B shows that replotting the data (from Figure 4.7A) as ρ_{Net} vs t_{NS} reveals the expected linear behaviour. Fitting the data allows us to extract both ρ_{NS} and R_{J} using the value of P_{Net} obtained above. We obtained values of $\rho_{\text{NS}} = (3.5 \pm 0.6) \times 10^{-5} \Omega\text{m}$ which is broadly consistent with expected values for multilayer graphene or graphite flakes.^{6, 243} In addition, the junction resistance within the networks was determined to be $R_{\text{J}} = 7.8 \pm 0.5 \text{ k}\Omega$. These values

are consistent with the few reports on the junction resistance in LPE graphene networks, which fall in the range 1 – 100 k Ω .^{6, 151}

We can use the known dimensions of the graphene nanosheets, combined with the nanosheet resistivities to estimate the nanosheet resistance, R_{NS} , in each size fraction. To do this, we assume the carriers travel, on average, half the lateral length of the nanosheets during intra-sheet transport,⁶ leading to $R_{NS} = \rho_{NS} / 2t_{NS}$. This allows for the calculation of R_J/R_{NS} , a parameter which determines if the networks are junction limited, nanosheet limited or both, for each of our size fractions. We found values of R_J/R_{NS} ranging from 0.56 to 6.11 for the smallest to largest fractions, respectively (Figure 4.7C). We note that the networks of larger, thicker nanosheets are clearly junction limited, leaving room for improvements in the future.

4.5 Conclusion

This chapter demonstrates a robust and generalised methodology to decouple and quantify the contributions of intra- and inter-nanoparticle resistances in nanomaterial networks using simple DC measurements. By systematically varying the nanomaterial dimensions, the length for AgNWs and the thickness for graphene nanosheets, we validated our model from Chapter 3 that enables the extraction of both the intrinsic resistivity of the nanomaterial and the junction resistance. The approach confirmed the predominantly junction-limited nature of both the AgNW and graphene networks. Moreover, this technique is broadly applicable, where size dependent studies are possible, and does not face the challenges imposed on the impedance-based method, as discussed in the following chapter (Chapter 5). The ability to directly assess the limiting factors in network conductivity represents a significant step toward the rational design and optimisation of high-performance nanomaterial based electronic devices.

*"I begin to speak only when I'm certain
what I'll say isn't better left unsaid"*

Cato

CHAPTER 5

IMPEDANCE SPECTROSCOPY OF NANOMATERIAL NETWORKS

5.1 Introduction

Measuring R_{NP} and R_J as described in [Chapter 4](#) is time-consuming, requiring extensive sample preparation in the form of the size-selection procedure. We propose that AC impedance spectroscopy, a powerful tool for device and materials characterisation,^{207, 244} can leverage the intrinsic capacitance associated with the particle-particle junctions to extract information about nanosheet and junction resistances. A similar approach has been utilised for both grain/grainboundary²⁴⁵⁻²⁴⁷ and 2D systems²⁴⁸. However, because such measurements probe all junctions in all current paths, these measurements have, up to now, yielded R_{NP} and R_J in arbitrary units (but not absolute values), limiting useful analysis.

In this chapter, we develop and validate the impedance spectroscopy method to extract R_{NP} and R_J in nanomaterial networks. We apply and expand this method to LLID networks of EE MoS₂, MoSe₂, Nb:MoSe₂ and WS₂ and corroborate our results with various other techniques. We then discuss the limitations currently imposed on this technique and define a "sweet spot" of accessible systems with a view to broadening its applicability in future work.

5.2 Experimental Procedure

Electrochemical Exfoliation and Ink Preparation

An electrochemical cell with two electrodes is utilized to intercalate the crystals. A small crystal piece measuring $\sim 0.1 \times 1 \times 1$ mm serves as the cathode, while a platinum foil (Alfa Aesar) is employed as the anode. The electrodes are secured using copper crocodile clips. The electrolyte solution is prepared by dissolving tetrapropylammonium (TPA) bromide (5 mg/mL, Sigma-Aldrich) in approximately 50 mL of propylene carbonate. An 8 V voltage is applied across the electrodes for 30 minutes to intercalate the 2D crystal with TPA⁺ cations. Following this process, the 2D crystal expands to more than twice its original volume, confirming successful intercalation. The expanded 2D crystal is subjected to bath sonication (Fisherbrand 112xx series) in a solution of 1 mg/mL poly(vinylpyrrolidone) (PVP, molecular weight $\sim 40,000$) dissolved in dimethylformamide (DMF) for 5 minutes. This is followed by centrifugation (Hettich Mikro 220, 1195-A, radius 87 mm) at 500 rpm ($24 \times g$) for 20 minutes to remove unexfoliated crystals. To size-select the dispersion, the supernatant (top 90%) is centrifuged at 1000 rpm ($97 \times g$) for 1 hour, and the sediment is collected. To remove the PVP, the sediment obtained at $97 \times g$ is diluted with 2 mL of DMF and centrifuged at 10,000 rpm ($9744 \times g$) for 1 hour. This process is repeated twice, with the sediment being collected each time. A third washing step (to remove the DMF) involves diluting the sediment in 0.5 mL of isopropanol (IPA) and centrifuging at 10,000 rpm ($9744 \times g$), after which the sediment is collected. The final sediment is redispersed in approximately 0.5 mL of IPA, which is used in the study for each 2D crystal.

Langmuir–Schaefer Deposition

The Langmuir–Schaefer setup involves a Teflon stand where a patterned fused silica substrate (25×25 mm JGS2, MicroChemicals) is placed on top. The stand is placed in a 100 mL beaker of deionized water. About 20 mL of distilled hexane is

drop-cast onto the surface of the deionized water to create a water/hexane interface, under which the substrate on the Teflon stand is submerged. Ink was drop-cast ($\sim 120 \mu\text{L}$) onto the surface of the hexane until no gaps in the interface could be seen. A needle attached to a vacuum pump is used to extract the deionized water from the bottom of the Langmuir-Schaefer set-up, which extrudes the substrate through the 2D crystal layer at a reproducible and consistent rate. A diagram of the setup can be found in our previous work.³¹ The process is repeated to build the subsequent layers of the networks. The 2D nanosheet networks are annealed at 120°C for 1 h on a hot plate in an N_2 glovebox (Jacomex GP campus) for each layer of deposition to remove residual solvent and improve the adhesion of the 2D nanosheets to the substrate.

AC Electrical Characterisation

Impedance spectra were taken using a Keysight E4990A analyser with a 30 MHz maximum frequency. A test fixture (16047E) was used to connect the samples to the analyser as this allowed as short a wire distance as possible (down to $\sim 50 \text{ mm}$) to avoid inductive or capacitive artefacts at high frequency. A spring-loaded probe attachment (Sensepeek SP10) was used to connect the analyser to the contact pads on the substrates. Ti/Au (5 nm/95 nm) electrodes were deposited by evaporation (FC-2000 Temescal Evaporator) through a shadow mask ($L_{\text{Ch}} = (50 - 200) \mu\text{m}$, $W_{\text{Ch}} = 19.4 \text{ mm}$) for AC electrical characterisation. For contact resistance measurements, electrodes with five different channel lengths ($L_{\text{Ch}} = 50, 80, 100, 150$ and $200 \mu\text{m}$, $W_{\text{Ch}} = 19.4 \text{ mm}$) were used. The spectra were acquired with a 500 mV amplitude using a precision speed of 3. A DC voltage sweep was first run on the sample to ensure the response is linear through the origin in the range of the AC amplitude.

THz Spectroscopy

A titanium-doped regenerative amplifier (Libra), the foundation of our THz spectroscopy apparatus, generates 60 fs laser pulses with an 800 nm central

wavelength. Optical photoexcitation of the sample, THz creation, and THz detection are the three separate uses for the amplifier's output. The first part of the beam is optically transformed by frequency doubling in a BBO crystal to a pump wavelength of 400 nm (photon energy 3.1 eV). Optical rectification at 800 nm is utilised in the second half to generate a THz waveform in a nonlinear ZnTe crystal with a duration of around 1 ps. The third component (at 800 nm) uses electro-optic sampling to detect the THz waveform after it has passed through the sample in a different ZnTe crystal. Mechanical delay stages regulate the time delays between the THz generation and detection pulse (t) as well as between the photoexcitation pump pulse and the THz detection pulse (τ). All of the experiments were carried out in a closed box with an N₂ environment at room temperature.

Transistor Measurements on a Nanosheet Networks

After a single Langmuir–Schaefer deposition the MoS₂ networks had a film thickness of ~15 nm. Interdigitated electrodes (Ti/Au, 5 nm/95 nm) were then deposited (FC-2000 Temescal Evaporator) through a shadow mask ($L_{\text{Ch}} = 50 \mu\text{m}$, $W_{\text{Ch}} = 19.4 \text{ mm}$) onto the sample. The ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIM-TFSI, 98 %, HPLC, Sigma Aldrich) was utilised to regulate ion injection into the semiconducting channel. The ionic liquid was first heated under vacuum at 100 °C for 6 h to degas any absorbed water. Subsequently, a small amount of EMIM-TFSI was carefully pipetted onto the transistor, ensuring the gate and channel were adequately covered. To remove any remaining water, the devices were left in a Janis probe station under vacuum conditions overnight, lasting 12 h. After this step, the devices were returned to atmospheric pressure in preparation for measurements. For electrical characterisation, a Keithley 2612 A dual channel source measuring unit was used. The transfer characteristics were undertaken within a gate voltage window of –3 to 3 V, employing a scan rate of 50 mV s⁻¹. Additionally, V_{DS} was set to 1 V for all the devices during the measurements.

Transistor Measurements on an Individual Nanosheet

For the electrical measurements of the individual EE MoS₂ nanosheet devices a Keithley 2636 A dual source-meter was used with an Instec compact vacuum probe station. The measurements were performed under low vacuum (10^{-2} mbar) and at 300 K. For each device electrical transfer curves ($I_D(V_{SG})$) were measured with varied V_{SD} bias, and apparent linear mobility was extracted by considering the channel geometries and the capacitance of a 300 nm thick global SiO₂/Si gate.

Kelvin Probe Force Microscopy

In-operando KPFM experiments were performed on the AIST NT scanning probe microscopy system under ambient conditions and in a frequency modulated regime. The contact potential difference (CPD) maps were recorded in a two-pass mode, using lift height of 20 nm. Potential drop maps were extracted from the CPD maps by subtracting the reference grounded measurement of the same area, following the procedure described in Refs.^{223, 249} Nu-Nano SPARK probes were used with a Pt coating, spring constant of ≈ 42 N m⁻¹, and tip radius below 30 nm. The external bias was provided via a custom-built electrical holder and by using a Keithley 2636 A dual source metre. The ground of the KPFM probe was connected also to the ground of the device (source electrode).

Note: The electrochemical exfoliation and ink preparation, as well as the Langmuir-Schaefer deposition presented in this chapter were carried out by Dr. Kevin Synnatschke and Dr. Tian Carey. The THz spectroscopy was carried out by Dr. Goutam Ghosh, Dr. Sachin Kinge and Prof. Laurens D. A. Siebbeles at Delft University of Technology. The KPFM and individual nanosheet mobility measurements were carried out by Dr. Muhammad Awais Aslam and Prof. Aleksandar Matkovic at Montanuniversität Leoben. Network mobility measurements were carried out by Dr. Tian Carey.

5.3 Verifying the Impedance Method

In Chapter 3, we established that extracting absolute values for the nanosheet resistance (R_{NS}) and junction resistance (R_J) in nanomaterial networks requires transforming the measured network impedance spectrum (Z_{Net}) into a form representing the impedance an average single nanosheet-junction pair (Z_{NS-J}). These NS-J spectra can then be analysed to extract physical parameters based on a microscopic model of the network.

Equation 3.3 introduced an expression linking the DC resistivity of a nanosheet network (ρ_{Net}) to the sum of the junction and nanosheet resistances, effectively capturing the contribution of a single nanosheet junction-pair. We assume that a similar scaling relation must apply in the AC regime, such that the complex resistivity of a network (ρ_{Net}^*) can be directly related to Z_{NS-J} . The complex resistivity will be defined as $\rho_{Net}^* = Z_{Net} A_{Net} / L_{Ch}$, where A_{Net} is the network cross-sectional area and L_{Ch} is the channel length. This leads to the expression

$$Z_{NS-J} = \rho_{Net}^* \frac{(1 - P_{Net})}{2t_{NS}} \left[1 + \frac{2}{n_{NS} t_{NS} l_{NS}^2} \right]^{-1} \quad [5.1]$$

which converts the real and imaginary parts of ρ_{Net}^* to those representing a single average nanosheet-junction pair, once P_{Net} , t_{NS} , l_{NS} and n_{NS} are known (although when n_{NS} is large enough the square bracket term can be neglected).

This impedance-based approach was applied to liquid-liquid interface deposited (LLID) networks of electrochemically exfoliated MoS₂ nanosheets, which display low porosity¹⁸ and large area junctions,³¹ as shown in Figure 5.1A. Although such networks are intensively studied, thanks in part due to their high field-effect mobilities ($>1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for printed networks),^{31, 116, 250, 251} the values for R_J and R_{NS} remain completely unknown. Initially, the networks were deposited in a transistor geometry and the (peak) field-effect mobility of these networks was measured from field-effect transistor curves such as those in Figure 5.1B, obtaining an average of $\mu_{Net} = 6.6 \pm 0.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, consistent with literature reports.³¹

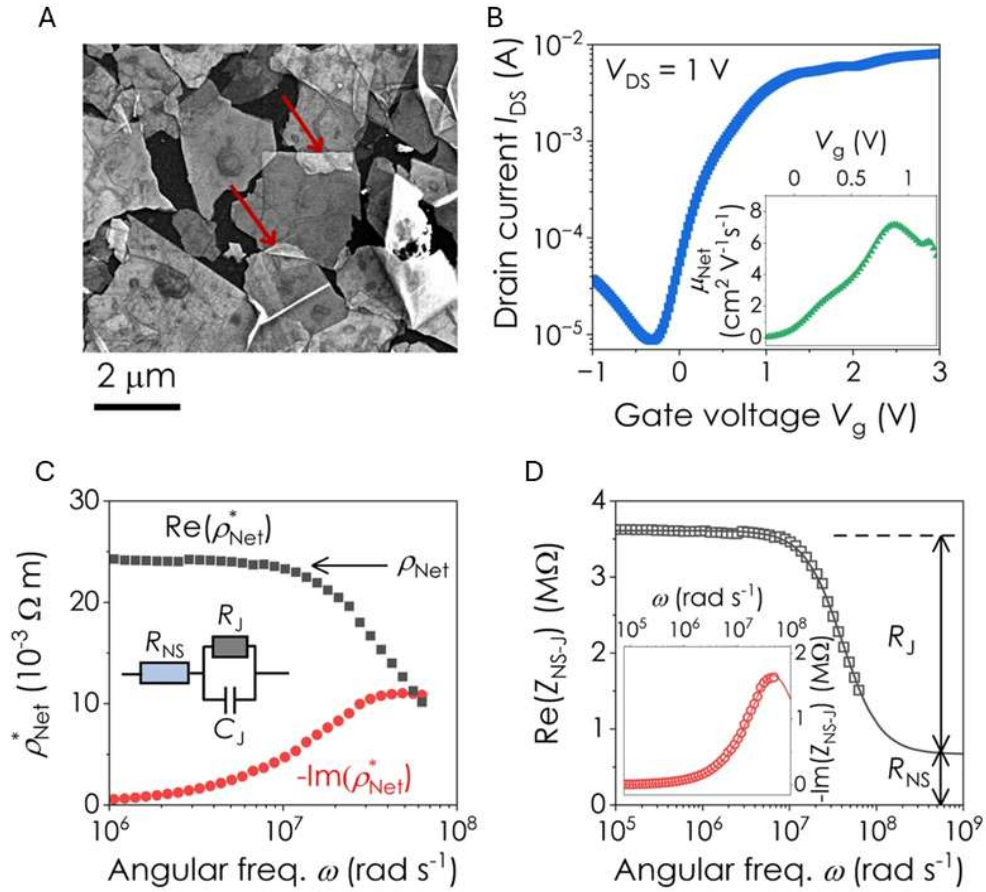


Figure 5.1: Impedance Spectra of MoS₂ Network. **A)** SEM surface image of a network of electrochemically exfoliated (EE) MoS₂ nanosheets. The arrows point to two well-defined junctions. **B)** Field effect transfer curve for an electrolytically gated EE MoS₂ network using a drain-source voltage of $V_{DS} = 1$ V. Inset: Plot of the network mobility, μ_{Net} , as a function of gate voltage. Averaging over four devices yields a mean (peak) mobility of $\mu_{Net} = (6.6 \pm 0.6) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. **C)** Real (Re) and imaginary (Im) parts of the complex network resistivity, ρ^*_{Net} , plotted as a function of angular frequency, ω , for a network of EE MoS₂ nanosheets.

Inset: The circuit element representing a nanosheet-junction pair. Here, R_{NS} is the nanosheet resistance while R_J and C_J are the junction resistance and capacitance respectively. **D)** The real part of the impedance of a nanosheet-junction pair, $\text{Re}(Z_{NS-J})$, plotted versus ω . The data has been fitted using Equation 5.2 (3.25) and the contributions of the junction and nanosheet resistances are indicated by the arrows. Inset: $-\text{Im}(Z_{NS-J})$ plotted as a function of ω . The solid line is a fit to Equation 3.26. [Adapted from Ref. ⁶]

The impedance of the networks was then measured and the real (Z') and imaginary (Z'') components of the network resistivity were extracted as a function of frequency, ω , shown in Figure 5.1C. As key spectral features occur above ~ 10 kHz, it was necessary to minimise background artefacts such as stray capacitances and inductances (as discussed later in this chapter). The low

frequency plateau in $\text{Re}(\rho_{\text{Net}}^*)$ from Figure 5.1C, gives a DC resistivity of $\rho_{\text{Net}} = 0.024 \Omega\text{m}$. Combining this with the measured network mobility yields a carrier density of $n \approx 3.8 \times 10^{23} \text{ m}^{-3}$, consistent with prior reports on electrochemically exfoliated MoS₂.^{116, 252}

With these values now known, Equation 5.1 can be used to convert the impedance of a network into the impedance of a single, average nanosheet-junction pair. Figure 5.1D shows the real part of $Z_{\text{NS-J}}$ with the imaginary part shown in the inset. These curves can be fit to an equivalent circuit to extract quantitative values for R_{NS} and R_{J} . In Chapter 3, we showed that a nanosheet-junction pair can be modelled as a Randles' circuit in the AC regime, where R_{NS} is in series with a parallel combination of R_{J} and C_{J} (Figure 5.1C, inset). Fitting the Z' vs ω plot, known as the real impedance Bode plot, yielded the most accurate fit parameters compared to fitting other spectra (as shown later in this chapter). Such spectra can be fitted using equations appropriate to the Randles circuit to yield values of R_{NS} , R_{J} , and C_{J} . However, as discussed in Chapter 3, this would assume all $R_{\text{J}}C_{\text{J}}$ values for all junctions to be identical, whereas we expect some variation in junction morphology. This distribution in $R_{\text{J}}C_{\text{J}}$ was accounted for by substituting the capacitor in the Randles' circuit with a constant phase element²⁵³ giving the expression

$$Z'_{\text{NS-J}}(\omega) = R_{\text{NS}} + \frac{R_{\text{J}} \left[1 + (\omega R_{\text{J}} C_{\text{J}})^n \cos(n\pi / 2) \right]}{1 + 2(\omega R_{\text{J}} C_{\text{J}})^n \cos(n\pi / 2) + (\omega R_{\text{J}} C_{\text{J}})^{2n}} \quad [5.2]$$

where n is an ideality factor accounting for the distribution of $R_{\text{J}}C_{\text{J}}$ values across the network.²¹¹

Fitting our data with Equation 5.2 yielded excellent fits with values of $R_{\text{J}} = 2.9 \pm 0.1 \text{ M}\Omega$, $R_{\text{NS}} = 0.67 \pm 0.07 \text{ M}\Omega$, $C_{\text{J}} = (8.4 \pm 0.4) \times 10^{-15} \text{ F}$ and $n = 0.985$. Across five devices on a single substrate, R_{NS} varied by less than 20%, while R_{J} and C_{J} showed broader distributions (with a standard deviation/mean of <60%), likely due to spatial

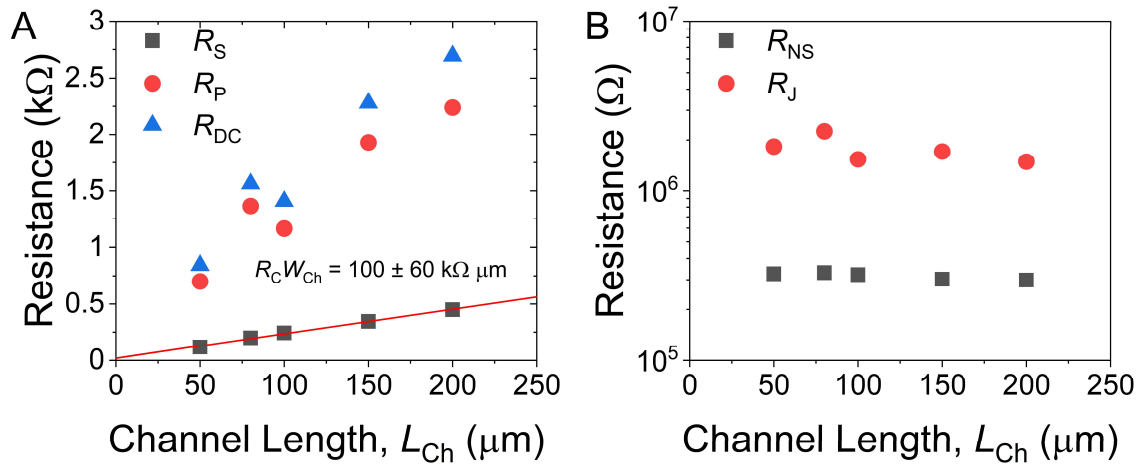


Figure 5.2: Measurement of Contact Resistance **A)** A plot of the total DC resistance, R_P and R_S versus channel length, L_{Ch} . The red line is a linear fit to the R_S data. **B)** Contact resistance corrected nanosheet and junction resistance, R_{NS} and R_J , plotted versus

variations in junction morphology. The extracted $R_J/R_{NS} = 4.4 \pm 0.2$ indicates that these networks are not significantly junction-limited, especially when compared to LPE networks which typically show values >10 as shown in Chapter 4. Using $\rho_{NS} = 2R_{NS}t_{NS}$ gives a nanosheet resistivity of $\rho_{NS} = (4.4 \pm 0.5) \times 10^{-3} \Omega\text{m}$. Given the porosity of networks of electrochemically exfoliated nanosheets are typically very low (~ 0.02),^{18, 31} we assume the carrier density in the network is approximately equal to that in the nanosheets themselves ($n_{Net} \approx n_{NS}$).²⁵⁴ This leads to a nanosheet mobility of $\mu_{NS} = 37 \pm 4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is in line with values reported for electrochemically exfoliated MoS_2 nanosheets.^{88, 116}

The impedance method presented here is especially sensitive to any contact resistances present in the network. Using this method, the nanosheet resistance, R_{NS} , is related to the series resistance, R_S , of the equivalent Randles circuit, while the junction resistance, R_J , is associated with the parallel resistance, R_P . An important issue associated with this procedure is that the extracted R_S will contain all resistances in series within the network, including the contact resistance, R_C , associated with the interface between the nanosheet network and the electrodes. Therefore, the value extracted for R_S is the sum of the contact resistance and the resistance associated with the nanosheets within the network.

