Structure and Ordering in Solvents and Solutions of Carbon Nanotubes

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A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy

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October 2018
Dedicated to my parents
Declaration

I, Nadir Basma, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated, and that appropriate credit has been given where reference has been made to the work of others.

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Abstract

Our lack of understanding of interactions between nanoparticles in liquids is impeding our ability to controllably produce and manipulate nanomaterials. Traditionally, nanoparticle dispersions are treated using classical colloidal theories originally developed for micron-scale particles. These theories have recently been called into question as significant deviations from micro-scale models are routinely seen as dimensions of the dispersed particle are reduced.

The deviations are prominent in the liquid phase where low-dimensional nanomaterials are often processed to produce individualised species with which desirable properties are associated. In this context, a few solvents have proven to more effective than others. Yet, their liquid structures, which ultimately underpins their solvation properties, has not been established. In the first part of this work, advanced neutron scattering methods was used to probe the structure of three solvents: N-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF) and dimethylacetamide (DMA). Monte Carlo molecular modelling was used to analyse the neutron data. In NMP, an unusually well-developed mix of interactions is uncovered and its dipole moment was found to have a profound effect on its structure, inducing molecular organisation extending into the nanometer range. In the case of DMF and DMA, structural information pertaining to spatial and orientational correlations in each of the solvents was revealed. The results demonstrate a variety of differences between these two structurally-analogous solvents. Most notably, a higher degree of ordering was found in DMF, dictated by its polar moment, though stronger hydrogen bonding interactions were found in DMA. The intrinsic order in all of these solvents enables a range of local solvent-solute interactions, rationalising their ability to coordinate to and solvate a variety of species.

The influence of a nanoparticle on both local and system solvent structures is then investigated in the second part of this work. Solutions of nanomaterials provide a unique system to explore local solvent ordering effects at smaller particle dimensions, and examine the crossover from colloidal to solution behaviour, allowing comparison to classical models. The investigation represents the first atomistically-resolved neutron scattering measurement of a nanomaterial solution. Single-Walled Carbon Nanotubes (SWCNTs) have been shown to thermodynamically dissolve to high concentrations in aprotic solvents, though the underpinning mechanisms to their dissolution are unknown. Thus, the system studied was of a concentrated solution of SWCNTs in DMF. The findings provide experimental evidence of enhanced solvent ordering near the nanoparticle’s surface, and contributes crucial insights that differ from conventional standpoints in understanding nanoparticle dissolution.
Nanomaterials promise to have a huge impact on many technologies, in areas as diverse as healthcare, energy infrastructure, and multifunctional composites. However, their widespread use has been historically hampered by issues of synthesis, agglomeration, and manipulation. Processing can be facilitated by dispersion of the nanomaterials in a liquid; such dispersions can be used to apply the nanomaterials over large areas at low costs. However, while promising, little is known about the underpinning forces and mechanisms at the atomic level for such dispersions to form and stabilise. This work uses neutron scattering methods to uncover local order in such liquids and finds far more developed solvent ordering and structure than as is proposed in conventional models and traditional understandings. The work not only points us a new direction in understanding nanoparticle dispersions, but develops a versatile methodology which is applicable to a wide range of similar systems, which range from electrochemical to biological devices.
Acknowledgements

I take the opportunity to express my gratitude to many whom have in some way or another contributed to this thesis.

First and foremost, to Chris Howard, for his supervision, support and guidance that have been paramount over the course of the project. His positive outlook and his confidence in my research have truly inspired me. His enthusiasm was contagious and motivational, and translated into my immense enjoyment of the process.

To Milo Shaffer, for his supervision and counsel, and his commendable knowledge of all chemistry things which was invaluable to me from the beginning till the end of the project. I am thankful for many of his ideas and suggestions at various stages.

To Tom Headen, with whom I collaborated with for most of the work in this thesis. I owe Tom a debt of gratitude for sharing his expertise so willingly and lending me his intuition. To Neal Skipper too, for his counsel and valuable input during the entire process. To Tristan Youngs, Daniel Bowron and Alan Soper whom during beam-time experiments at the Rutherford Appleton Laboratory provided a great deal of help. To post-doctoral researchers, David Buckley for showing me the ropes at the beginning of the journey, and Adam Clancy for timely advice, as well as thoughtful and detailed feedback on the thesis.

To colleagues at the London Centre for Nanotechnology, and to members of both the Howard and the Shaffer groups at UCL and Imperial College. To many at the ACM doctoral training centre, and indeed the centre’s directors, Neil Curson and Stephen Skinner, for their management and direction.