We can leverage this feature to our advantage by performing channel length dependence studies on our networks, which should allow the use of the transfer length method (TLM) to determine the contact resistance associated with the network.

To test this, we measured impedance spectra on an EE MoS₂ nanosheet network which had been contacted with five sets of electrodes, each with a different channel length, L_{Ch} . These network spectra were fitted to a (CPE modified) Randles circuit from which R_{P} and R_{S} were extracted. Figure 5.2A shows the extracted R_{P} and R_{S} as well as the network DC resistance, R_{DC} . While there is a considerable amount of scatter in both R_{P} and R_{DC} , the R_{S} data increases monotonically with channel length. The TLM method predicts $R_{\text{S}} = 2R_{\text{C}} + \rho_{\text{NS,Net}} L_{\text{Ch}} / W_{\text{Ch}} t_{\text{Net}}$, where $\rho_{\text{NS,Net}}$ is the part of the network resistivity associated with the nanosheets and L_{Ch} , W_{Ch} and t_{Net} are the channel length, width and network thickness. Fitting our data reveals a contact resistance of $R_{\text{C}} W_{\text{Ch}} \approx 100 \text{ k}\Omega \mu\text{m}$, which is similar to, but slightly higher than values of $R_{\text{C}} W_{\text{Ch}} \approx 400 \text{ k}\Omega \mu\text{m}$ reported by Chen et al. for similar networks.²⁵⁵

Using the extracted R_{C} , the contact resistance corrected nanosheet and junction resistances were calculated, as shown in Figure 5.2B. R_{NS} and R_{J} remains constant with channel length, however, we observe significant scatter in R_{J} . We attribute this scatter to the spatial variation in junction morphology, and hence R_{J} , which is the dominant contribution to the network resistance. Therefore, this scatter could also be observed in the R_{DC} data (Figure 5.2A), making it impossible to extract R_{C} using the traditional TLM method from DC measurements on a single network. In principle, this means that the impedance measurement of R_{S} is the best way to extract the contact resistance from systems that are not completely homogeneous over the device area, as is common for LLID networks.

As this technique is novel to the field of nanomaterial networks, further measurements are needed to support these results. First, we used time resolved

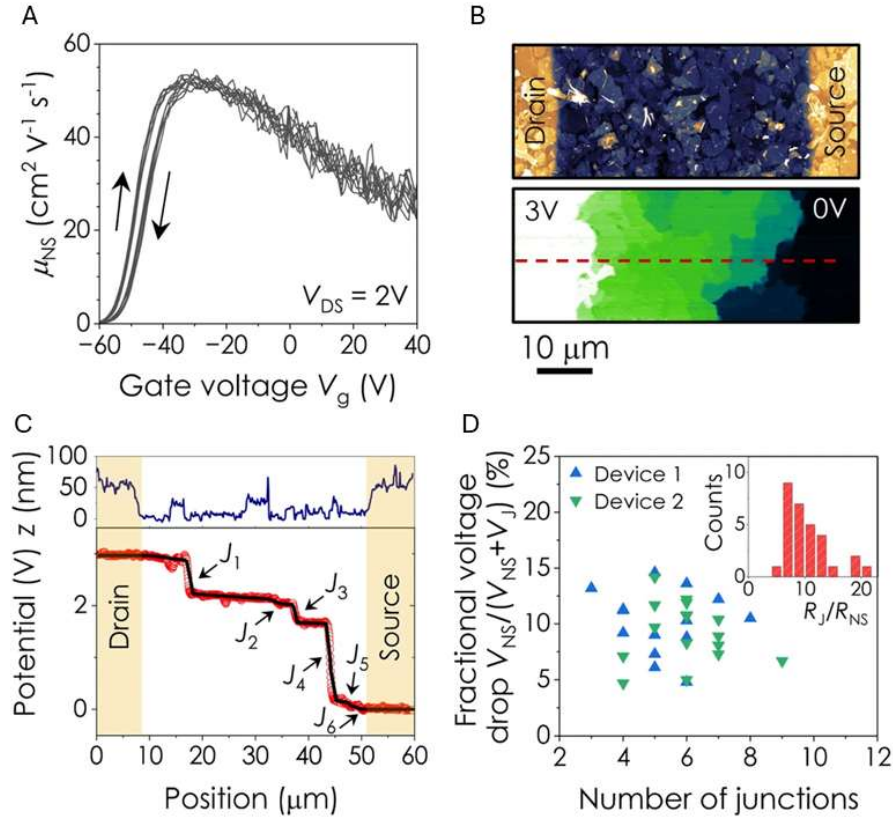


Figure 5.3: Backup Characterisation of MoS₂ Network. **A)** Gate-voltage-dependent mobility, μ_{NS} , for a representative individual EE MoS₂ nanosheet. Arrows indicate the sweep direction. **B)** Topographic AFM image (top) and in-operando KPFM image (bottom) of a section of an EE MoS₂ network between source and drain electrodes. **C)** Topographic line profile (top) and potential profile (bottom) associated with the red dashed line in (B). In this section of channel, 6 sharp drops associated with inter-sheet junctions can be seen, labelled as J_1 to J_6 . The nearly flat regions represent the gradual drop of potential across nanosheets. The black line represents fits to the linear regions. **D)** Fractional voltage dropped across nanosheets in a given portion of channel plotted versus the number of junctions observed in that section. The fractional voltage drop is given by $V_{NS}/(V_{NS} + V_J)$ where V_{NS} and V_J describe voltage drops across nanosheets and junctions respectively. Inset: Histogram of R_J/R_{NS} values calculated from the fractional voltage drops in (D). [Adapted from Ref. 6]

pump-probe terahertz spectroscopy to determine the room-temperature AC mobility of photogenerated charge carriers. A mobility of $\mu_{NS} = 40 \pm 2 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at 1 THz was observed, consistent with the value extracted from the impedance method. Additionally, field-effect mobility measurements were performed on individual MoS₂ nanosheets (Figure 5.3A), obtaining a zero-gate-bias value of $42 \pm$

$6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, again consistent with the impedance result. Reformulating Equation 3.3 from Chapter 3 gives the scaling relation $(R_J / R_{NS}) \approx (\mu_{NS} / \mu_{Net}) - 1$. Using the mobility values obtained above, we estimate $R_J/R_{NS} = 5.3 \pm 1.4$ which is once again consistent with the results given by the impedance method.

Finally, to independently verify these results, our collaborators performed in-operando Kelvin probe force microscopy (KPFM) under frequency modulation to map the potential drop across an MoS₂ network, as shown in Figure 5.3B,C.^{249, 256, 257} These measurements revealed potential drops across both the junctions and the individual nanosheets. Figure 5.3D demonstrates that summing the voltage drops associated with the junctions along the channel length, we can extract the overall fraction of potential dropped within the nanosheets, which yields a mean value of $R_J/R_{NS} = 10 \pm 4$, broadly consistent with our previous analyses. While morphological variations can shift these values, the agreement across all methods strongly supports the application of impedance spectroscopy for the characterisation of nanomaterial networks.

5.4 Fitting Impedance Spectroscopy Data

Typically, fitting impedance spectroscopy data to equivalent circuits can come with many pitfalls,^{205, 207} and impedance spectra from nanomaterial networks are

	$R_J \text{ (M}\Omega\text{)}$	$R_{NS} \text{ (k}\Omega\text{)}$	R^2
$ Z $ Bode	6.60 ± 0.02	340 ± 10	0.999
Nyquist	6.94 ± 0.03	92 ± 19	0.996
Z' Bode	6.90 ± 0.01	97 ± 5	0.999

Table 5.1: Fit parameters for the various plotting methods to extract R_J and R_{NS} from impedance spectra. The values for the junction resistance, R_J , and nanosheet resistance, R_{NS} , were extracted by fitting the Bode plots of $|Z|$ and Z' and the Nyquist plot of $-Z''$ vs Z' in Figure 5.4.

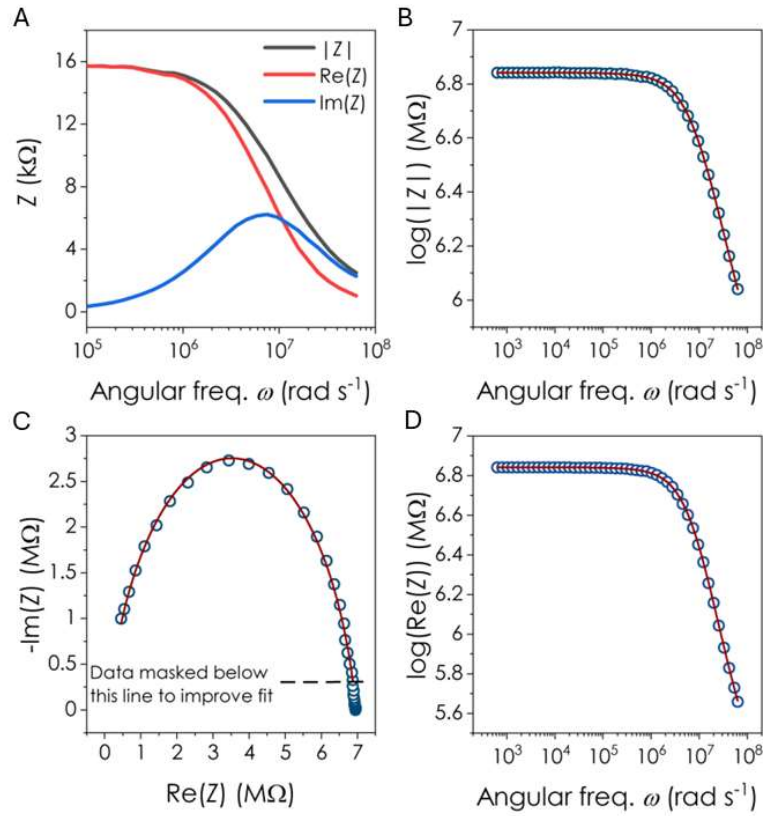


Figure 5.4: Fitting Impedance Spectra of Nanomaterial Networks. **A)** Plots of $|Z|$, Z' and $-Z''$ as a function of angular frequency, ω . **B)** Bode plot of $|Z|$ vs ω . **C)** Nyquist plot of $-Z''$ vs Z' . **D)** Bode plot of Z' vs. ω . Here (A) represents network data, while (B-D) are converted to NS-J.

no different. Areas of particular concern for these systems include background capacitances or inductances and the frequency range of interest.⁶ However, to assess the effects of these issues, it is first necessary to establish the fitting of which data provides the most accurate results. The most common technique for fitting spectra to equivalent circuits in the literature involves fitting a Nyquist plot of $-Z''$ against Z' , however, fitting the $|Z|$, Z' and $-Z''$ Bode plots are also commonly chosen.²⁰⁷ For a (CPE modified) Randles circuit, the imaginary impedance does not contain any information on the series resistance, only that of the parallel resistance and capacitance (R_pC_p). Therefore, the $-Z''$ Bode plot can be neglected for the primary fitting technique, however, it is still very useful to fit the $-Z''$ Bode plot to verify results from other fitting techniques.

Figure 5.4A shows a plot of the $|Z|$, Z' and $-Z''$ Bode plots for a sample of LLID electrochemically exfoliated MoS_2 . At low frequencies the $|Z|$ plot is dominated by the Z' contribution and at intermediate frequencies it is dominated by the Z'' contribution, as expected for a Randles circuit. Therefore, if the series resistance is extract from $|Z|$ Bode plot where the entire spectrum is not available (due to the maximum frequency of the impedance analyser), the value of R_s (R_{NS}) will be overestimated.

Figure 5.4B-D shows the Bode plot of $|Z|$ vs ω , the Nyquist plot of $-Z''$ vs Z' and the Bode plot of Z' vs ω , respectively. As these values typically stretch multiple orders of magnitude, the y-axis has been displayed as the log of the impedance. The fit parameters of each of these plots is shown in Table 5.1, along with the coefficient of determination, R^2 . This table shows that while the R_J values may be similar for each of these fitting techniques, R_{NS} can have some variance. As predicted, fitting the $|Z|$ Bode plot resulted in an overestimation of R_{NS} . Fitting of the Nyquist plot results in a large uncertainty in R_{NS} and a lower R^2 . Therefore, we primarily fit our equivalent circuits to Z' Bode when extracting R_{NS} , R_J and C_J in nanomaterial networks.

Junction Characteristic Frequency Limitations

An inherent challenge in measuring the impedance of nanomaterial networks is that the characteristic frequency associated with the junctions often lies beyond the upper frequency limit of standard impedance analysers. Typical commercially available instruments are limited to frequencies below $\sim 10 - 100$ of MHz, beyond which specialised equipment and more complex experimental setups are required, significantly complicating the measurement process.²⁵⁸ In a Randles circuit, the characteristic relaxation time, τ , is given by the product $R_P C_P$, and the corresponding relaxation frequency is $f_r = 1/\tau$. At this frequency there is a peak in the $-Z''$ vs ω Bode plot and an inflection point in Z' vs ω Bode plot. Even when this relaxation frequency lies outside the accessible range, partial features of the

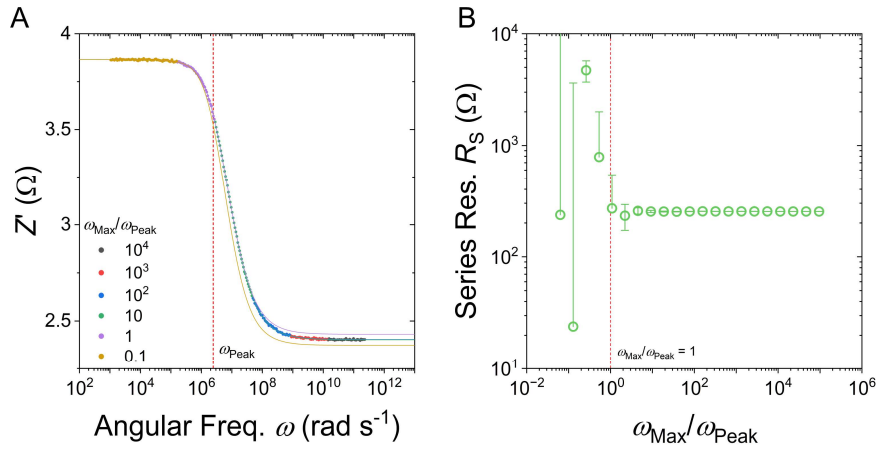


Figure 5.5: Fitting Different Frequency Ranges of Impedance Spectra. A) Plot of generated Z' vs ω data with varying degrees of curvature ($\omega_{\text{Max}}/\omega_{\text{Peak}}$) fit to a Randles circuit (with a CPE). **B)** The resulting series resistance, R_s , plot against the degree of curvature ($\omega_{\text{Max}}/\omega_{\text{Peak}}$). There is a clear deviation from the $R_s = 253 \Omega$ below $\omega_{\text{Max}}/\omega_{\text{Peak}} = 1$.

associated inflection (or peak) may still appear within the measurement window, allowing extraction of R_s , R_P and C_P . However, the degree of curvature required in these features to ensure a reliable fit remains unclear. Establishing quantitative criteria for when fitting produces reliable results (particularly in cases where only a portion of the relaxation feature is observed) would be highly valuable for analysing nanomaterial networks, where incomplete impedance spectra are common.

To investigate this, we began by generating data for a representative network with $R_s = 253 \Omega$, $R_P = 7089 \Omega$, $C_P = 5.79 \times 10^{-11} \text{ F}$ and $n = 0.85$ at 0.2% noise, matching a network of LLID electrochemically exfoliated SnSe_2 nanosheets. The impedance analyser used in this work (Keysight E4990A) reaches a maximum frequency of 30 MHz ($1.9 \times 10^8 \text{ rad s}^{-1}$) so the data generated between $10^3 \text{ rad s}^{-1} < \omega < 2.3 \times 10^{11} \text{ rad s}^{-1}$ to ensure both the high and low frequency plateaus were entirely visible (Figure 5.5A). The data was then fit for a range of maximum frequencies, ω_{Max} (i.e., the fits ranged from 10^3 rad s^{-1} to ω_{Max}). In Figure 5.5B, the extracted R_s is plot as a function of $\omega_{\text{Max}}/\omega_{\text{Peak}}$ (where $\omega_{\text{Peak}} = 1/R_P C_P = 2.4 \times 10^6 \text{ rad s}^{-1}$), from which it is clear that for $\omega_{\text{Max}}/\omega_{\text{Peak}} < 1$ the fit becomes very unreliable. This result suggests, if the measured impedance does not reach ω_{Peak} (i.e., display a peak in the $-Z''$ Bode

plot) then the fit will not be reliable, providing a simple, quick route to verifying the reliability of the impedance method.

However, this results also implies that there is a limit to which nanomaterial networks are suitable for impedance spectroscopy. Impedance spectra from networks with a peak frequency ($1/R_P C_P$) greater than the maximum frequency of the impedance analyser cannot be reliably fit to an equivalent circuit to extract values of R_J and R_{NS} . This means networks of more conductive materials, where transport across junctions can proceed more freely (i.e., networks that display small R_J and hence C_J), will not be measurable using the impedance method without the use of high frequency impedance analysers, which typically introduces major experimental difficulties.²⁵⁹

IDE Capacitance

Another key limitation in performing impedance spectroscopy on nanomaterial networks, particularly for more resistive semiconducting materials, is the use of high aspect ratio interdigitated electrodes (IDEs), such as those shown in [Figure 5.6A](#). IDEs are widely used in printed electronics as they provide a way to maximise channel width, and thus reduce network resistance, while maintaining a compact device footprint and short channel length. However, upon closer inspection, it becomes clear that IDEs inherently introduce a background capacitance due to their geometry. The alternating metal fingers separated by dielectric gaps (air and/or resistive nanomaterials) form a planar capacitor. Furthermore, this parasitic capacitance is increased once dielectric or semiconducting nanosheets are deposited over top the electrodes. Some studies have even exploited this planar geometry to design high-capacitance, low-footprint devices.²⁶⁰ When this IDE-related capacitance becomes too large relative to the network capacitance, it can dominate the impedance response, particularly at higher frequencies.

The total capacitance of an IDE can be understood as a combination of two components: the interior capacitance (C_i) and the exterior capacitance (C_e); C_i

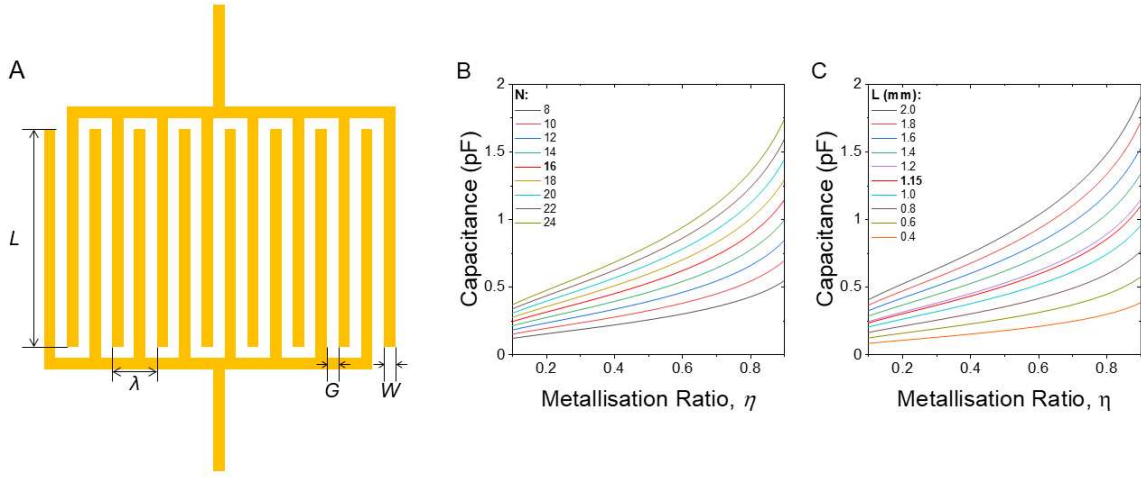


Figure 5.6: Capacitance of an IDE. **A)** Schematic of an IDE layout **B)** Plot of the capacitance of an IDE as a function of the metallisation ratio, η , for various values of N . **C)** Plot of the capacitance of an IDE as a function of the metallisation ratio, η , for various values of L .

represents half the capacitance of an interior electrode with respect to ground, while C_E accounts for the capacitance of an outer electrode relative to the adjacent ground plane. The total IDE capacitance is then given by

$$C_{\text{IDE}} = (N-3) \frac{C_1}{2} + 2 \frac{C_1 C_E}{C_1 + C_E} \quad [5.3]$$

where N is the number of electrode fingers, as shown in Figure 5.6A. To calculate C_1 and C_E , conformal mapping techniques can be used to transform the IDE geometry into an equivalent parallel plate configuration, for which analytical solutions exist for both the capacitance and the field lines.²⁶¹ This yields

$$C_1 = \epsilon_0 \epsilon_r L \frac{K(k_1)}{K(k_1')}, \quad C_E = \epsilon_0 \epsilon_r L \frac{K(k_E)}{K(k_E')} \quad [5.4]$$

where, ϵ_r is the relative permittivity of the overlying dielectric layer, L is the length of the IDE fingers, and $K(k)$ is the complete elliptic integral of the first kind. k' is the complementary modulus defined as $k' = \sqrt{1-k^2}$. Assuming an infinitely thick dielectric layer, these expressions depend only on the metallisation ratio of the IDE, defined as:

$$\eta = \frac{W}{W + G} \quad [5.5]$$

where W is the electrode finger width and G is the gap width between adjacent electrodes, or in our case, the channel length, L_{Ch} . Therefore, the IDE capacitance is governed by L , N , ϵ_r , and η . Figure 5.6B,C shows how the total IDE capacitance varies with metallisation ratio for different values of N and L , respectively. Lower metallisation ratios (i.e., narrower electrodes and/or wider gaps) result in reduced background capacitance.

In practice, large-area devices are often required to achieve usable conductivity in semiconducting nanosheet networks. As a result, both L and N must remain relatively large ($N = 16$, $L = 1.15$ mm in this work). Consequently, minimising the metallisation ratio becomes essential to reduce the impact of IDE capacitance on impedance measurements. However, there are physical and fabrication-related limits to how small W and how large G (l_{Ch}) can be made. For example, extremely narrow fingers may lead to high contact resistance due to reduced contact overlap between the nanosheets and the electrodes, as well as fabrication challenges depending on the resolution of the patterning technique. Furthermore, the influence of IDE capacitance becomes more significant at higher frequencies, as the impedance of a capacitor decreases with frequency according to $Z_C = -i / \omega C$. Thus, any future efforts to extend impedance spectroscopy into the high MHz or GHz regime must carefully consider and minimise IDE-related capacitance to ensure accurate measurement of the nanomaterial network's intrinsic properties.

5.5 Material Suitability for Impedance Spectroscopy

Having established both an upper limit (set by IDE background capacitance) and a lower limit (set by the junction's characteristic frequency, $R_J C_J$), the next logical step is to identify which nanomaterial networks fall within this window of

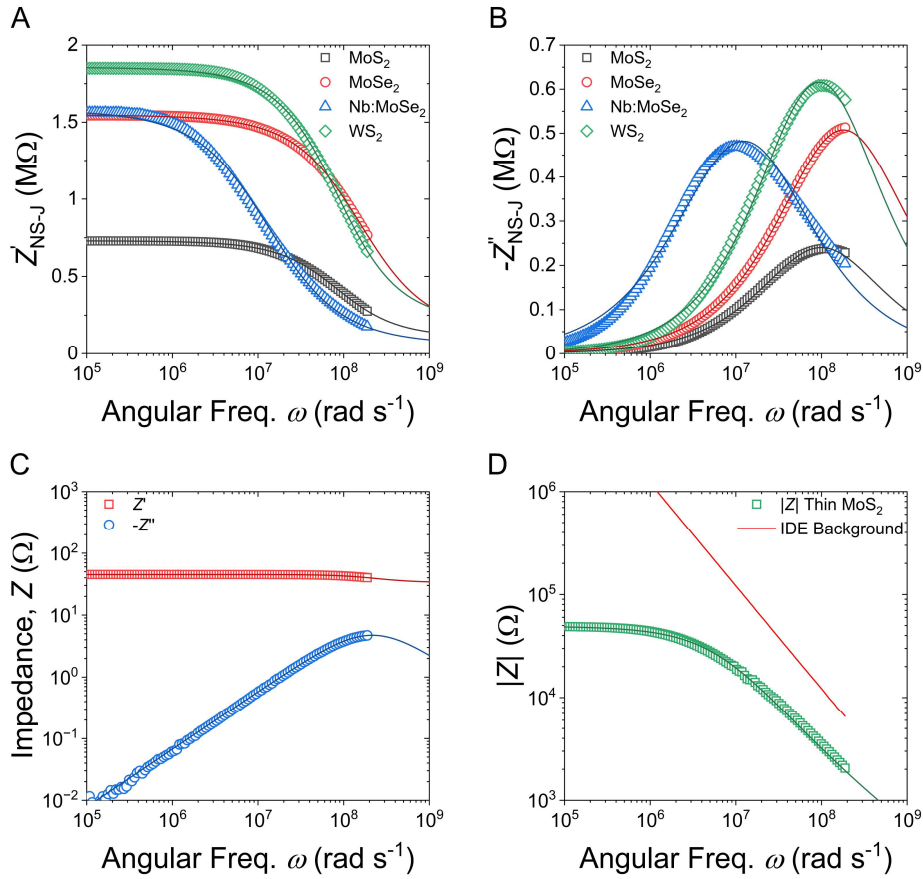


Figure 5.7: Material Suitability for Impedance Spectroscopy **A)** Z'_{NS-J} vs ω Bode plot measured on LLID EE TMD networks. **B)** $-Z''_{NS-J}$ vs ω Bode plot measured on LLID EE TMD networks. In both (A) and (B) the spectra have been converted to the single average nanosheet-junction pair representation. The solid lines are fits to a Randles circuit with a CPE. **C)** Z' and $-Z''$ vs ω Bode plots for a 4-layer ($t_{Net} \approx 60$ nm) LLID EE MoS₂ network. The Z' data shows very little curvature while the $-Z''$ data falls just short of the peak from the fit. **D)** $|Z|$ vs ω Bode plot for a 1-layer ($t_{Net} \approx 15$ nm) LLID EE MoS₂ network alongside the background impedance measured on a bare IDE device. At higher frequencies the measured impedance becomes dominated by the IDE capacitance.

accessibility. An ideal system should feature large junction overlap areas to maximise the junction capacitance, while being conductive enough to avoid the IDE background capacitance, but not too conductive so that $R_J C_J$ is below the frequency limit of the impedance analyser; certainly, a complex balancing act! Liquid-liquid interface deposited networks of electrochemically exfoliated semiconducting nanosheets are a highly suitable candidate for this. The combination of large area nanosheets produced by EE with the large overlap area junctions produced by LLID results in a significant junction capacitance.

Furthermore, the junction resistance typically falls in just the right range, being resistive enough to keep the characteristic junction frequency ($R_J C_J$) below the frequency limit of the analyser, while producing networks which are conductive enough to avoid the IDE background.

Figure 5.7A,B shows the real and imaginary Bode plots of (the nanosheet-junction converted) impedance for multiple liquid-liquid interface deposited electrochemically exfoliated transition metal dichalcogenides. These materials all display junction resistances on the order $\sim 1\text{ M}\Omega$, and nanosheet resistances around $\sim 100\text{ k}\Omega$. In all cases we find $R_J/R_{NS} > 1$, indicating the networks are junction limited, despite their high electrical performance.^{31, 82} Networks of LLID EE TMDs appear to be in the current sweet spot for impedance spectroscopy measurements, with $1/R_J C_J < 30\text{ MHz}$ (30 MHz being the maximum frequency attainable by our Keysight E4990A impedance analyser) and a network impedance which falls below the background capacitance of the IDEs.

However, not all EE TMDs are created equally. Figure 5.7C,D shows two cases of EE TMDs networks which are not suitable for impedance spectroscopy. The first sample is a thicker MoS_2 network which was annealed at $200\text{ }^\circ\text{C}$. The annealing process removes inter-flake solvent residues, significantly reducing the junction resistance. Additionally, the increased network thickness introduces more parallel conductive pathways for charge transport through the network, further lowering the average junction resistance. This reduction in R_J (and C_J) shifts the characteristic peak in the imaginary impedance beyond the 30 MHz upper limit of our impedance analyser, as shown by Figure 5.7C. Fitting of this data will therefore result in an overestimation of R_{NS} and a slight underestimation of R_J as previously discussed.

Conversely, Figure 5.7D shows the impedance for a thin ($<15\text{ nm}$), unannealed sample of MoS_2 . In this case, the junction resistance is much larger due to the presence of solvent residue and the decreased network thickness, resulting in the

network displaying a large resistance/impedance. Figure 5.7D shows the $|Z|$ Bode plot alongside the measured bare IDE $|Z|$ Bode plot. At higher frequencies, the sample impedance approaches that of the IDE impedance and the IDE capacitance begins to dominate the spectrum. Fitting this spectrum using a Randles model reveals an unphysically low $R_s = 0$, suggesting the IDE capacitance has completely dominated the measurement at high frequency. In this regime, the device behaves more like a parallel resistor-capacitor circuit where the resistor represents the network, and the capacitor reflects the background IDE capacitance.

5.6 Conclusion

In this chapter, we developed and validated an impedance spectroscopy-based method to extract the junction and nanosheet resistance in nanomaterial networks. By converting the measured network impedance into that of an average nanosheet-junction pair, we were able to directly extract meaningful physical parameters by modelling the system with an equivalent Randles circuit. This method was applied to LLID networks of electrochemically exfoliated MoS_2 , where the values for R_{NS} , R_{J} and C_{J} were extracted and found to be consistent with independent measurements from THz spectroscopy, field-effect mobility and in-operando KPFM. More broadly, we demonstrated that this approach works for a range of EE TMD networks.

However, some practical limitations currently remain. Most notably, the background capacitance introduced by the IDEs can obscure the sample response at higher frequencies, particularly in more resistive networks with larger impedances. Conversely, high conductivity networks with low R_{J} and/or C_{J} can push the characteristic frequencies beyond the range of standard impedance analysers. These two effects define a “sweet spot” between an upper and lower limit on the materials and devices currently accessible using this technique. Future

work should focus on addressing these constraints, either by improved electrode design or junction engineering, allowing the method to be extended to a broader range of materials.

"Time is the wisest counsellor of all"

Pericles

CHAPTER 6

ELECTRICAL TRANSPORT IN NANOMATERIAL NETWORKS

6.1 Introduction

Measuring the temperature-dependent electrical characteristics of systems such as networks of nanomaterials is crucial to understanding their primary conduction mechanisms. Numerous studies have reported the temperature-dependent conductivity or resistivity of networks composed of solution processed nanomaterials such as graphene, AgNWs,²⁶² SWCNTs^{89, 181} and MoS₂.^{212, 213} However, these reports investigate the conduction mechanisms of the network as a whole and cannot separate inter- from intra-particle effects. Consequently, such measurements primarily probe the rate-limiting step in the conduction process, which is usually inter-particle charge transport across junctions. However, in many systems, where the rate-limiting step is not completely dominant, it can be difficult to arrive at a conclusion for the transport within the network. For a broader understanding of the transport within the network, it is necessary to decouple the contribution from the junctions and from the nanoparticles themselves. The chapter aims to simultaneously assess the inter-particle (junction) and intra-particle (nanomaterial) transport within nanomaterial networks to provide a comprehensive understanding of the conduction phenomena at play.

Building on [Chapter 4](#) and [Chapter 5](#), we apply two complementary approaches. First, using AgNWs and LPE graphene nanosheet networks, we exploit the size-dependent DC measurements discussed in [Chapter 4](#), but now as a function of temperature enabling the extraction of the temperature-dependent R_J and ρ_{NW} (or ρ_{NS}). Then, using EE MoS₂ networks, we perform temperature-dependent impedance spectroscopy and extract R_{NS} , R_J and C_J , as we did in [Chapter 5](#), for each temperature across the full temperature range. In both cases, the transport mechanisms present in both the nanoparticles and the junctions were understood using existing physical interpretations and useful parameters were determined. This work establishes a general framework to understand the inter- and intra-particle conduction mechanisms in nanomaterial networks using both DC and AC measurements.

6.2 Experimental Procedure

Nanomaterial Network Production and Characterisation

AgNW and LPE graphene nanosheet networks were produced as detailed in [Chapter 4](#). MoS₂ networks were produced as detailed in [Chapter 5](#). SEM and FIB-SEM NT were carried out as detailed in [Chapter 4](#). THz spectroscopy was carried out as detailed in [Chapter 5](#).

DC Temperature Dependent Conductivity Measurements

The low frequency real component of the sample impedance was measured from a frequency of 10 to 1000 Hz in the temperature range 20 to -120 °C using a broadband Alpha High-Resolution impedance Analyzer (Novocontrol GmbH, Germany), which utilizes a capacitance bridge technique to calculate impedance. The low frequency real impedance is expected to be identical to the DC resistance in samples such as these. The samples were placed inside a sample holder which has a fitted Pt 100 Ω resistance temperature sensor in contact with the electrodes. The temperature of the sample was controlled inside a double wall

cryostat and maintained by a heated N₂ jet produced by evaporating liquid nitrogen inside a 50 L dewar (Apollo 50 by Messer Griesheim GmbH). The Quatro temperature controller controls the power supplied to the dewar and gas heater. The AC measuring voltage applied to the sample was set at 0.5 V.

AC Temperature Dependent Impedance Measurements

Temperature-dependent impedance measurements were performed using a broadband Alpha High-Resolution Impedance Analyser (Novocontrol GmbH, Germany), which utilizes a capacitance bridge technique to calculate impedance. The real and imaginary components of impedance were measured from a frequency of 100Hz to 10MHz in the temperature range 20 °C to –120 °C. The samples were placed inside a sample holder which has a fitted Pt 100Ω resistance temperature sensor in contact with the electrodes. The temperature of the sample was controlled inside a double wall cryostat and maintained by a heated N₂ jet produced by evaporating liquid nitrogen inside a 50 L dewar (Apollo 50, Messer Griesheim GmbH). The Quatro temperature controller controls the power supplied to the dewar and gas heater. The AC measuring voltage applied to the sample was set at 0.1V.

Note: The electrochemical exfoliation and ink preparation, as well as the Langmuir-Schaefer deposition for the MoS₂ networks presented in this chapter were carried out by Dr. Kevin Synnatschke and Dr. Tian Carey. The THz spectroscopy was carried out by Dr. Goutam Ghosh, Dr. Sachin Kinge and Prof. Laurens D. A. Siebbeles at Delft University of Technology.

6.3 Results and Discussion: Transport in Silver Nanowire Networks

In Chapter 4, we used AgNW networks as a benchmark system as they are a relatively well studied system and are already being adapted for industry use.^{42, 43,}

²²⁵ We showed that we could extract R_J and ρ_{NW} in these networks using simple DC

measurements and the networks were predominantly junction limited. Here, we build upon this work by extracting the temperature dependent R_J and ρ_{NW} to separately assess their contribution to the electrical transport within AgNW networks. We achieve this by measuring the temperature dependence of the network resistivity for networks comprising nanowires of different lengths. We note that for technical reasons we used two-probe rather than 4-probe measurements, meaning our resistivity values are slightly overestimated. However, this does not affect the general validity of the method. Figure 6.1A,B shows the temperature dependence of the resistivity of AgNW networks for three different nanowire lengths, both for AgNWs with $D_{NW} = 38$ and 57 nm, respectively. The data shows that the network resistivity increases with increasing temperature, as is characteristic of metallic materials. Such data has been reported before by various authors.^{213, 263}

Our novel contribution is to replot this data, not as ρ_{Net} versus T for various nanowire lengths, but as ρ_{Net} versus $1/l_{NW}$ for various temperatures (Figure 6.1C,D). This allows us to fit the data for each temperature using Equation 4.2, as we did in Chapter 4. In this way, values of R_J and ρ_{NW} can be extracted for each temperature (Figure 6.1E,F). This allows us to examine the temperature dependence of R_J and ρ_{NW} individually, which enables the separate examination of intra-nanowire and inter-nanowire conduction mechanisms.

Figure 6.1E shows the extracted ρ_{NW} vs temperature data, as well as literature data for ρ_{NW} vs temperature measured on individual AgNWs for comparison. We find our ρ_{NW} data (extracted from network measurements) to be consistent to the published data measured on individual nanowires.^{4, 5}

The temperature dependence of individual AgNWs has been extensively studied and it is well understood that, within certain limitations,⁵ it can be described by a combination of the Bloch–Grüneisen (BG) formula^{4, 5, 216}

$$\rho(T) = \rho_0 + \rho_{e-ph}(T) \quad [6.1]$$

$$\rho_{e-ph}(T) = \alpha_{e-ph} \left(\frac{T}{\Theta_D} \right)^5 \times \int_0^{\Theta_D/T} \frac{x^5}{(e^x - 1)(1 - e^{-x})} dx \quad [6.2]$$

where ρ_0 is the residual resistivity due to defect scattering, ρ_{e-ph} is the resistivity arising from electron-phonon (e-ph) interactions, α_{e-ph} is a constant characterizing e-ph coupling and Θ_D is the Debye temperature. Equation 6.2 assumes that the dominant source of temperature dependence is the scattering of electrons by phonons and predicts that the resistivity of a material increases with increasing temperature. This is because the increased thermal energy allows the phonons to scatter electrons more effectively, which reduces the mean free path of electrons.

Our $\rho_{NW}(T)$ data shows a good fit to the BG equation over our temperature range (Figure 6.1E), which confirms that the primary mode of scattering in our AgNWs is due to phonons. The Debye temperature for AgNWs with $D_{NW} = 38$ and 57 nm were found to be 181 and 133 K, respectively, which aligns well with the reported range of 128 – 215 K for AgNWs^{4, 5, 216} and demonstrates the expected higher Debye temperature for smaller nanowires.^{4, 216} The extracted residual resistivities were $8.9 \times 10^{-9} \Omega m$ for the 38 nm nanowires and $4.8 \times 10^{-9} \Omega m$ for the 57 nm nanowires, both consistent with the typical reported range of 1.7×10^{-9} to $2.0 \times 10^{-8} \Omega m$ for AgNWs^{4, 5, 216} and consistent with previously reported nanowire diameter scaling.⁴ Additionally, the electron-phonon coupling constants were determined to be 9.6 and $3.0 \times 10^{-8} \Omega m$ for the $D_{NW} = 38$ and 57 nm AgNWs, respectively, which also scale with D_{NW} as expected⁴ and fall within the reported range of 3.5 to $9.9 \times 10^{-8} \Omega m$.^{4, 5, 216} This clearly shows that the $\rho_{NW}(T)$ data extracted using our method is consistent both with other reported experimental data and with the standard theoretical framework (the BG equation) used to analyse such data.

A plot of R_J vs temperature is shown in Figure 6.1F. The data are quite linear in T , consistent with metallic behaviour at temperatures above the Debye temperature. We interpret this as meaning the junctions consist of silver welds as

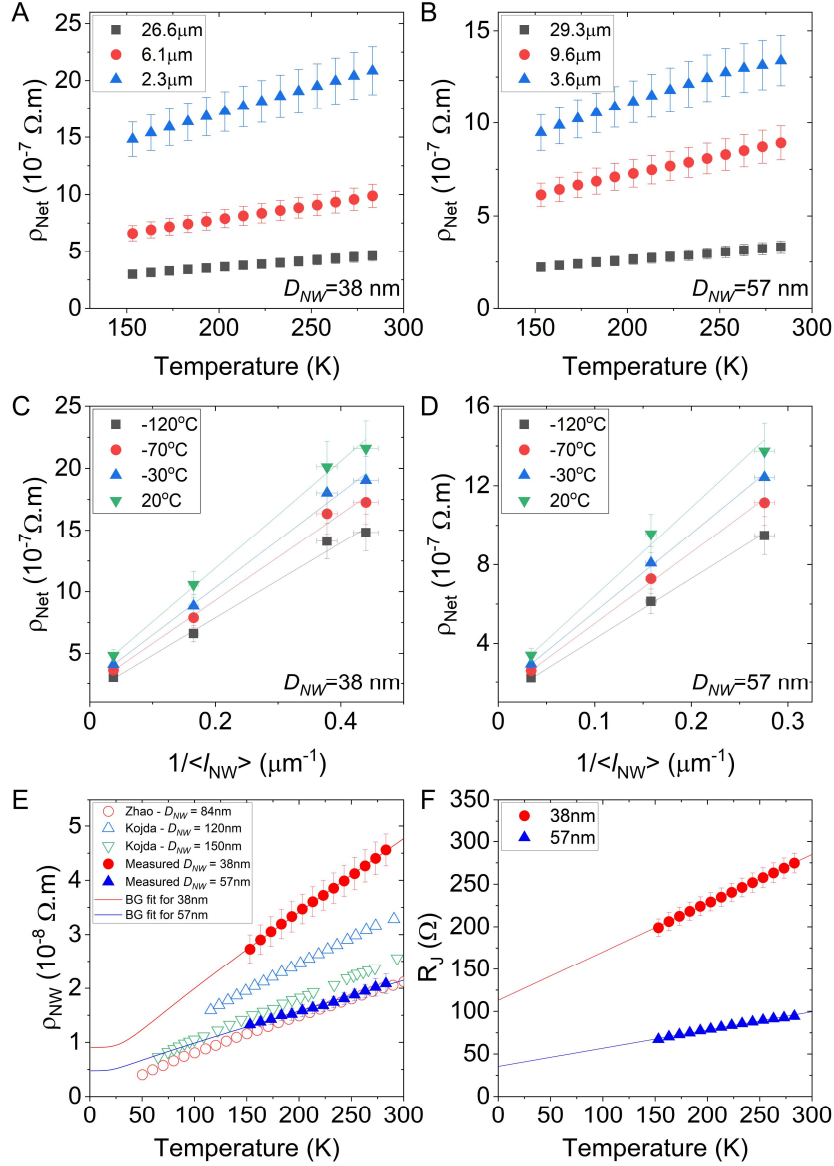


Figure 6.1: Temperature Dependence of AgNW Networks. A-B) Examples of network resistivity, ρ_{Net} , vs temperature, T , for networks with various AgNW lengths for nanowires with $D_{\text{NW}} = 38 \text{ nm}$ (A) and $D_{\text{NW}} = 57 \text{ nm}$ (B). **C-D)** Examples of network resistivity, ρ_{Net} , measured at various temperatures plotted versus the inverse of the nanowire length, $\langle l_{\text{NW}} \rangle^{-1}$, for AgNWs of diameter 38 nm (C) and 57 nm (D). The lines are fits to Equation 4.2. **E)** The extracted nanowire resistivity plotted versus temperature for our AgNW networks compared to temperature dependent resistivity of individual silver nanowires reported in the literature^{4,5}. The lines are a fit to Equation 6.2. **F)** The extracted junction resistance versus temperature for our AgNW networks. The lines are a fit to Equation 6.4.

previously reported for annealed networks.^{264, 265} However, this linearity, coupled with the limited temperature range, makes it impossible to apply the BG fit accurately. Nevertheless, we can roughly analyse the data by taking the high

temperature approximation to Equation 6.2 (expanding the exponentials to first order and integrating) which yields

$$\rho(T) = \rho_0 + \frac{\alpha_{e-ph}}{4\Theta_D} T \quad [6.3]$$

We then assume that the junction resistance can be related to the resistivity of the material making up the junctions via $R_J = \rho / b$. Here b is a parameter with dimensions of length which describes the geometric properties of the junction. We can then write

$$R_J = \frac{\rho_0}{b} + \frac{\alpha_{e-ph}}{4b\Theta_D} T \quad [6.4]$$

We estimate b by comparing the values for junction resistance and nanowire resistivity at room temperature, yielding $b = 1.65$ and 2.18×10^{-10} m for the 38 and 57 nm diameter nanowires, respectively.

We can use Equation 6.4 to fit the data in Figure 6.1F. From the intercepts we find the residual resistivities to be 1.9×10^{-8} Ωm for the 38 nm nanowires and 7.7×10^{-9} Ωm for the 57 nm nanowires, both consistent with the values extracted from the ρ_{NW} data. From the slopes, we find the ratio of the electron-phonon coupling and the Debye temperature, α_{e-ph} / Θ_D , obtaining values of 3.8 and 1.9×10^{-10} ΩmK^{-1} , for the 38 and 57 nm diameter nanowires respectively, close to the values of 5.3 and 2.3×10^{-10} ΩmK^{-1} found from the ρ_{NW} data. This result shows that the temperature dependence of our junction resistance values is fully consistent with the expected behaviour of metallic silver junctions. We reiterate that such metallic junctions are expected to occur in annealed networks of silver nanowires such as those used here.²⁶⁵ These results fully support the effectiveness of our method to extract both nanowire and junction resistance from length-dependent network resistivity measurements.

6.4 Results and Discussion: Transport in Graphene Nanosheet Networks

Expanding on our work with AgNW networks and our work with graphene nanosheet networks in [Chapter 4](#) we aim to extract and separately assess the contributions of R_J and ρ_{NS} in LPE graphene nanosheet networks, currently a very important system in the literature.²⁶⁶ We achieve this by measuring the temperature dependent resistivity of multiple networks, each with different nanosheet thickness. For technical reasons, we once again performed two-probe temperature-dependent resistivity measurements, so we expect the resistivity values to be slightly overestimated, but we do not expect this to have a substantial effect on the validity of our results. The temperature dependent resistivity of a subset of the measured networks are displayed in [Figure 6.2A](#). The network resistivity of the graphene networks decreases with increasing temperature, as expected for networks of LPE graphene.^{213, 267} In addition, such behaviour is observed for many types of graphite above ~ 50 K.^{65, 243} It is also worth noting that the resistivity does not vary much within our experimental window, typical of both graphite flakes and graphene networks.^{65, 213, 243}

The temperature dependence of the nanosheet resistivity (ρ_{NS}) and the junction resistance (R_J) can be extracted from the data using the same technique displayed above for AgNWs and in [Chapter 4](#). Instead of plotting the data in [Figure 6.2A](#) as graphs of ρ_{Net} versus temperature for different flake thicknesses, we replot this data as graphs of ρ_{Net} versus nanosheet thickness (t_{NS}), each at a different temperature ([Figure 6.2B](#)). Once again, this allows for the calculation of both the nanosheet resistivity and junction resistance at each temperature by fitting each curve using [Equation 4.4](#), enabling the extraction and inspection of the temperature dependent ρ_{NS} and R_J individually, so that the inter- and intra-nanosheet transport mechanisms can be separately examined.

The extracted nanosheet resistivity as a function of temperature is shown in [Figure 6.2C](#) while the temperature dependence of the junction resistance is shown in

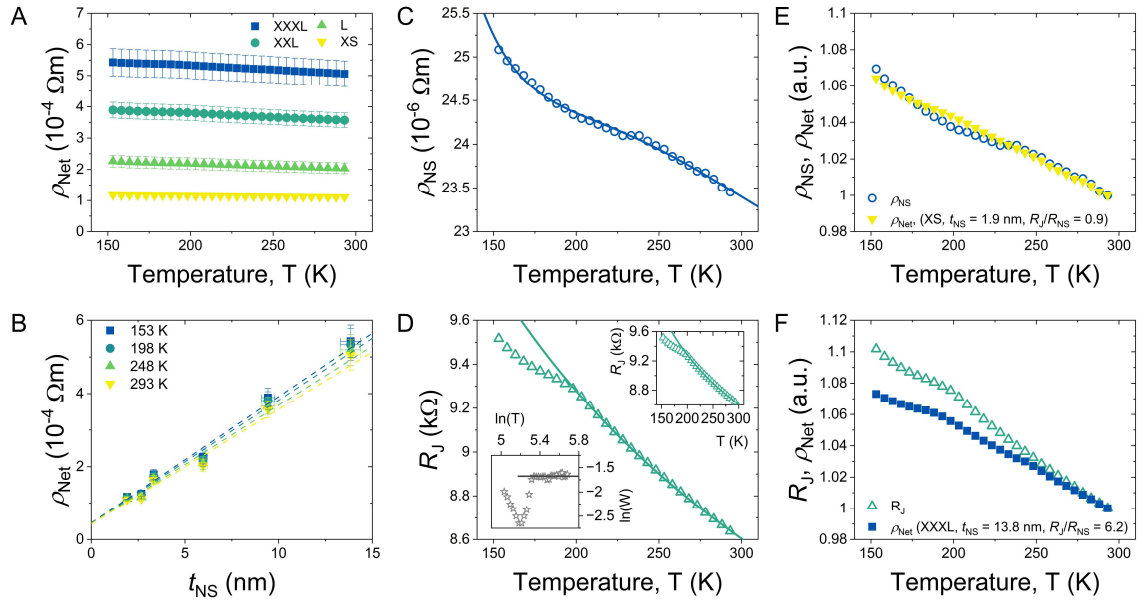


Figure 6.2: Temperature Dependence of graphene network resistivity. **A)** Examples of network resistivity versus temperature for various nanosheet thicknesses. **B)** Examples of network resistivity measured at various temperatures plotted against nanosheet thickness. The lines are fits to Equation 4.4. **C)** The extracted nanosheet resistivity plotted versus temperature. The line is a fit to Equation 6.8. **D)** The extracted junction resistance versus temperature for our graphene nanosheet networks. In the top inset, the line is a fit to a 3D-VRH model while in the main panel, the line is a power law fit. The bottom inset shows reduced activation energy (W) analysis as described in the text. **E)** A plot of ρ_{NS} and ρ_{Net} (both normalised to room temperature values) versus temperature. **F)** A plot of R_J and ρ_{Net} (both normalised to room temperature values) versus temperature.

Figure 6.2D. In both cases, the data show weak temperature dependence with ρ_{NS} and R_J falling slightly as temperature is increased. We note that both curves have subtle but clear differences to their shapes. To test the validity of our method, recall that in Chapter 4 we showed networks containing the largest nanosheets are clearly junction limited, while networks containing the smallest nanosheets display junction resistances slightly below that of the constituent nanosheets, so are predominately limited by the nanosheet properties. Therefore, we expect the temperature dependence of ρ_{Net} for the largest nanosheets to be similar to that of R_J and the temperature dependence of ρ_{Net} for the smallest nanosheets to be similar to that of ρ_{NS} . To test this, we plot both ρ_{NS} and ρ_{Net} for the smallest fraction ($t_{NS} = 1.91$ nm), normalised to their room temperature values, versus T in Figure 6.2E.

As expected, both are very similar in shape. In addition, we plot R_J and ρ_{Net} for the largest fraction ($t_{\text{NS}} = 13.9 \text{ nm}$), normalised to their room temperature values, versus T in [Figure 6.2F](#). Again, both curves are very similar in shape. This strong correlation between the extracted parameters and the corresponding network resistivities provides independent confirmation of the robustness of our extraction method.

We can now consider both the intra-sheet and inter-sheet transport mechanisms, obtained by analysis of the temperature dependence of ρ_{NS} and R_J , to determine if they align with expectations. Although many studies on the temperature dependent transport within few-layer graphene/graphite nanosheets find it hard to reach a consensus on the transport mechanism within these systems, Zoraghi et al.⁶⁵ have previously been able to completely describe the transport of these systems and have shown it is governed by the different stacking orders present in graphite layers. They found the temperature dependence of the in-plane resistance of their graphite samples, and many samples from the literature, can be very well explained between 2 and 1100 K assuming three contributions in parallel: two semiconducting phases, attributed to the Bernal and rhombohedral stacking orders, and a third metallic-like contribution arising from the interface between the two crystallographic regions. This means the total graphite nanosheet resistivity (ρ_t) can be described by the following

$$\rho_t(T)^{-1} = \rho_i(T)^{-1} + \rho_{s1}(T)^{-1} + \rho_{s2}(T)^{-1} \quad [6.5]$$

where ρ_i , ρ_{s1} and ρ_{s2} are the contributions from the interface, 3R and Bernal phase, respectively. It is worth noting that the authors found that the metallic contribution is rarely seen for thinner graphite samples ($< 30 \text{ nm}$), and when it is, it is only at very low temperatures. Therefore, we can assume its contribution to be negligible in our case. We assume the transport within the crystalline components behaves as intrinsic semiconductors, given as

$$\rho_s(T) = a(T) \exp\left(\frac{E_g}{2k_B T}\right) \quad [6.6]$$

where E_g is the semiconducting energy gap, k_B is the Boltzmann constant, and $a(T)$ is a mobility dependent prefactor which can be written as

$$a(T) = \frac{1}{N(\mu_h + \mu_e)T^{3/2}} \quad [6.7]$$

Here, N is a temperature independent constant and μ_h and μ_e are the hole and electron mobilities. Experimental studies^{268, 269} in graphite flakes have shown $\mu_{h,e} \propto T^{-3}$, allowing us to obtain $a(T) = a_0 T^{3/2}$. Combining this with Equation 6.5 and Equation 6.6 we arrive at the following

$$\rho_t(T)^{-1} = \left(a_{0,1} T^{3/2} \exp\left(\frac{E_{g,1}}{2k_B T}\right) \right)^{-1} + \left(a_{0,2} T^{3/2} \exp\left(\frac{E_{g,2}}{2k_B T}\right) \right)^{-1} \quad [6.8]$$

where the subscripts 1 and 2 refer to the 3R and Bernal components, respectively. As shown in Figure 6.2C, fitting Equation 6.8 to our data results in a very good fit across the entire temperature range, confirming the presence of both 3R and Bernal phase stacking in our graphite samples. We find the semiconducting bandgaps to be 195 meV and 42 meV for the 3R and Bernal phases respectively. These values agree well with reported values of 90 - 154 meV for 3R and 25 - 61 meV for Bernal phases respectively.⁶⁵

The extracted junction resistance as a function of temperature is shown in Figure 6.2D. Unlike the nanosheet resistivity, which reflects the intra-flake transport, R_J captures the transport processes across the inter-nanosheet junctions. At first glance, the data above 200 K is consistent with 3D Mott variable range hopping (VRH), as previously observed by Piatti et al.²¹³ for networks of nanosheets very similar to these. 3D-VRH is consistent with $R \propto \exp(T_0 / T)^{1/4}$, where $T_0 = 24 / (\pi k_B N(E_f) \xi^3)$ and $N(E_f)$ is the density of states at the Fermi energy, while ξ is the electron localisation length. Fitting this equation to the R_J vs. T data (Figure

6.2D, top inset) yields a value of $T_0 = 75.8$ K, which is lower than room temperature and below the temperature range of our experiment. Such behaviour has been reported in networks composed of metallic regions when the transport is dominated by inter-region hopping,²⁷⁰⁻²⁷² as is plausible for networks of LPE graphene. In addition, by approximating the density of states via the carrier density, n , as $N(E_f) = n / k_B T$, and taking $n \approx 10^{25} \text{ m}^{-3}$ (Ref. ^{213, 273}), we obtain $\xi = 14$ nm. This value is similar to a previously reported value of $\xi = 13$ nm for an inkjet-printed LPE graphene network²¹³ and within the range observed for networks of reduced graphene oxide.²⁷⁴

However, identifying the hopping mechanism by directly fitting temperature-dependent transport data is challenging. For example, different hopping models such as 3D VRH and 2D VRH regularly give almost equally good fits.^{275, 276} To avoid this problem, the reduced activation energy (W) method is often used.^{213, 276} This involves calculating W , which is defined here as $W(T) = -d(\ln R_j)/d(\ln T)$. Then, plotting $\ln W$ versus $\ln T$ should result in a straight line, from which fitting of the slope allows unambiguous identification of the appropriate hopping model. Such a plot is shown in Fig 2D, lower inset. The high temperature portion of this graph is clearly a flat line (slope = 0) which is the hallmark of a power-law relationship: $R_j \propto T^{-\alpha}$.²⁷⁴ The dip below $\ln T = 5.35$ is most probably a transition region. Future work will investigate the lower temperature regime.

A power-law relationship has been fitted to the data in the main panel of Figure 6.2D, yielding a good fit consistent with $\alpha = 0.1866 \pm 0.0005$. Such behaviour has been observed in networks of reduced graphene oxide²⁷⁴, nanocrystalline graphene,²⁷⁷ and graphene nano-ribbons²⁷⁸ as well as various polymeric systems.²⁷⁹⁻²⁸¹ Although such power-law behaviour can have multiple origins,²⁸⁰ two stand out. Richter et al.²⁷⁸ observed power-law scaling of resistance with temperature in graphene nano-ribbon networks. The data was very well described by the so-called nuclear tunnelling mechanism, where the inter-ribbon hopping was modelled via phonon-mediated tunnelling between biased potential wells

separated by a potential barrier. Conceptually, this model appears well suited to inter-nanosheet transport, however, when applied to nano-ribbon networks²⁷⁸ it yields an exponent of $\alpha \sim 3$ and for polymeric systems²⁷⁹ it yields $\alpha \sim 1-7$, which are much higher than our value.

The second notable power-law mechanism tends to occur in partially disordered systems in which a mobility edge²⁸² separates extended (delocalised) states at higher energy from localised states at lower energy.²⁸¹ In such a scenario, a metal-insulator-transition (MIT) can occur if the Fermi energy falls below the mobility edge. Power-law scaling has been observed in such systems just above the MIT with expected values of α in the range 0.33-1,²⁸¹ much closer to our value. Kovtun et al.²⁷⁴ studied temperature dependent conduction in networks of reduced graphene oxide with different degrees of reduction, observing power-law behaviour with exponents varying from 0.19 up to 4. Interestingly, the lowest exponents, closest to ours, were found for the most highly graphitised, lowest resistivity networks, similar to those used here. Taken together, this implies that our nanosheets display a mobility edge slightly below the Fermi energy. Inter-sheet hopping occurs via delocalised states just above the mobility edge, which in turn implies the presence of localised states that must be associated with disorder, perhaps basal plane defects or the effects of nanosheet edges. It would be interesting to determine how the mobility edge relates to the band edges associated with the bandgaps of the Bernal and 3R stacked phases discussed above.

6.5 Results and Discussion: Transport in MoS₂ Nanosheet Networks

In Chapter 5 we showed that impedance spectroscopy enables the simultaneous extraction of R_J and R_{NS} . Similar to the DC case, we can build upon this work to extract the temperature dependent R_J and R_{NS} , however, with the power of the impedance technique, these values can be obtained significantly faster and with

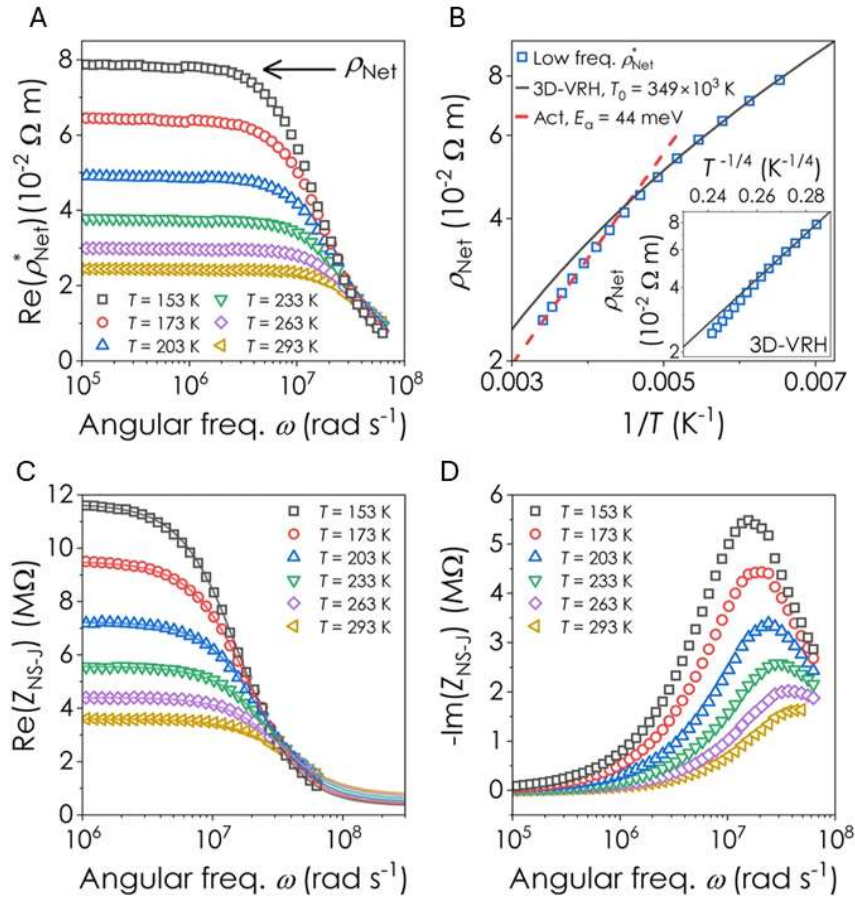


Figure 6.3: Measurement of Temperature-Dependent Network Impedance. A) Real part of the complex network resistivity, $\text{Re}(\rho_{\text{Net}}^*)$, plotted versus angular frequency, ω , for a network of EE MoS₂ nanosheets at a range of temperatures, T . The arrow indicates that the DC network resistivity was found from $\rho_{\text{Net}} = \text{Re}(\rho_{\text{Net}}^*)_{\omega \rightarrow 0}$. **B)** DC network resistivity, ρ_{Net} , plotted as a function of temperature as $1/T$ and $T^{-1/4}$ (inset). The dashed line is an activated (Act) fit while the solid line is a fit to the 3D variable-range hopping (VRH) model. **C-D)** Real (C) and imaginary (D) parts of the impedance spectrum of a single (average) nanosheet junction pair, $Z_{\text{NS-J}}$, measured at various temperatures. The curves in (C) are fitted using Equation 5.2. [Adapted from Ref. 6]

far less sample preparation (such as producing nanomaterial length/thickness dependent networks). To demonstrate this, temperature-dependent impedance measurements were performed on a network of electrochemically exfoliated MoS₂ nanosheets (Figure 6.3A) from which the temperature dependent R_J and R_{NS} could be separated and analysed.

The DC resistivity of the network was obtained from the low frequency plateau of the real component of the of the ρ_{Net}^* spectrum and plotted as a function of $1/T$

in Figure 6.3B. Consistent with previous studies,²¹³ ρ_{Net} displays thermally activated behaviour near room temperature, described by $\rho_{\text{Net}}(T) = \rho_0 \exp(E_a / k_B T)$ (where ρ_0 and E_a are constants), while at lower temperatures, it transitions to 3D variable range hopping (3D-VRH), described by $\rho_{\text{Net}}(T) = \rho_0 \exp[(T_0 / T)^{1/4}]$ (where ρ_0 and T_0 are constants). The data and corresponding fits (Figure 6.3B and its inset) are consistent with this behaviour. However, as discussed, such conventional analysis does not distinguish the respective contributions of the nanosheets and the junctions.

To decouple these components, the network impedance spectra were converted into their equivalent $Z'_{\text{NS-J}}$ and $-Z''_{\text{NS-J}}$ spectra (Figure 6.3C,D), revealing clear and well-defined temperature dependencies. Fitting the $Z'_{\text{NS-J}}$ spectrum using the equivalent circuit model from Chapter 3 (Equation 3.22) provides quantitative values for R_{NS} , R_{J} and C_{J} at each temperature as shown in Figure 6.4A,B. Notably, R_{NS} and R_{J} exhibit opposing temperature dependencies indicating distinct transport mechanisms (band-like through the nanosheets and hopping through the junctions), with $R_{\text{NS}}/R_{\text{J}}$ increasing with temperature. Figure 6.4B shows that C_{J} remains relatively constant over the temperature range, implying that temperature-dependent changes in $Z'_{\text{NS-J}}$ primarily reflect variations in R_{J} .

Extracted values of C_{J} lie between 6-8 fF. Using SEM analysis, the junction overlap area was found to be $A_{\text{J}} = 0.4 \mu\text{m}^2$ (Figure 6.4B inset) which gives $C_{\text{J}}/A_{\text{J}} = 2 \mu\text{Fcm}^{-2}$. This is significantly lower than typical quantum capacitance measurements of $\sim 10 \mu\text{Fcm}^{-2}$ ²⁸³ but is consistent with a geometric capacitance of the form $C_{\text{J}} / A_{\text{J}} = \epsilon_r \epsilon_0 / l_{\text{J}}$. Assuming $\epsilon_r = 1$ and an inter-sheet distance of $l_{\text{J}} = 0.6 \text{ nm}$,¹¹⁶ this yields $C_{\text{J}}/A_{\text{J}} = 1.5 \mu\text{Fcm}^{-2}$, comparable to the measured value. This permits the estimation of the network's effective dielectric constant (using a model which has been detailed in Appendix A.5), resulting in a value exceeding 10^4 , in agreement with the measured network capacitance.

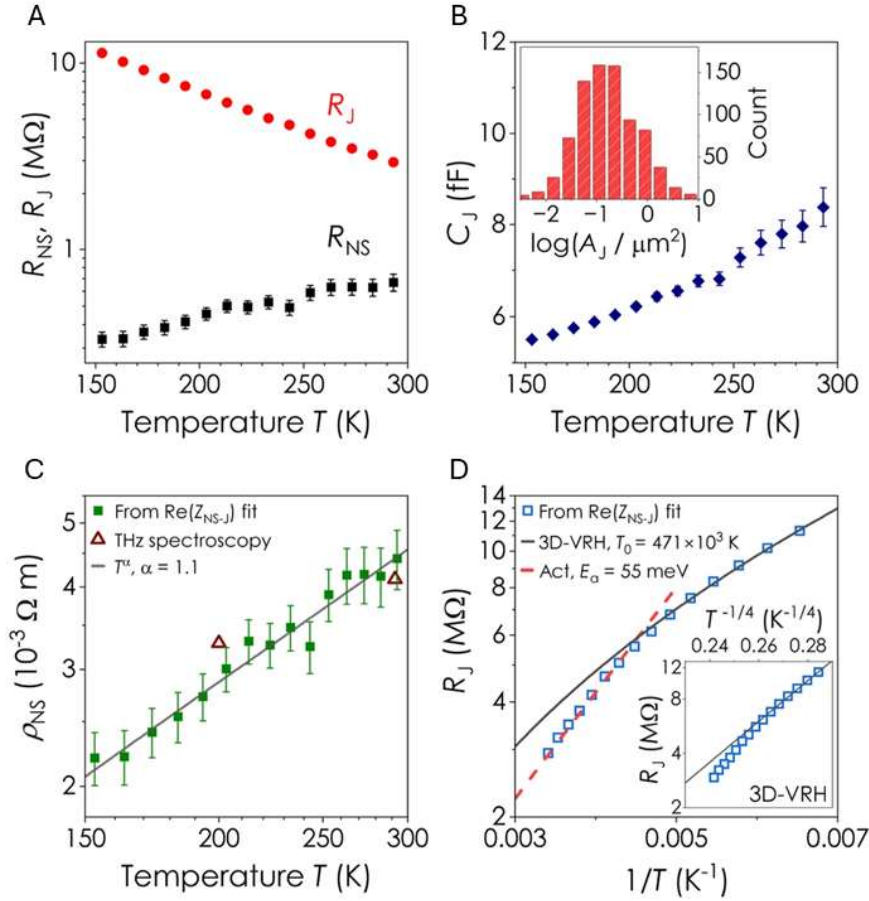


Figure 6.4: Nanosheet and Junction Transport Extracted from Impedance Spectroscopy Measurements. **A)** Nanosheet and junction resistances, R_{NS} and R_J , extracted from fits to the $\text{Re}(Z_{NS-J})$ spectra, plotted as a function of temperature. **B)** Junction capacitance, C_J , plotted versus temperature. Inset: Histogram of nanosheet junction areas, A_J , measured from SEM images and plotted as $\log(A_J / \mu\text{m}^2)$. This distribution showed $\langle A_J \rangle = 0.41 \mu\text{m}^2$ ($n = 807$). **C)** Resistivity of an (average) individual nanosheet, ρ_{NS} , extracted from R_{NS} ($\rho_{NS} \approx 2R_{NS}t_{NS}$) and plotted as function of temperature. The solid line is a power law with exponent $\alpha = 1.1$. The hollow triangles represent the THz mobility of the nanosheets converted into resistivity using the measured carrier density of $3.8 \times 10^{23} \text{ m}^{-3}$. **D)** Junction resistance plotted as a function of $1/T$ and $T^{-1/4}$ (inset). The dashed line is an activated-behaviour fit (Act) described by Equation 6.9, while the solid line is a fit to the 3D-VRH model (Equation 6.10). [Adapted from Ref. 6]

To investigate the distinct transport mechanisms in more detail, temperature dependence of ρ_{NS} and R_J were analysed individually (Figure 6.4C,D). Figure 6.4C shows the nanosheet resistivity follows a power law dependence, $\rho_{NS} \propto T^\alpha$, with $\alpha \approx 1.1$, in agreement with values reported for individual MoS_2 flakes (typically $\alpha = 0.5 - 1.9$).²⁸⁴⁻²⁸⁶ This behaviour suggests band-like transport limited by phonon

scattering,²⁸⁷ a mechanism commonly observed in MoS₂ flakes at high carrier densities,^{284, 288, 289} and is further supported by THz spectroscopy measurements (Figure 6.4C, triangles).

Since these networks are junction-limited, the temperature dependence of R_J closely mirrors that of ρ_{Net} , exhibiting a crossover from activated to hopping transport, as shown in Figure 6.4D. This can be rationalised by a Miller-Abrahams-type hopping model:²⁹⁰

$$R_J \approx R_{J,0} \exp\left(\frac{2l_J}{a}\right) \exp\left(\frac{E_a}{k_B T}\right) \quad [6.9]$$

where $R_{J,0}$ is a pre-exponential factor, a is the localisation length and E_a is the activation energy. In Appendix A.6, we propose an alternative version of the 3D-VRH model can be derived, which considers inter-nanosheet hopping from the conduction band-edge of one nanosheet to the conduction-band edge of another yielding:

$$R_J \approx R_{J,0} \exp\left(\frac{2l_J}{a}\right) \exp\left(\left[\frac{T_0}{T}\right]^{1/4}\right) \quad [6.10]$$

where T_0 is a constant given by $T_0 \approx 76\pi\hbar^2 d_0 / k_B a^3 m$, with d_0 representing the monolayer thickness and m is the effective electron mass. Fitting the experimental data to Equation 6.10 at lower temperatures and Equation 6.9 at higher temperatures yields $E_a = 55 \pm 2$ meV and $T_0 = (471 \pm 37) \times 10^3$ K. These values relate solely to the junctions and are in line with the relatively low R_J and high carrier mobility observed in these networks.²⁹¹ Using $m = 0.7m_e$ and $d_0 = 0.6$ nm, the extracted localisation length is $a = 0.7$ nm, within the range reported for MoS₂ (0.2 – 3 nm).^{213, 270, 292, 293} The most probable hopping distance was ~2 nm, again consistent with inter-sheet hopping.

6.6 Comparing Transport in AgNW, Graphene and MoS₂ Networks

Across the three representative nanomaterial systems studied, temperature dependent measurements reveal distinctly different transport regimes, reflecting the intrinsic transport of the materials themselves and the transport across the junctions. In AgNW networks, the nanowire resistivity increases monotonically with temperature, characteristic of metallic systems where electron-phonon scattering dominates. In contrast, LPE graphene nanosheet networks show only weak temperature dependence, with ρ_{NS} decreasing with temperature consistent with semiconducting/graphitic behaviour. MoS₂ nanosheet networks present a markedly different case with the nanosheet resistivity increasing with temperature following a power-law, indicating band-like transport limited by phonon scattering.

The junctions in AgNW networks also display a monotonic increase with temperature, confirming that the sintered silver junctions behave as bulk-like metallic contacts. The junction resistance in LPE graphene nanosheet networks once again shows a weak temperature dependence, slightly decreasing with increasing temperature. Here, this decrease is attributed to inter-sheet transport

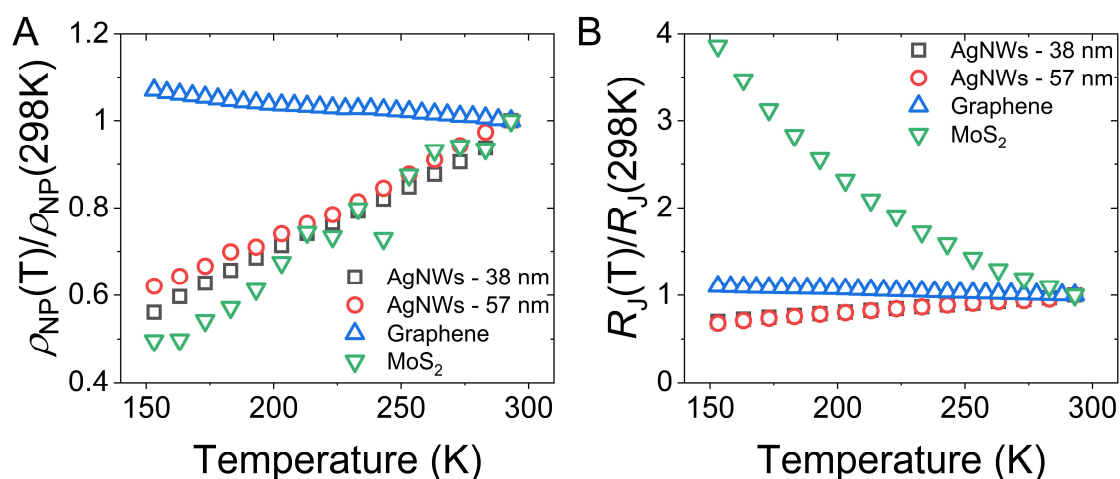


Figure 6.5: Comparing Transport in AgNW, Graphene and MoS₂ Networks. **A)** Nanoparticle resistivity normalised to 298K plotted as a function of temperature for both AgNW diameters, LPE graphene nanosheets and EE MoS₂ nanosheets. **B)** Junction resistance normalised to 298K plotted as a function of temperature for both AgNW diameters, LPE graphene nanosheets and EE MoS₂ nanosheets.

near a mobility edge. The junction resistance in MoS₂ networks decreasing significantly with increasing temperature, exhibiting a transition from 3D-VRH to activated behaviour.

The three systems we have discussed show three different distinct combinations of nanoparticles and junction transport. This comparative analysis not only underscores the versatility of our extraction methodologies, but it also illustrates the importance of a comprehensive insight into the balance between junction and nanoparticle transport in nanomaterial networks.

6.7 Conclusion

This chapter has demonstrated complimentary techniques for the extraction and analysis of the temperature-dependent inter-particle (R_J) and intra-particle (R_{NS}) transport mechanisms in nanomaterial networks. We used AgNW networks as a model system and found the nanowire resistivity, ρ_{NW} , to be consistent with the Bloch-Grüneisen model and with literature values measured on individual nanowires. The junctions, R_J , showed metallic transport confirming the presence of metallic welds at the junctions and validating the robustness of our method. Applying the same approach to LPE graphene networks revealed the nanosheet transport is consistent with parallel semiconducting phases associated with mixed Bernal and rhombohedral stacking, consistent with literature results on graphite samples, while the junctions are power law dominated which is attributed to inter-sheet transport near a mobility edge. EE MoS₂ networks were analysed using impedance spectroscopy which enabled the rapid temperature-dependent extraction of R_{NS} , R_J and C_J without the need for laborious sample preparation. This revealed band-like transport limited by phonon scattering in the MoS₂ nanosheets while the junctions transition from a 3D Mott variable range hopping mechanism to activated hopping with increasing temperatures.

Together these results establish a general framework for comprehensively understanding the transport phenomena in printed nanomaterial networks using both AC and DC techniques. By decoupling and quantitatively analysing the inter- and intra-particle transport, this methodology provides deeper physical insight than conventional temperature dependent-dependent measurements. Beyond the systems studied here, these approaches can be readily extended to other nanomaterial types and device architectures, offering a versatile platform for understanding and optimising network performance in emerging printed nanomaterial network technologies.

*"You let the hours slip through your fingers
like dust, then curse the wind for taking
them"*

Seneca

CHAPTER 7

CONCLUSION AND FUTURE WORK

Over the past few decades, the insatiable hype for nanomaterials has reflected their seemingly limitless potential to reshape a wide range of technologies. The exceptional intrinsic properties of nanomaterials have driven intense research in the field. While some nanomaterial systems have achieved niche industrial adoption, many promising attributes have yet to make the transition from the lab to widespread use. However, given the expeditious pace of progress in the field, the gap between promise and practice will surely begin to narrow in the coming years.

Within this landscape, printed nanomaterial networks are particularly attractive for electronic applications, but a central limitation persists; inter-particle junctions inhibit conduction across networks and typically dominate charge transport. Considerable effort has therefore focused on reducing junction resistance to improve film conductivity,^{20, 31, 114, 151} however characterisation remains challenging. Conventional electrical metrics, such as sheet resistance, conductivity or mobility, report on the overall network response, conflating inter- and intra-particle contributions. This thesis aims to develop a methodology to simultaneously quantify the transport in both the junctions and the nanoparticles, to provide a rational basis for network electrical optimisation.

We introduce a simplistic model for conduction in nanomaterial networks based on a resistor chain picture. In this model, each conduction pathway consists of a series of alternating resistors (nanoparticle-junction (NP-J) pairs, $R_{NP} + R_J$) representing the nanoparticles, R_{NP} , and junctions, R_J . Building upon this minimal picture, we derive a completely general expression which relates the network resistivity to R_J and R_{NP} and geometric descriptors of the network. Crucially, this expression can be applied to almost any nanomaterial or network geometry.

This model yields two practical routes for parameter extraction. First, it predicts scaling relations between network resistivity and nanoparticle size (nanowire length for 1D systems and nanosheet thickness for 2D systems), enabling the extraction of R_J and R_{NP} from size-dependent DC studies. Second, the same expression can be modified to show that AC impedance spectroscopy can produce quantitative values for both R_J and R_{NP} . By converting the measured network spectrum into the impedance of an average NP-J pair, the direct extraction of R_{NP} , R_J and the associated junction capacitance can be achieved from a single device.

We used AgNW networks as a benchmark system to verify the DC methodology owing to the large volume of literature available on these networks. We carried out a nanowire length-dependence study and found the network resistivity scales with the inverse of nanowire length, as predicted by our model. We extracted nanowire resistivities in the range $\rho_{NW} \approx 1 \times 10^{-8} \Omega m$, comparing well to bulk silver ($\rho_{Ag} = 1.6 \times 10^{-8} \Omega m$) and determined the junction resistance to be $R_J \approx 200 \Omega$, broadly in line with literature results. From this, we found values of R_{NW}/R_J ranging from 0.03 to 0.7 noting the predominantly junction limited nature of these networks. Following this, we used liquid phase exfoliated (LPE) graphene nanosheets and carried out a nanosheet thickness-dependence study. We confirmed the linear trend between ρ_{Net} and t_{NS} , using it to obtain values of $\rho_{NS} = (3.5 \pm 0.6) \times 10^{-5} \Omega m$, broadly consistent with expected values for multilayer graphene or graphite flakes.^{6, 243} In addition, the junction resistance was determined to be $R_J = 7.8 \pm 0.5$

k Ω . This leads to values of R_J/R_{NS} ranging from 0.56 to 6.11 for the smallest to largest fractions, respectively.

Building on the DC electrical characterisation of AgNWs and LPE graphene we perform temperature-dependent measurements on size-dependent networks to comprehensively understand the transport mechanisms present in these systems. This enabled the extraction of both ρ_{NP} and R_J as a function of temperature. In AgNW networks, we found metallic junctions composed of silver, suggesting sintering at the junctions. The AgNW resistivity followed literature trends and was well described by the Bloch–Grüneisen (BG) formula.^{4, 5, 216} For LPE graphene networks, the nanosheets displayed two parallel semiconducting phases attributed to the different stacking orders (3R and Bernal) present in graphite.⁶⁵ The junctions displayed a power-law behaviour with an exponent, $\alpha = 0.1866 \pm 0.0005$. This is consistent with a mobility edge scenario in which the Fermi level lies slightly below the mobility edge. Inter-sheet hopping occurs via delocalised states just above the edge, which in turn implies the presence of localised states that must be associated with disorder, perhaps basal plane defects or the effects of nanosheet edges.^{274, 281, 282}

Nanomaterial size-dependent studies can prove laborious and time-consuming. Therefore, we used AC impedance spectroscopy to rapidly extract R_J and R_{NS} from a single device using EE MoS₂ networks. We found the impedance spectrum could be well described by a modified Randles circuit with a constant-phase element. From this, we obtained values of $R_J = 2.9 \pm 0.1$ M Ω , $R_{NS} = 0.67 \pm 0.07$ M Ω , $C_J = (8.4 \pm 0.4) \times 10^{-15}$ F and $n = 0.985$. The extracted $R_J/R_{NS} = 4.4 \pm 0.2$ indicates that these networks are not significantly junction limited. We were able to verify our results using a combination of network and nanosheet mobility measurements, along with Kelvin probe force microscopy and THz spectroscopy. Performing temperature-dependent impedance measurements enabled the extraction of R_J and R_{NS} as a function of temperature. The MoS₂ nanosheets follows a power-law dependence with an exponent $\alpha \approx 1.1$, in agreement with values reported for

individual MoS₂ flakes, suggesting band-like transport limited by phonon scattering.²⁸⁴⁻²⁸⁹ We further support this using THz spectroscopy measurements. We find the junction resistance to display a 3D-VRH to activated hopping transition with increasing temperature, yielding $E_a = 55 \pm 2$ meV and $T_0 = (471 \pm 37) \times 10^3$ K for the MoS₂ junctions.

Feature	DC Size-Dependence Route	AC Impedance Route
Strengths	Simple and universal.	Rapid and information rich.
Limitations	Laborious sample preparation.	Instrument bandwidth and electrode parasitic capacitance limit the "sweet spot".
Model Assumptions/ Requirements	Requires network morphology to be independent of particle size.	Assumes junctions can be modelled using a Randles equivalent circuit.
Hardware Requirements	Standard DC source-meter and temperature stage.	High-frequency impedance analyser.
Future Improvements	Expand the materials envelope and temperature range.	Explore higher-frequency (>GHz) instruments such as vector network analysers and expand materials envelope.

Table 7.1: Positives, Negatives and Future work of both the DC and AC Routes

Future Work: DC technique

Chapter 4 demonstrates that simple DC size-dependent studies can be used to extract the temperature dependence of both the nanomaterial resistivity and junction resistance. To date, we have applied this approach to AgNW and LPE graphene networks. A natural next step is to extend it to additional systems. For example, mobility measurements on length-dependent semiconducting single-walled carbon nanotube (s-SWCNT) transistors could be used to quantify the SWCNT mobility, μ_{NT} , and R_J as a function of temperature. Such studies would provide a more complete picture of transport in networks that are especially promising for future technologies. Expanding the temperature window under investigation would further clarify mechanism crossovers. More broadly, the

method lends itself to building a comprehensive portfolio across many printed materials and systems, providing a database to predict trends in future works.

Future Work: Impedance Method

Chapter 5 establishes impedance spectroscopy as a rapid route to quantify R_J and R_{NS} from a single device, but they also expose practical limits. The instrument bandwidth constrains the highest observable junction relaxation frequency, which typically exceeds ~ 100 s MHz in many networks. In addition, background capacitance from interdigitated electrodes (IDEs) can dominate the spectra at higher frequencies or larger impedances. Together, these effects define a window of applicability within which LLID networks of electrochemically exfoliated nanosheets sit. Future work should map which materials fall inside this window and explore whether optimising particle dimensions and deposition conditions can shift systems into the accessible regime.

Pushing the technique to higher frequencies would greatly expand its reach. To achieve this, minimising IDE parasitic capacitance is key. By reducing metallisation ratio, and optimising finger number and length, the IDE capacitance could be reduced to enable GHz-range impedance measurements on nanomaterial networks. While this requires significant design and calibration effort, it would capture junction relaxations currently beyond standard analysers and open the method to a broader set of materials.

Finally, the versatility of impedance spectroscopy can be explored by combining it with external stimuli or complementary techniques. For example, under optical excitation or gate-voltage modulation, changes in carrier density may affect R_{NS} or R_J . Measuring these changes would deliver deeper, mechanism-level insight and provide a practical pathway to optimise networks under operating conditions.

A.1 AgNW Length and Diameter Statistics

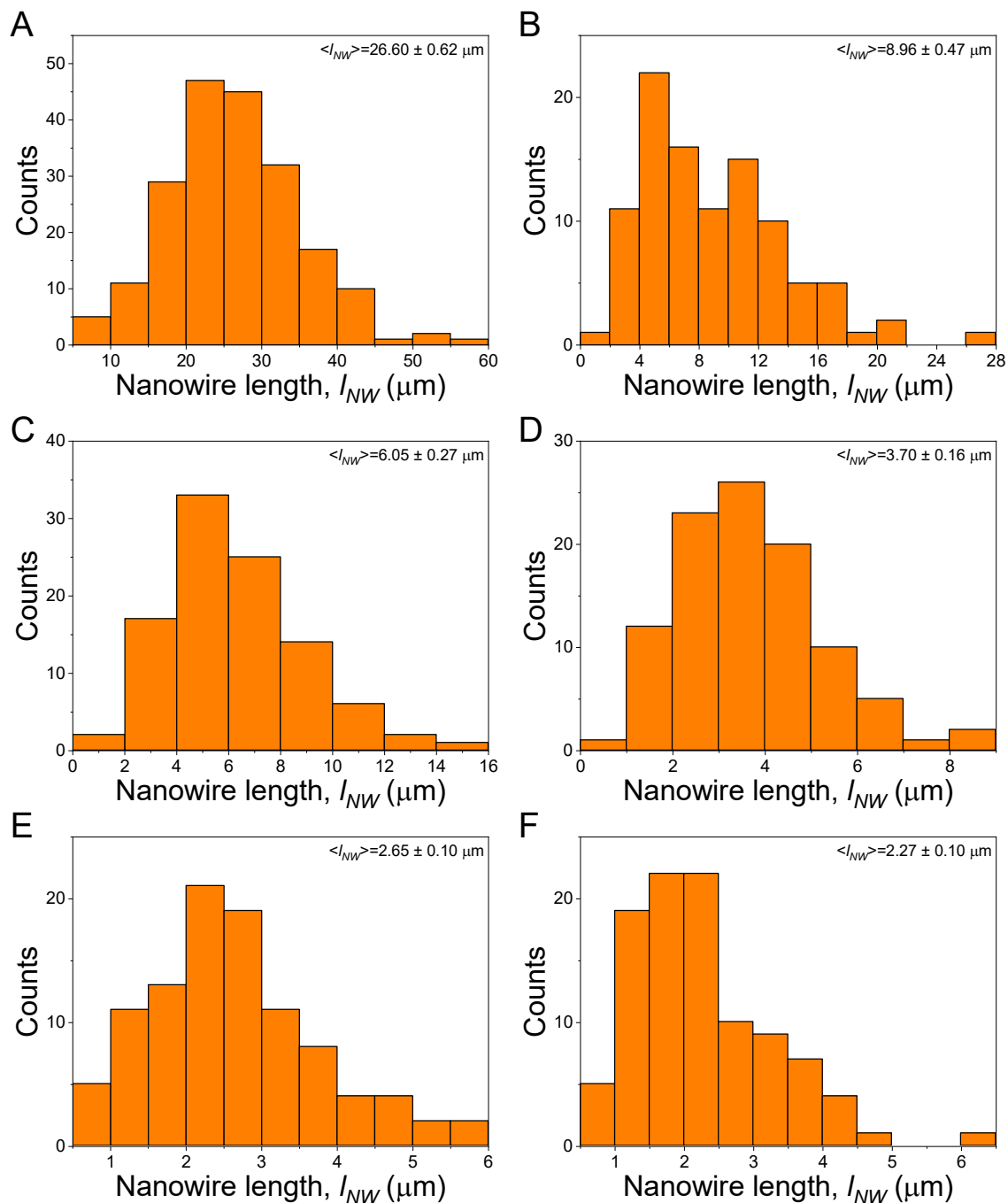


Figure A1.1: (A-F) SEM histograms of l_{NW} for AgNWs with a 38nm diameter having increasing sonication times of **(A)** 0, **(B)** 0.25, **(C)** 0.5, **(D)** 1, **(E)** 1.5 and **(F)** 2 hours.

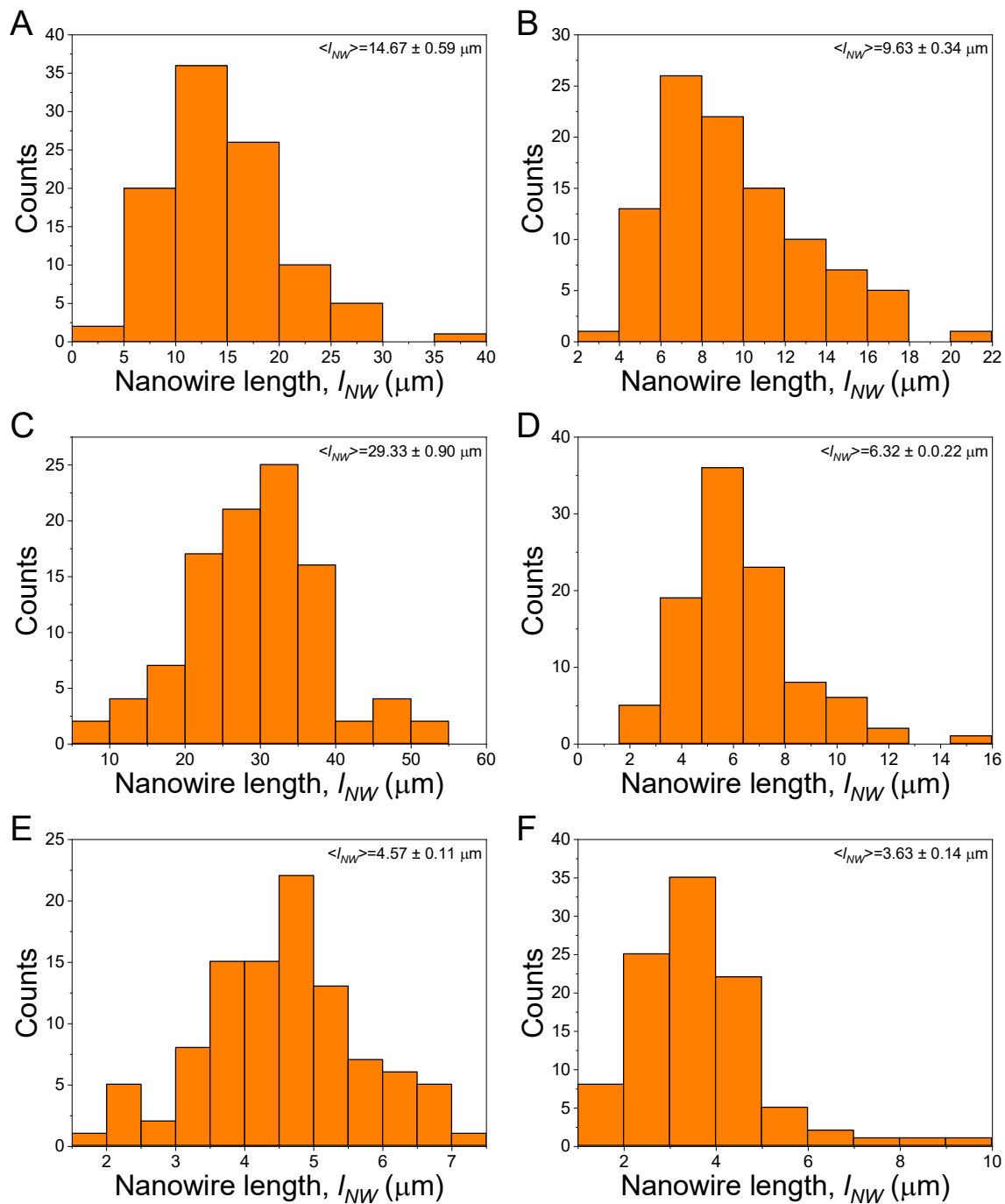


Figure A1.2: (A-F) SEM histograms of l_{NW} for AgNWs with a 57nm diameter having increasing sonication times of (A) 0, (B) 0.25, (C) 0.5, (D) 1, (E) 1.5 and (F) 2 hours.

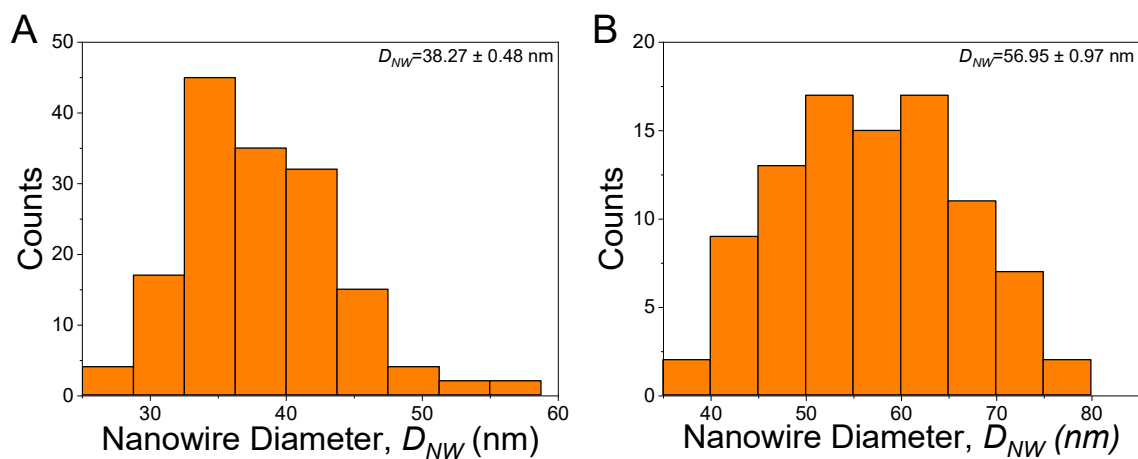


Figure A1.3: (A-F) SEM histograms of D_{NW} for AgNWs labelled **(A)** 38nm and **(B)** 57nm throughout this study.

A.2 Graphene Nanosheet Length and Thickness Statistics

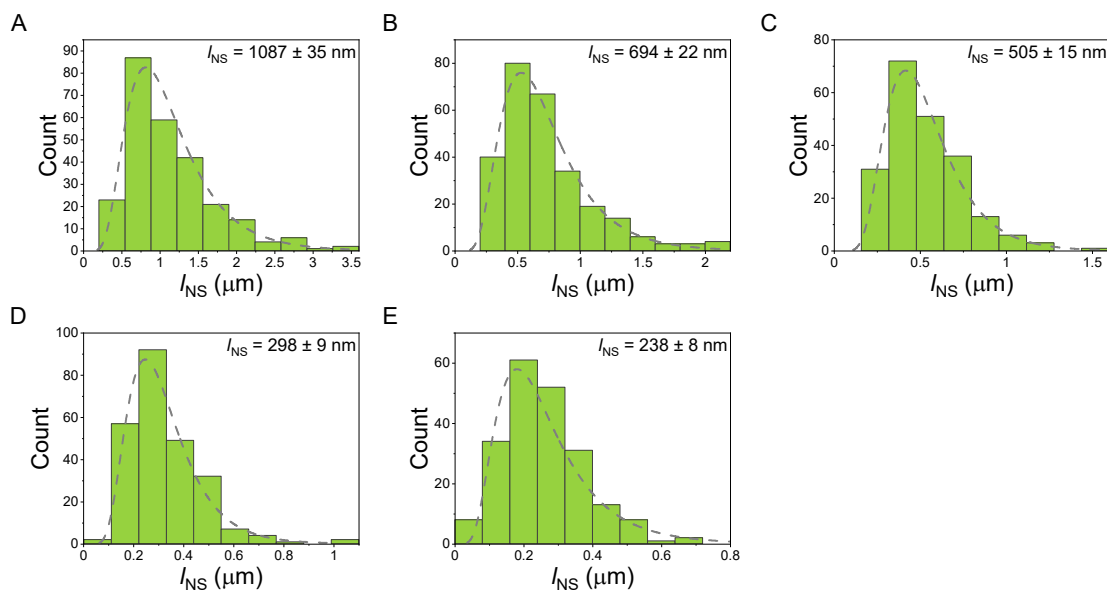


Figure A2.1: Nanosheet Length Statistics. A-E) Distributions of nanosheet length, l_{NS} , measured using AFM for size-selected graphene inks. The distributions are sorted by decreasing l_{NS} .

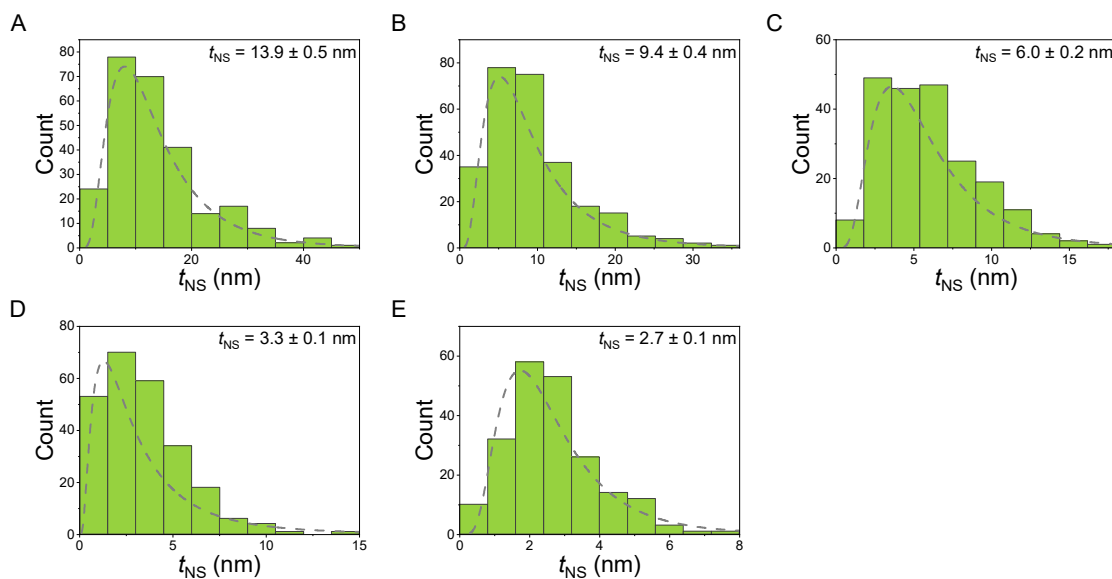


Figure A2.2: Nanosheet thickness Statistics. A-E) Distributions of nanosheet length, t_{NS} , measured using AFM for size-selected graphene inks. The distributions are sorted by decreasing t_{NS} .

A.3 Contact Resistance in Graphene Networks

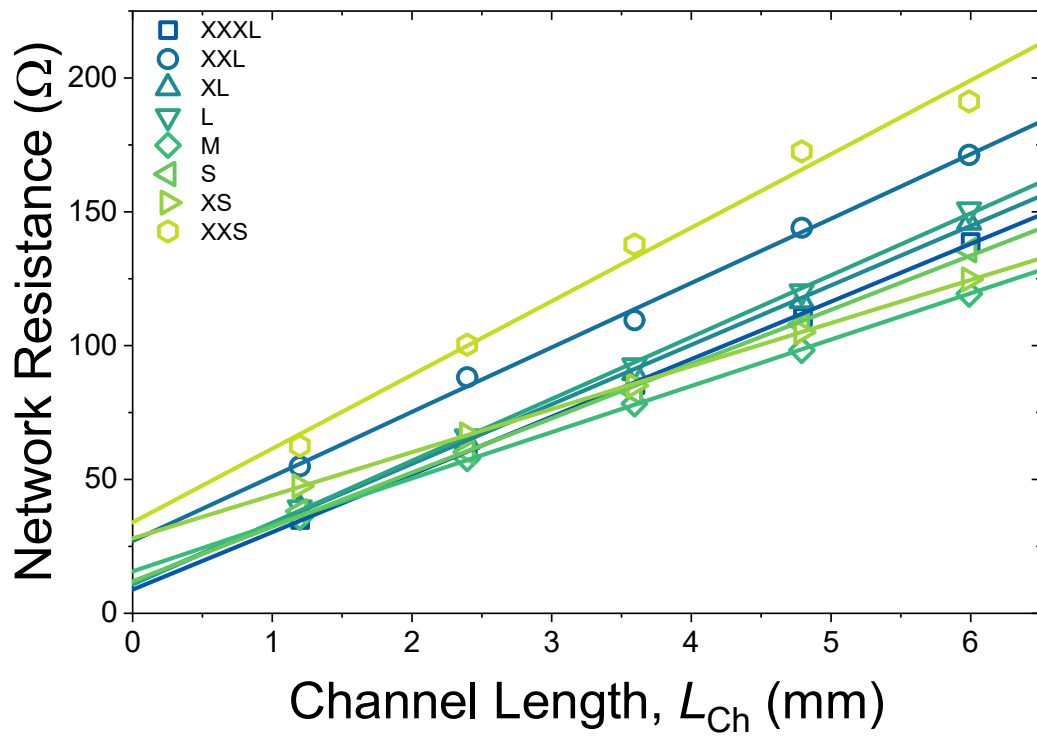


Figure A3.1: Contact Resistance. Graph of network resistance, R_{Net} , versus channel length, L_{Ch} . The lines are linear fits with the contact resistance extract from the intercept in each case.

A.4 Model Development

Here we develop a simple model describing the conductivity and mobility of networks of 1D (nanotubes, nanowires etc.), 2D (nanosheets, nanoplatelets etc.), or 0D (nanodots etc.) nano-particles as a function of both particle (e.g. size) and network (e.g. porosity, junction resistance, tortuosity) properties. We note that we expect these models to apply to networks that are thick enough that the disorder associated with local thickness fluctuations (often referred to as percolation effects)¹⁹ is not dominant. Such films are in the bulk-like regime and demonstrate thickness-independent conductivity.^{19, 39}

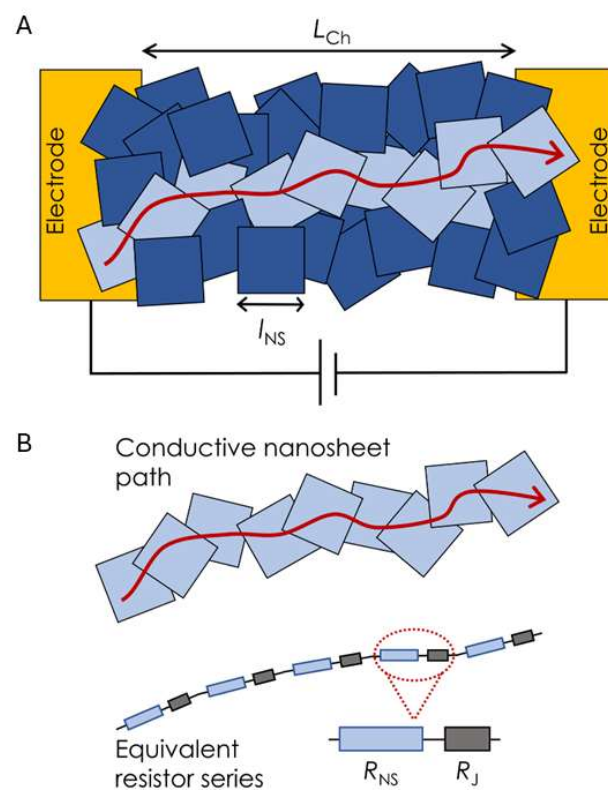


Figure A4.1: Model schematic for a nanosheet network. (a) Schematic illustrating a nanosheet network connected to two electrodes with channel length, L_{Ch} , under an applied voltage. A single conducting path consisting of a linear array of nanosheets is shown spanning the channel length (red arrow). The nanosheet lateral size is l_{NS} . While this schematic depicts a nanosheet network, a similar diagram could easily be produced to represent a 1D or 0D network. (b) This conducting path can be considered as a chain of resistor pairs, with each pair consisting of a resistance representing a nanosheet, R_{NS} , and the inter-sheet junction, R_J .

A4.1 Calculation of network conductivity using a random-resistor model

We begin by discussing the general case of networks of nanoparticles. Here, by nanoparticles we mean those with any dimension on the nanometer scale, for example 2D nanosheets, 1D nanowires or 0D nanodots. The basic principle of this model is that carriers flow along conductive paths, the basic unit of which is the nanoparticle/junction pair (Figure A4.1). When moving along a current path, a carrier travels a distance L from one electrode to another. This is greater than the electrode-to-electrode channel length because the conductive path is not straight and is related to the channel length, L_0 , via the tortuosity factor, k ,²⁹⁴ such that $L = L_0 \sqrt{\kappa}$. We include the tortuosity factor in our calculations here for completeness however we expect $K_{\text{Net}} \approx 1$ so we neglect it in the main manuscript.

Every time an electron passes through a nanoparticle, it must also pass through a junction to get to the next nanoparticle. A current path is made up of many of these pairs in series. Here, the average resistances experienced by an electron moving through individual nanoparticles and junctions are R_{NP} and R_{J} . When a voltage, V , is applied to a network, we can consider its effect on a current path. In a given path, the voltage will be dropped over the entire set of nanoparticle-junction pairs. The minimum number of pairs in a conductive path is $N = L / (d_{\text{NP}} + d_{\text{J}})$ where d_{NP} is the distance the electron travels on average through a single nanoparticle before jumping to the next nanoparticle and the forward distance travelled during the inter-particle jump is d_{J} (where we expect $d_{\text{J}} \ll d_{\text{NP}}$). The average voltage drop across one junction-nanoparticle pair is

$$V_{\text{p}} = V / N = V \times (d_{\text{NP}} + d_{\text{J}}) / L$$

This voltage drop can then be separated into separate contributions due to the junction and the nanoparticle, $V_{\text{p}} = V_{\text{J}} + V_{\text{NP}}$. The voltage drop across a junction is given by

$$V_{\text{J}} = \frac{R_{\text{J}}}{R_{\text{J}} + R_{\text{NP}}} V \frac{(d_{\text{NP}} + d_{\text{J}})}{L}$$

And the voltage drop across a nanoparticle is

$$V_{\text{NP}} = \frac{R_{\text{NP}}}{R_{\text{J}} + R_{\text{NP}}} V \frac{(d_{\text{NP}} + d_{\text{J}})}{L}$$

These equations can now be used to calculate some conduction properties. The time taken for an electron to cross the entire network is the channel length, L_{Ch} , divided by the effective carrier speed

$$\tau_{\text{Net}} = \frac{L_0}{\mu_{\text{Net}} E_{\text{A}}} = \frac{L_{\text{Ch}} L_{\text{Ch}}}{\mu_{\text{Net}} V}$$

where $E_{\text{A}} = V / L_{\text{Ch}}$ is the applied field. Since a current path has N nanoparticle-junction pairs

$$\tau_{\text{Net}} \approx N(\tau_{\text{NP}} + \tau_{\text{J}}) = \frac{L}{(d_{\text{NP}} + d_{\text{J}})} (\tau_{\text{NP}} + \tau_{\text{J}})$$

where τ_{NP} and τ_{J} are the times taken to cross a nanoparticle and a junction, respectively. The time to cross a nanoparticle is given by

$$\tau_{\text{NP}} = \frac{d_{\text{NP}}}{\mu_{\text{NP}} E_{\text{NP}}} = \frac{d_{\text{NP}}^2}{\mu_{\text{NP}} V_{\text{NP}}} = \frac{d_{\text{NP}}^2}{\mu_{\text{NP}}} \frac{R_{\text{J}} + R_{\text{NP}}}{R_{\text{NP}}} \frac{L}{(d_{\text{NP}} + d_{\text{J}}) V}$$

The time to cross the junction can be related to the current flowing across the junction

$$\tau_{\text{J}} = \frac{e}{I_{\text{J}}} = \frac{e R_{\text{J}}}{V_{\text{J}}}$$

Using the above expression for V_{J} , we find

$$\tau_{\text{J}} = \frac{e}{I_{\text{J}}} = \frac{e R_{\text{J}}}{V_{\text{J}}} = e(R_{\text{J}} + R_{\text{NP}}) \frac{L}{(d_{\text{NP}} + d_{\text{J}}) V}$$

Then

$$\tau_{\text{Net}} = \frac{L_{\text{Ch}}^2}{\mu_{\text{Net}} V} \approx \frac{L}{(d_{\text{NP}} + d_{\text{J}})} \left[\frac{d_{\text{NP}}^2}{\mu_{\text{NP}}} \frac{R_{\text{J}} + R_{\text{NP}}}{R_{\text{NP}}} \frac{L}{(d_{\text{NP}} + d_{\text{J}}) V} + e(R_{\text{J}} + R_{\text{NP}}) \frac{L}{(d_{\text{NP}} + d_{\text{J}}) V} \right]$$

Tidying terms then gives (where $\kappa_{\text{Net}} = (L / L_{\text{Ch}})^2$ is the tortuosity factor)

$$\frac{1}{\mu_{\text{Net}}} \approx \kappa_{\text{Net}} \frac{R_J + R_{\text{NP}}}{(d_{\text{NP}} + d_J)^2} \left[\frac{d_{\text{NP}}^2}{\mu_{\text{NP}} R_{\text{NP}}} + e \right]$$

Or

$$\mu_{\text{Net}} = \frac{(d_{\text{NP}} + d_J)^2 / d_{\text{NP}}^2}{\left(1 + \frac{R_J}{R_{\text{NP}}}\right)} \frac{\mu_{\text{NP}} / \kappa_{\text{Net}}}{\left[1 + \frac{\mu_{\text{NP}} e R_{\text{NP}}}{d_{\text{NP}}^2}\right]}$$

When d_J is very small compared to d_{NP} , this reduces to

$$\mu_{\text{Net}} \approx \frac{\mu_{\text{NP}} / \kappa_{\text{Net}}}{\left(1 + \frac{R_J}{R_{\text{NP}}}\right) \left[1 + \frac{R_{\text{NP}} e \mu_{\text{NP}}}{d_{\text{NP}}^2}\right]} = \frac{\mu_{\text{NP}} / \kappa_{\text{Net}}}{\left(1 + \frac{R_J}{R_{\text{NP}}}\right) \left[1 + \frac{\sigma_{\text{NP}} R_{\text{NP}}}{n_{\text{NP}} d_{\text{NP}}^2}\right]} = \frac{\mu_{\text{NP}} / \kappa_{\text{Net}}}{\left(1 + \frac{R_J}{R_{\text{NP}}}\right) \left[1 + \frac{d_{\text{NP}} / A_{\text{NP}}}{n_{\text{NP}} d_{\text{NP}}^2}\right]}$$

where A_{NP} is the effective nanoparticle cross-sectional area, with $R_{\text{NP}} = d_{\text{NP}} / \sigma_{\text{NP}} A_{\text{NP}}$ and $\sigma_{\text{NP}} = n_{\text{NP}} e \mu_{\text{NP}}$. Here μ_{NP} , σ_{NP} and n_{NP} are the nanoparticle mobility, conductivity and carrier density, respectively.

It is important to note that we have discussed the equations above as describing the mobility of the network. However, strictly speaking they describe the mobility of carriers along a single current path (a linear array of nanoparticles). Because we are considering the network as an array of many parallel current paths, we assume the mobility of the network is the same as the mobility along an average current path.

The equations above show explicitly that $\mu_{\text{Net}}^{-1} \propto (R_J + R_{\text{NP}})$, which implies that the network resistivity also scales with the sum of junction and nanosheet resistances: $\rho_{\text{Net}} \propto (R_J + R_{\text{NP}})$. This is a fundamental feature of this model and reflects the fact that every time a charge carrier travels through a nanosheet it must then travel across a junction. It should be noted that this feature has been proposed previously^{151, 295} and has independently been deduced empirically from experimental data.²⁹⁶

A4.2 Converting network mobility to network conductivity (or resistivity)

Method 1: Although this equation for network mobility will certainly be useful, it would be more useful to have an equation for network conductivity or resistivity. To achieve this, we need an expression for the carrier density of a network. In the simplest case, charge carriers exist only in the nanoparticles making up the network and not the pores in between. Then the network carrier density is given by $n_{\text{Net}} = n_{\text{NP}}(1 - P_{\text{Net}})$, where P_{Net} is the network porosity.

It is worth noting that a more complicated scenario is possible. Studies on mixed networks of graphene and WS₂ nanosheets²⁹⁷ have shown that the carrier density in the graphene network is given by $n_{\text{Net}} = n_{\text{NP}}(\phi - \phi_c)^a$, where ϕ is the graphene volume fraction, ϕ_c is the graphene percolation threshold and a is an exponent. Converting ϕ into porosity for a single-material nanoparticle network would imply: $n_{\text{Net}} = n_{\text{NP}}(P_c - P)^a$ where P_c is the porosity at the percolation threshold. This expression is a generalised version of $n_{\text{Net}} = n_{\text{NP}}(1 - P_{\text{Net}})$ but has the disadvantage that it has two extra variables. On balance, we believe $n_{\text{Net}} = n_{\text{NP}}(1 - P_{\text{Net}})$ is a reasonable approximation, especially in a single-material nanoparticle network (e.g. a network of silver nanowires or a network of MoS₂ nanosheets) as percolation effects such as the presence of dead ends are minimal.

Thus, in a network, we hypothesise that the carrier density scales as: $n_{\text{Net}} = n_{\text{NP}}(1 - P_{\text{Net}})$, where P_{Net} is the network porosity. This implies that $\sigma_{\text{Net}} = n_{\text{NP}}e\mu_{\text{Net}}(1 - P_{\text{Net}})$, or

$$\sigma_{\text{Net}} \approx \frac{\sigma_{\text{NP}}(1 - P_{\text{Net}}) / \kappa_{\text{Net}}}{\left[1 + \frac{R_j}{R_{\text{NP}}}\right] \left[1 + \frac{d_{\text{NP}} / A_{\text{NP}}}{n_{\text{NP}} d_{\text{NP}}^2}\right]} \quad [\text{A4.1}]$$

We use the subscript “Net” because the tortuosity factor refers to the nanoparticle network. The $(1 - P_{\text{Net}}) / \kappa_{\text{Net}}$ part of this equation is consistent with models used for ion transport in electrolyte-filled pore networks²⁹⁸ where the conductivity within a pore network is related to the conductivity in the bulk electrolyte by $\sigma_{\text{pore}} = \sigma_{\text{bulk}} P / \kappa_{\text{pore}}$. Here, we are considering transport in the nanoparticle network we use $(1 - P_{\text{Net}})$, the volume fraction of nanosheets instead of P_{Net} , the volume

fraction of pores. We expect k_{Net} to be a dimensionless number slightly larger than 1 and so can be approximated as 1 to first order.¹⁸

It is important to note that Equation A4.1 is general. Up to this point we have not incorporated the nanoparticle geometry into the model. The geometric parameters, d_{NP} (the mean distance travelled by an electron within a nanoparticle) and A_{NP} (the effective cross-sectional area of the nanoparticle) are written in a geometry-independent way. This means Equation A4.1 could be applied to networks of 0D, 1D or 2D particles just by using appropriate values of d_{NP} and A_{NP} .

Method 2: We can derive the same equation more explicitly by considering that charge carriers flow along many parallel current paths, each one consisting of a linear chain of nanoparticle-junction pairs. Then the overall resistance of the network is $R_{\text{Net}} = R_{\text{Path}} / m$. Here R_{Path} is the resistance of a single current path and m is the number of current paths which we must consider in parallel. We can find m from the cross-sectional area of the film, A_{Net} , divided by the cross-sectional area occupied by each nanoparticle: $m = A_{\text{Net}} / (A_{\text{NP}} / (1 - P_{\text{Net}}))$ where the factor $(1 - P_{\text{Net}})$ accounts for the free space between nanosheets. This means $R_{\text{Net}} = R_{\text{Path}} A_{\text{NP}} / ((1 - P_{\text{Net}}) A_{\text{Net}})$.

The resistance of a single current path is

$$R_{\text{Path}} = \frac{1}{\sigma_{\text{Path}}} \frac{L}{A_{\text{Path}}} = \frac{1}{n_{\text{NP}} e \mu_{\text{Path}}} \frac{L}{A_{\text{Path}}}$$

Where L is the channel length, σ_{Path} is the conductivity of the current path and A_{Path} is the cross-section area of the path (which is just a chain of nanoparticles). Combining equations for R_{Net} and R_{Path}

$$R_{\text{Net}} = \frac{1}{n_{\text{NP}} e \mu_{\text{Path}}} \frac{L}{A_{\text{Path}}} \frac{A_{\text{NP}}}{((1 - P_{\text{Net}}) A_{\text{Net}})}$$

Now, we note that because the current path is just a chain of nanoparticles, $A_{\text{Path}} = A_{\text{NP}}$. In addition, as discussed above, μ_{Path} and μ_{Net} are identical. This allows us to rearrange

$$\sigma_{\text{Net}} = n_{\text{NP}} e \mu_{\text{Net}} (1 - P_{\text{Net}})$$

which is the same equation we used in method 1.

We will now develop this model for the specific cases of 2D, 1D, and 0D nanoparticles.

A4.3 2D Nanosheet Networks

While $R_{\text{NP}} = d_{\text{NP}} (\sigma_{\text{NP}} A_{\text{NP}})^{-1}$ is geometry-independent, we can make it specific to nanosheets (assuming they are square) by writing the cross-sectional area as $A_{\text{NS}} = l_{\text{NS}} t_{\text{NS}}$ where t_{NS} and l_{NS} are the mean nanosheet thickness and length. In addition, we need to relate d_{NS} (the mean distance travelled by an electron within a nanosheet) to the nanosheet length, l_{NS} . Depending on the stacking arrangement of nanosheets, d_{NS} could vary from close to zero (junctions where electron entered and left the nanosheet were very close together) to close to the entire nanosheet length (junctions where electron entered and left the nanosheets were very close to each end). Thus, on average, the distance travelled through the nanosheet is roughly half the nanosheet length such that $d_{\text{NS}} = l_{\text{NS}} / 2$ (although this will not apply in cases such as Langmuir-Blodgett edge-to-edge connected monolayer networks²⁹⁹). This gives $d_{\text{NS}} / A_{\text{NS}} = (2t_{\text{NS}})^{-1}$. We can then obtain an equation for the conductivity of a nanosheet network as

$$\sigma_{\text{Net}} \approx \frac{\sigma_{\text{NS}} (1 - P) / \kappa_{\text{Net}}}{\left[1 + \frac{R_{\text{J}}}{R_{\text{NS}}}\right] \left[1 + \frac{2}{n_{\text{NS}} t_{\text{NS}} l_{\text{NS}}^2}\right]} \quad [\text{A4.2a}]$$

Alternatively, this equation can be written in terms of network resistivity.

$$\rho_{\text{Net}} \approx \frac{\rho_{\text{NS}} \kappa_{\text{Net}}}{(1 - P_{\text{Net}})} \left[1 + \frac{R_{\text{J}}}{R_{\text{NS}}}\right] \left[1 + \frac{2}{n_{\text{NS}} t_{\text{NS}} l_{\text{NS}}^2}\right] = \frac{2 t_{\text{NS}} \kappa_{\text{Net}}}{(1 - P_{\text{Net}})} [R_{\text{NS}} + R_{\text{J}}] \left[1 + \frac{2}{n_{\text{NS}} t_{\text{NS}} l_{\text{NS}}^2}\right] \quad [\text{A4.2b}]$$

Or

$$\rho_{\text{Net}} \approx \frac{\kappa_{\text{Net}}}{(1 - P_{\text{Net}})} [\rho_{\text{NS}} + 2 t_{\text{NS}} R_{\text{J}}] \left[1 + \frac{2}{n_{\text{NS}} t_{\text{NS}} l_{\text{NS}}^2}\right]$$

where we use $R_{\text{NS}} = d_{\text{NS}}(\sigma_{\text{NS}}A_{\text{NS}})^{-1} = (\sigma_{\text{NS}}2t_{\text{NS}})^{-1} = \rho_{\text{NS}}(2t_{\text{NS}})^{-1}$ and $\sigma_{\text{NS}} = en_{\text{NS}}\mu_{\text{NS}}$.

Or

$$\sigma_{\text{Net}} \approx \frac{n_{\text{NS}}e\mu_{\text{NS}}(1-P_{\text{Net}})/\kappa_{\text{Net}}}{\left[1 + 2R_{\text{J}}n_{\text{NS}}e\mu_{\text{NS}}t_{\text{NS}}\right] \left[1 + \frac{2}{t_{\text{NS}}l_{\text{NS}}^2n_{\text{NS}}}\right]} \quad [\text{A4.2c}]$$

We note that the combination of parameters found in the denominator of the final term of this equation $(t_{\text{NS}}l_{\text{NS}}^2n_{\text{NS}})$ represents the number of free carriers in the nanosheet.

Equations A4.2a-c are general equations for conductivity in nanosheet networks. It is very important to note that we have taken a classical approach, treating the nanosheets as classical objects where $R_{\text{NS}} = d_{\text{NS}}(\sigma_{\text{NS}}A_{\text{NS}})^{-1}$. However, one could easily take a semi-quantum approach, for example by using $R_{\text{NS}} = R_{\text{Q}}d_{\text{NS}}/\zeta$ where R_{Q} is the resistance quantum and ζ is the scattering length.

Conduction Regimes

Looking at the second bracketed term in the denominator in equation (S2a), there are two main regimes that this model can reduce to depending on the carrier density. We elucidate this explicitly for 2D nanosheets but the same could be done for other geometries. For a network of 2D nanosheets, the resistivity is given by

$$\rho_{\text{Net}} \approx \frac{2t_{\text{NS}}\kappa_{\text{Net}}}{(1-P)} [R_{\text{NS}} + R_{\text{J}}] \left[1 + \frac{2}{n_{\text{NS}}t_{\text{NS}}l_{\text{NS}}^2}\right]$$

For nanosheets with a low carrier density such as semiconductors, $n_{\text{NS}} \ll 2(t_{\text{NS}}l_{\text{NS}}^2)^{-1}$. Then

$$\rho_{\text{Net}} \approx \frac{4(R_{\text{NS}} + R_{\text{J}})\kappa_{\text{Net}}}{(1-P_{\text{Net}})n_{\text{NS}}l_{\text{NS}}^2} \quad \text{or} \quad \sigma_{\text{Net}} \approx \frac{(1-P_{\text{Net}})n_{\text{NS}}l_{\text{NS}}^2}{4(R_{\text{NS}} + R_{\text{J}})\kappa_{\text{Net}}}$$

For this to be the case, the number of carriers per nanosheet $n_{\text{NS}}t_{\text{NS}}l_{\text{NS}}^2 = n_{\text{NS}}V_{\text{NS}} = N_{\text{NS}}$ must be very small ($\ll 2$).

For nanosheets with a high carrier density such as highly doped semiconductors or conductors, $n_{NS} \gg 2(t_{NS}l_{NS}^2)^{-1}$. Then

$$\rho_{Net} \approx \frac{2t_{NS}\kappa_{Net}}{(1-P_{Net})}[R_{NS} + R_J] \quad \text{or} \quad \sigma_{Net} \approx \frac{(1-P_{Net})}{2t_{NS}(R_{NS} + R_J)\kappa_{Net}}$$

For this to be the case, the number of carriers per nanosheet $n_{NS}t_{NS}l_{NS}^2 = n_{NS}V_{NS} = N_{NS}$ must be very large ($\gg 2$).

By now considering the relative magnitudes of R_{NS} and R_J , we can further develop these equations in five cases:

Case 1: A nanosheet network with a low carrier density and limited by inter-sheet junctions.

Then, $1 \ll 2(n_{NS}t_{NS}l_{NS}^2)^{-1}$ and $R_J / R_{NS} \gg 1$ which gives

$$\sigma_{Net} \approx \frac{(1-P_{Net})l_{NS}^2 n_{NS}}{4R_J \kappa_{Net}}$$

e.g. the case of junction-limited semiconductor. This equation is similar (but not identical) to one proposed in ref³⁰⁰ and found via dimensional analysis. However, this equation contains l_{NS} whereas the previously proposed version wrongly included t_{NS} . The version presented here is correct.

Case 2: A nanosheet network with light doping and low junction resistance:

Then, $1 \ll 2(n_{NS}t_{NS}l_{NS}^2)^{-1}$ and $R_J / R_{NS} \ll 1$ which gives

$$\sigma_{Net} \approx \frac{(1-P_{Net})n_{NS}l_{NS}^2}{4R_{NS}\kappa_{Net}} = \sigma_{NS}(1-P_{Net})t_{NS}l_{NS}^2 n_{NS} / 2\kappa_{Net}$$

e.g. the case of a material-limited system with few carriers.

Case 3: A nanosheet network with a high carrier density and limited by inter-sheet junctions:

Then, $1 \gg 2(n_{NS}t_{NS}l_{NS}^2)^{-1}$ and $R_J / R_{NS} \gg 1$ which gives

$$\sigma_{\text{Net}} \approx \frac{(1 - P_{\text{Net}})}{2t_{\text{NS}}R_{\text{J}}\kappa_{\text{Net}}}$$

e.g. the case for junction-limited conductor like graphene or silver nanoplatelets, or a heavily doped semiconductor. This equation is very similar to one proposed in ref³⁰⁰ and found via dimensional analysis. The version presented here is correct.

Case 4: A nanosheet network with a high carrier density and low junction resistance:

Then, $1 \gg 2(n_{\text{NS}}t_{\text{NS}}l_{\text{NS}}^2)^{-1}$ and $R_{\text{J}} / R_{\text{NS}} \ll 1$ which gives

$$\sigma_{\text{Net}} \approx \sigma_{\text{NS}}(1 - P_{\text{Net}}) / \kappa_{\text{Net}}$$

e.g. the case for material limited system with lots of carriers (for example, heavily doped TMDs as published by Lin et al³⁰¹.)

Special Case: Networks of nanosheets prepared by liquid-phase exfoliation (LPE)

A specific case which is particularly important here is that of networks of LPE nanosheets as used in [Chapter 5](#) and [Chapter 6](#). Owing to the mechanics of the ultrasonication-based exfoliation process,²³⁵ LPE nanosheets tend to have a roughly constant aspect ratio, k_{NS} , (defined by nanosheet mechanics) allowing us to define a well-defined relationship between nanosheet length and thickness $k_{\text{NS}} = l_{\text{NS}} / t_{\text{NS}}$. In this case, [Equation A.2a](#) becomes

$$\sigma_{\text{Net}} \approx \frac{n_{\text{NS}}e\mu_{\text{NS}}(1 - P_{\text{Net}})}{\left[1 + 2R_{\text{J}}n_{\text{NS}}e\mu_{\text{NS}}l_{\text{NS}} / k_{\text{NS}}\right] \left[1 + \frac{2k_{\text{NS}}}{l_{\text{NS}}^3 n_{\text{NS}}}\right]} \quad [\text{A4.3}]$$

A4.4 1D Nanotube/Nanowire Networks

Similar to the 2D case, [Equation A4.1](#) can be modified to describe conduction in 1D networks. We take R_{NS} as the resistance (on average) of the portion of the nanowire the electron passes through between junctions (length, d_{NW}). Assuming each nanowire has many junctions with other nanowires, this distance could vary from close to zero (junctions where electron entered and left the nanowire were very close together) to close to the nanowire length (l_{NW}) where junctions were

electron entered and left the nanowire were very close to each end. The average distance travelled through the nanowire is roughly half the nanowire length allowing us to replace d_{NS} with $l_{NW}/2$. Then R_{NS} can be replaced by

$$R_{NW} = (l_{NW} / 2) / (\sigma_{NW} \pi D_{NW}^2 / 4) = (2l_{NW}) / (\sigma_{NW} \pi D_{NW}^2)$$

where we take $A_{NS} = \pi D_{NW}^2 / 4$. Then

$$\sigma_{Net} \approx \frac{\sigma_{NW}(1-P_{Net})/\kappa_{Net}}{\left[1 + \frac{R_J \sigma_{NW} \pi D_{NW}^2}{2l_{NW}}\right] \left[1 + \frac{8}{n_{NW} l_{NW} \pi D_{NW}^2}\right]}$$

or

$$\rho_{Net} \approx \frac{\pi D_{NW}^2 \kappa_{Net}}{2l_{NW}(1-P_{Net})} [R_{NW} + R_J] \left[1 + \frac{8}{n_{NW} l_{NW} \pi D_{NW}^2}\right]$$

Which simplifying further gives

$$\rho_{Net} \approx \frac{\kappa_{Net}}{(1-P_{Net})} \left[\rho_{NW} + \frac{\pi D_{NW}^2 R_J}{2l_{NW}} \right] \left[1 + \frac{8}{n_{NW} l_{NW} \pi D_{NW}^2}\right]$$

If the 1D objects are conductors, n_{NW} is very large and meaning the above equation reduces to

$$\sigma_{Net} \approx \frac{\sigma_{NW}(1-P_{Net})/\kappa_{NW}}{\left[1 + \frac{R_J \sigma_{NW} \pi D_{NW}^2}{2l_{NW}}\right]} \quad \text{or} \quad \rho_{Net} \approx \frac{\left[\rho_{NW} + \frac{R_J \pi D_{NW}^2}{2l_{NW}} \right]}{(1-P_{Net})/\kappa_{NW}} \quad [A4.4]$$

A4.5 0D Nanoparticle Networks

We can also use [Equation A4.1](#) to describe arrays of large, weakly coupled nanoparticles of diameter D_{NP} . Again, assuming bulk-like transport within the nanoparticle, we replace d_{NS} with D_{NP} , and R_{NS} can be replaced by $R_{NP} \approx D_{NP} / (\sigma_{NP} D_{NP}^2) = 1 / (\sigma_{NP} D_{NP})$. We assume unity tortuosity factor. Then

$$\sigma_{Net} \approx \frac{\sigma_{NP}(1-P_{Net})}{\left[1 + \sigma_{NP} D_{NP} R_J\right] \left[1 + \frac{1}{n_{NP} D_{NP}^3}\right]}$$

If the 0D nanoparticles are conducting, n_{NP} is very large and

$$\sigma_{\text{Net}} \approx \frac{\sigma_{\text{NP}}(1 - P_{\text{Net}})}{\left[1 + \sigma_{\text{NP}} D_{\text{NP}} R_{\text{J}}\right]}$$

Which can alternatively be written as

$$\rho_{\text{Net}} \approx \frac{D_{\text{NP}} \left[R_{\text{NS}} + R_{\text{J}} \right] \left[1 + \frac{1}{n_{\text{NP}} D_{\text{NP}}^3} \right]}{(1 - P_{\text{Net}})}$$

A.5 The Effective Permittivity of an MoS₂ network.

In [Chapter 3](#) we showed that both the network as a whole and the NS-J pair can both be described by Randles circuits. This means that we can consider certain frequency limits. As the frequency approaches zero, the impedance of the capacitor approaches infinity while as the frequency approaches infinity, the impedance of the capacitor approaches zero.²⁰⁷ This means

$$\begin{aligned}\lim(Z'_{\text{Net}})_{\omega \rightarrow 0} &= R_p + R_s \\ \lim(Z'_{\text{Net}})_{\omega \rightarrow \infty} &= R_s \\ \lim(Z'_{\text{NS-J}})_{\omega \rightarrow 0} &= R_J + R_{\text{NS}} \\ \lim(Z'_{\text{NS-J}})_{\omega \rightarrow \infty} &= R_{\text{NS}}\end{aligned}\tag{A5.1}$$

Keeping in mind the [Equation 3.22](#) linking $Z_{\text{NS-J}}$ to Z_{Net} as

$$Z_{\text{NS-J}} = Z_{\text{Net}} \frac{A_{\text{Net}}}{L_{\text{Ch}}} \frac{(1 - P_{\text{Net}})}{2t_{\text{NS}}\kappa_{\text{Net}}} \left[1 + \frac{2}{n_{\text{NS}}t_{\text{NS}}l_{\text{NS}}^2} \right]^{-1}$$

We can write

$$R_{\text{NS}} = (Z'_{\text{NS-J}})_{\omega \rightarrow \infty} \approx (Z'_{\text{Net}})_{\omega \rightarrow \infty} \frac{A_{\text{Net}}}{L_{\text{Ch}}} \frac{(1 - P_{\text{Net}})}{2t_{\text{NS}}\kappa_{\text{Net}}} \left[1 + \frac{2}{n_{\text{NS}}t_{\text{NS}}l_{\text{NS}}^2} \right]^{-1}$$

And

$$R_J + R_{\text{NS}} = (Z'_{\text{NS-J}})_{\omega \rightarrow 0} \approx (Z'_{\text{Net}})_{\omega \rightarrow 0} \frac{A_{\text{Net}}}{L_{\text{Ch}}} \frac{(1 - P_{\text{Net}})}{2t_{\text{NS}}\kappa_{\text{Net}}} \left[1 + \frac{2}{n_{\text{NS}}t_{\text{NS}}l_{\text{NS}}^2} \right]^{-1}\tag{A5.2}$$

Combining [Equations A5.1](#) and [A5.2](#) we find that

$$R_J + R_{\text{NS}} = \frac{A_{\text{Net}}}{L_{\text{Ch}}} \frac{(1 - P_{\text{Net}})}{2t_{\text{NS}}\kappa_{\text{Net}}} \left[1 + \frac{2}{n_{\text{NS}}t_{\text{NS}}l_{\text{NS}}^2} \right]^{-1} (R_p + R_s)$$

For simplicity we consider a situation where $R_J \gg R_{\text{NS}}$ and n_{NS} is large. Then

$$R_J = \frac{A_{\text{Net}}}{L_{\text{Ch}}} \frac{(1 - P_{\text{Net}})}{2t_{\text{NS}}\kappa_{\text{Net}}} R_p$$

We also found in [Chapter 5](#) that $\omega_{\text{peak}} = (R_p C_p)^{-1} = (R_J C_J)^{-1}$ so $R_p C_p = R_J C_J$. We note that C_p is the effective capacitance of the nanosheet network as $C_p = R_J C_J / R_p$.

This allows us to use the equation above to find

$$C_p = \frac{A_{\text{Net}}}{L_{\text{Ch}}} \frac{(1 - P_{\text{Net}})}{2t_{\text{NS}}\kappa_{\text{Net}}} C_J$$

In the main text, we utilise $C_J = \epsilon_0 A_J / l_J$. In addition, the effective network permittivity is defined via $C_p = \epsilon_0 \epsilon_{r,\text{Net}} A_{\text{Net}} / L_{\text{Ch}}$, so

$$\epsilon_{r,\text{Net}} = \frac{(1 - P_{\text{Net}}) A_J}{2t_{\text{NS}}\kappa_{\text{Net}} l_J}$$

Taking $P_{\text{Net}} = 0.5$, $A_J = 0.5 \text{ mm}^2$, $l_J = 0.6 \text{ nm}$, $t_{\text{NS}} = 3.3 \text{ nm}$, and $\kappa_{\text{Net}} = 1$, we find a value for $\epsilon_{r,\text{Net}}$ of 6×10^4 , which is extremely large.

To check this, we note that the C_p value found from fitting the Z'_{Net} spectrum measured for the MoS_2 network analysed in [Figure 5.1C,D](#) in the main text was $7 \times 10^{-12} \text{ F}$. Here, the channel length and width were $L_{\text{Ch}} = 50 \text{ }\mu\text{m}$ and $W_{\text{Net}} = 19.4 \text{ mm}$, while the network thickness was $t_{\text{Net}} = 15 \text{ nm}$. This implies a network permittivity of 14×10^4 , in reasonable agreement with the model (any discrepancies are due to inaccuracies in our parameter estimation). Despite these very high permittivity values, we don't expect MoS_2 networks to make good dielectrics due to the expected large leakage currents since R_J is large but not infinite.

A.6 Temperature-Dependent Transport in Nanosheet Networks

Literature

Several papers have now performed temperature-dependent conductivity measurements on nanosheet networks of solution-processed MoS₂, two using liquid-phase exfoliated MoS₂^{88, 302} and two using electrochemically exfoliated MoS₂,²¹³ including this work. The distinction between exfoliation methods is important to note as both types of nanosheet show a change in transport behaviour in the range of 160-200 K; liquid-phase exfoliated nanosheets transition from tunnelling to hopping as temperature is increased^{88, 302} while electrochemically exfoliated nanosheets transition from variable-range hopping to an activated behaviour.^{213, This work}

The difference here is caused by the dominating effect of the inter-sheet junctions which is strongly mediated by nanosheet aspect ratio³⁰³, where electrochemically exfoliated nanosheets tend to have a much higher aspect ratio than liquid-phase exfoliated nanosheets. The relative rigidity of the low aspect-ratio, liquid-phase exfoliated nanosheets prevents intimate contact at the junctions thus creating a large junction resistance. The resistance associated with hopping depends exponentially on both the distance between hopping sites and temperature, meaning that a wide inter-sheet distance combined with a low temperature produces an excessively high inter-sheet hopping resistance which rules it out below a critical temperature. Below this temperature, transport can only occur by inter-sheet tunnelling which is a comparatively inefficient transport process that suppresses the conductivity of the network to $< 10^{-9} \text{ S m}^{-1}$.^{88, 302}

By contrast, the large area and conformal junctions between the electrochemically exfoliated nanosheets result in a very low junction resistance which allows a more efficient hopping transport to occur across the junctions at all temperatures. Variable-range hopping at lower temperatures ($< 200 \text{ K}$) is commonly seen in measurements of individual nanosheets³⁰⁴⁻³⁰⁶ as the energetic disorder of the nanosheet means a low energy site will always be accessible within a reasonable range of the carrier. To the best of the authors knowledge, intra-sheet tunnelling transport in MoS₂ has not been seen at low temperatures. The

presence of hopping transport in a nanosheet network at low temperatures is another indicator that junction resistances are low.

Activated hopping

Miller Abrahams theory shows that the resistance associated with hopping between two sites under an applied electric field is given by²⁹⁰

$$R_{ij} \approx \frac{kT}{e^2 \nu_0} \exp\left(\frac{2r_{ij}}{a}\right) \exp\left(\frac{\epsilon_{ij}}{k_B T}\right) \quad [\text{A6.1}]$$

Where r_{ij} and ϵ_{ij} are the spatial and energy distances between sites while a is the localisation length and ν_0 is an attempt frequency. In the simplest case, we can apply this to describe the junction resistance data at high temperature where activated behaviour is observed:

$$R_j \approx \frac{kT}{e^2 \nu_0} \exp\left(\frac{2l_j}{a}\right) \exp\left(\frac{E_a}{k_B T}\right) = R_{j,0} \exp\left(\frac{2l_j}{a}\right) \exp\left(\frac{E_a}{k_B T}\right)$$

Where l_j is the inter-sheet separation (distance across the junction) and E_a is the activation energy. The equation describes the R_j versus T data for $T > 235$ K reasonably well with $R_{j,0} \exp(2l_j / a) = 282 \text{ k}\Omega$ and $E_a = 58 \text{ meV}$. Approximating $\nu_0 = 10^{13} \text{ Hz}$ and taking $l_j = 0.6 \text{ nm}$ and $a = 0.7 \text{ nm}$ (see below) predicts $R_{j,0} \exp(2l_j / a) = 90 \text{ k}\Omega$, lower than the measured value. The discrepancy might be due to the limitations of the model, or inaccuracies in the values of l_j and a used.

At temperatures below 235 K, our data is consistent with 3D variable range hopping (3D-VRH). Activated hopping is often observed to transition to variable range hopping at low temperatures.^{307, 308} The reason for this is that the reduced temperature limits the number of states within a reasonable energy range that a carrier can hop to. This forces the carrier to hop to more distant states that are closer in energy. In the standard derivation of variable range hopping,²⁹⁰ we consider hopping between nearby localised states, usually in the band tail or within the bandgap.

However, when considering the junction resistance between two nanosheets, we must consider hopping across the van der Waals gap between the sheets. This defines a minimum hopping distance. In addition, because our data implies band-

like transport within the nanosheets, we must consider hopping from the conduction band edge of one nanosheet to the conduction band of another. These differences require modification to the standard VRH derivation which we outline here by modifying the derivation given Ref. 290.

Following Equation A6.1, the junction resistance can be written as

$$R_j \approx R_{j,0} \exp(\alpha)$$

where

$$\alpha = \frac{2r_{ij}}{a} + \frac{\varepsilon_{ij}}{k_B T}$$

Variable range hopping is the situation where the resistance is minimised by considering the factors which minimise α .

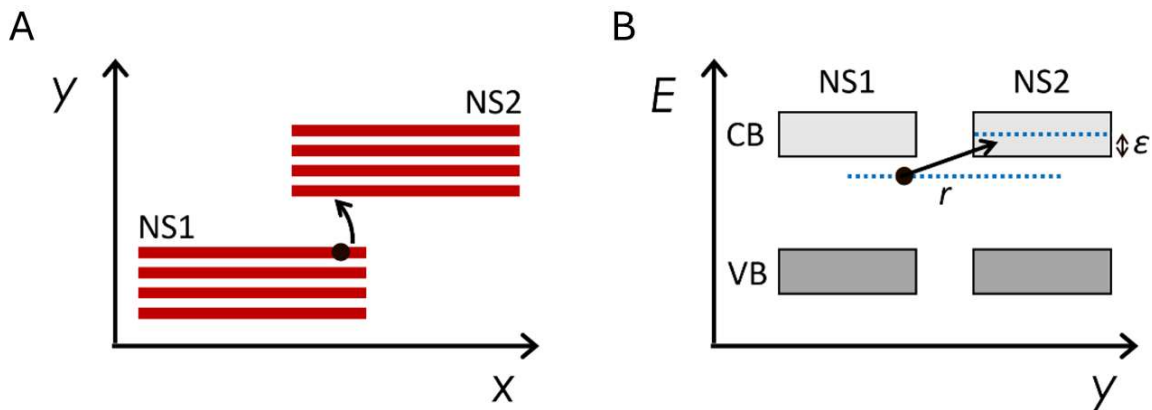


Figure A6.1: Electron Hopping Between Nanosheets. **A)** Schematic showing two multilayer nanosheets (NS1 and NS2) with a planar junction and an electron (black circle) hopping from one to another. **B)** Energy band diagram showing the conduction and valence bands of NS1 and NS2. Here, an electron is shown hopping from the conduction band of NS1 to the conduction band of NS2. The hopping distance is R . We assume the electron can hop into states within an energy ε of the bottom of the CB of NS2.

The hopping scheme we envisage is shown in Figure A6.1 where an electron hops from the conduction band-edge of one nanosheet to the conduction band of the other nanosheet. We assume it can hop into a range of states within an energy, ε , of the bottom of the conduction band of the second nanosheet. The minimum

hopping distance is the inter-sheet separation (l_J) with some hops being slightly longer than that depending on the final state. The number of states (per unit volume) accessible within the conduction band of the second nanosheet is $N = g\varepsilon$, where g is the density of states at the bottom of the conduction band. The average spatial separation between these states is $d = (g\varepsilon)^{-1/3}$. Thus, we assume the hopping distance to be the sum of the inter-sheet separation and the distance to the nearest state $r_{ij} = l_J + d = l_J + (g\varepsilon)^{-1/3}$ while we approximate $\varepsilon_{ij} = \varepsilon$. This yields:

$$\alpha = \frac{2}{a}(l_J + (g\varepsilon)^{-1/3}) + \frac{\varepsilon}{k_B T}$$

The minimum resistance is achieved when α is minimized. We identify the conditions for this via differentiation:

$$\frac{d\alpha}{d\varepsilon} = \frac{-2}{3a}(g)^{-1/3}(\varepsilon)^{-4/3} + \frac{1}{k_B T} = 0$$

Rearranging yields the most likely hopping energy

$$\varepsilon_o = \left[\left(\frac{3a}{2k_B T} \right)^3 g \right]^{-1/4}$$

Combining this value with $r_{ij} = l_J + (g\varepsilon)^{-1/3}$, yields the most probably hopping distance:

$$r_0 = l_J + \left[\frac{3a}{2k_B T g} \right]^{1/4}$$

Next, we replace ε_{ij} and r_{ij} in [Equation A6.1](#) with their most probable values, ε_0 and r_0

$$R_J \approx \frac{k_B T}{e^2 \nu_0} \exp\left(\frac{2}{a} l_J\right) \exp\left(\left[\frac{76}{k_B T g a^3} \right]^{1/4}\right)$$

yielding

$$R_J \approx R_{J,0} \exp\left(\frac{2l_J}{a}\right) \exp\left(\left[\frac{T_0}{T}\right]^{1/4}\right)$$

With

$$T_0 = \frac{76}{k_B g a^3}$$

These equations are almost identical to the standard 3D-VRH equation. However, here, g represents the density of states at the bottom of the conduction band (in the standard equation, it represents the DOS at the Fermi energy). We can approximate g within each monolayer using the equation for the density of states of a 2D electron gas

$$g_{2D} = \frac{m}{\pi \hbar^2}$$

However, the nanosheets themselves are a few nanometers thick and are essentially quasi-3D. We can convert this 2D density of states to an effective 3D density of states by dividing through by the monolayer thickness, d_0

$$g \approx g_{3D} = \frac{g_{2D}}{d_0} = \frac{m}{\pi \hbar^2 d_0}$$

This equation gives values which are in reasonable agreement with more sophisticated calculations³⁰⁹ and yields a final approximate expression for T_0

$$T_0 \approx \frac{76 \pi \hbar^2 d_0}{k_B a^3 m}$$

This equation is very different to the standard 3D-VRH expression for T_0 and we now use this equation to analyse our experimental data. Taking the fit value of $T_0 = 4.93 \times 10^5$ K and the effective mass known for MoS₂ ($m = 0.7m_e$) allows one to calculate the localisation length in MoS₂ to be a ~ 0.7 nm. This is similar to published data which varies between 0.2 and ~ 3 nm.^{213, 270, 304, 305} We can also compare this value to the Bohr radius in MoS₂ to which it should be similar to the localisation length³¹⁰

$$a_B = \frac{4\pi\hbar^2 \varepsilon_r \varepsilon_0}{e^2 m}$$

Taking $\varepsilon_r = 6$ (Ref. [311](#)) and $m = 0.7m_e$ yields $a_B = 0.45$ nm which is very similar to the value obtained above. We can modify the equation for the most probable hopping distance using the approximation for g given above:

$$r_0 = l_j + \left[\frac{3a\pi\hbar^2 d_0}{2mk_B T} \right]^{1/4}$$

Taking $d_0 = 0.6$ nm, this gives a value which is 1.7 nm larger than the inter-sheet distance at room temperature, leading to most probable hopping distance of 2.3 nm. Similarly, we modify the equation for the most probably hopping energy using the approximation for g given above:

$$\varepsilon_o = \left[\left(\frac{3a}{2k_B T} \right)^3 \frac{m}{\pi\hbar^2 d_0} \right]^{-1/4}$$

This yields a most probably hopping energy which increases with temperature roughly as $1.5 k_B T$, reaching 35 meV at 233 K, which is roughly where the behaviour transitions from VRH to activated. We note that this value is lower than the activation energy of 58 meV found in the activated region.

Discussion

It is worth noting that both the Miller-Abrahams and VRH equations describe hopping between localised states.[290](#) However, here we are considering a situation where the carriers undergo bandlike transport within the nanosheets, presumably via delocalised states, interspaced with hopping events between nanosheets. This means that on its journey, a carrier must transition between delocalised states (transport within the nanosheets) and localised states (during the inter-sheet transfer process) multiple times. Presumably this also applies in other networks, e.g. those of carbon nanotubes. We note that Schiessl et al.[312](#) successfully modelled inter-tube hopping in nanotube networks using the MA equation without considering the details of the transition between delocalised and localised states.

We note that it is likely that our nanosheets have localised states below the band edge, perhaps due to the presence of S-vacancies[313](#) or other defects created

during electrochemical exfoliation. Indeed, papers have shown hopping transport within individual nanosheets.^{213, 314, 315} However, like other papers on electrochemically exfoliated MoS₂,³¹⁶ we see high *n*-doping for reasons that are not fully understood. This doping pushes the Fermi energy up toward the conduction band edge, filling these trap states and allowing band-like transport to occur in the nanosheets themselves. Such band-like transport within nanosheets has also been seen in the literature by many authors^{285, 317, 318} with various papers showing transitions from hopping to band-like transport as the carrier density is increased.^{314, 319}

To explain the presence of hopping between localised states, one possibility is that immediately prior to the inter-sheet hop, carriers get trapped in a localised state close to the junction. Such “transit” states might be associated with the nanosheet edge or be due to band bending³²⁰ near the junction causing the Fermi energy to locally move into the band tail. From this localised state, the carriers hop, either directly into a delocalised state in the conduction band of the second nanosheet or to a similar localised “transit” state just below the mobility edge of the second nanosheet whence they can be rapidly promoted to a delocalised state. Understanding the details of this process will be an important part of the future work following this project.

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