Finally, to my parents. I’m indebted to you both. I am so much of what I learned from you. Thank you the for the values you instilled in me. I dedicate this thesis to you.
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Contributions

Publications:
N. Basma, T. Headen, M. Shaffer, N. Skipper and C. Howard
“Local Structure and Polar Order in Liquid N-methyl-2-pyrrolidone”

N. Basma, T. Headen, M. Shaffer, N. Skipper and C. Howard.
“The liquid structure of the solvents dimethylformamide and dimethylacetamide (DMF and DMA)” – In preparation

“Beyond the Double Layer: System Reorganization at Solvated Carbon Nanotube Surfaces” – In preparation


Poster: “The structure of NMP – a neutron diffraction study” N. Basma, T. Headen, M. Shaffer, N. Skipper and C. Howard; *European Conference for Neutron Scattering*, 2 September 2015, Zaragoza (Spain)


Invited Talk: “The liquid structures of polar aprotic solvents probed by neutron scattering”; N. Basma, T. Headen, M. Shaffer, N. Skipper and C. Howard; Universitat Politècnica de Catalunya, June 2016, Barcelona, Spain

Talk: “The liquid structures of polar aprotic solvents probed by neutron scattering” N. Basma, T. Headen, M. Shaffer, N. Skipper and C. Howard; World Congress and Expo on Nanotechnology and Nanoengineering, 4 April 2017, Dubai, UAE

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Chapter 1

Introduction

Recent advances in the production of low dimensional nanomaterials have provided access to a broad family of materials with novel functional properties and phenomena, alongside highly desirable physical, chemical, and biological properties. While their technological potential is clear, the road to their scalable implementation is littered with several significant obstacles, notably in synthesis (i.e. achieving monodispersity, controlled shape and size, reproducibility), processing, and assembly. The latter two issues are most commonly tackled through liquid phase processing, with solutions of nanoparticles an obvious route to purification, functionalization, and manipulation into desirable architectures and complex nanostructures.

One significant impeding factor is the difficulty in dispersing many nanoparticles in liquids, and indeed a lack of understanding of the fundamental interactions in the liquid that permit this. Historically, nanoparticle dispersions are treated with classical colloidal theories originally developed for micron-scale particles. However, significant deviations from behaviour predicted by micro-scale models and colloidal dispersions in terms of concentration, stability, phase behaviour, viscosity, and kinetics are routinely seen\cite{1-6}. It is now thought that these theories fail for nanoparticles as their complex shapes, morphologies and structural elements, and literal size being on the atomic scale, mean that contributing surface interactions (e.g. van der Waals, Coulombic and other solvation forces) do not add together linearly when treated separately to give the sum interaction energy, as is done in micro-scale models. The nuance
is particularly important in the liquid phase, since unlike mesoscale solutes which are particularly distinctive in their interaction with solvents, nanoparticle sizes are comparable to coordinating solvent molecules. Far from being a homogenous field of constant dielectric, the local orientation of the solvent molecules varies substantially and is thus important to consider when trying to understand nanoparticle dissolution[5–13].

In the case of low-dimensional (1d/2d) nanomaterials, agglomeration in the initially synthesised material leads to large intermolecular forces preventing processing of bulk materials into the individualised species with which desirable properties are associated. As such, liquid phase exfoliation (LPE) is ubiquitously performed, applying shear to the bulk solid mixed with a dispersing liquid. Various routes have been developed to forming dispersions and increase their metastable lifetimes, however, surprisingly, a few solvents have proven to be effective, a result which has stimulated many lengthy and systematic studies aimed at understanding the success and effectiveness of some solvents over others. These approaches have been used to select optimal solvents for a given nanomaterial (usually from a small family of typical solvents, notably amides), but little is understood about the underlying physics and thermodynamics as to why some few solvents are successful while others fail. What is desirable to better understand nanoparticle LPE and nanoparticle dispersions is a fuller description of the system organisation: how the presence of a nanoparticle influences both local and system solvent structures, and how the thermodynamics of this system compares to those of the initial pure solvent/solid agglomerated nanoparticle system(s).

Single-walled carbon nanotubes (SWCNTs) are prototypical 1-dimensional materials whose electronic nature has endowed them with exceptional material properties, and they remain the most studied low dimensional nanomaterial for LPE. Fortuitously, their size falls into the 0.5 to 40 nm range of length scales, within which the most vivid manifestations of effects and phenomena distinct to nanomaterials are exhibited. Exploring SWCNTs in solution therefore provides an important archetypal study to understand the local solvent ordering effects that become increasingly important for smaller particle dimensions - SWCNTs are a limiting example in the one dimension.
Comprehensive structural studies on nanoparticle dispersion and/or solution systems are rare, largely due to the complexity of the measurements involved, and the unavailability of experimental methods to probe these at the nanoscale, especially at the dilute concentrations intrinsic to nanoparticle dispersions. However, significant advances have now been made in the methods of neutron scattering, and to computational tools such as molecular modelling, making it is feasible to experimentally probe structure in liquids and complex solution systems.

Structure of Thesis

This thesis is split into 7 chapters that are structured as follows:

- Chapter 2 covers the literature upon which this work is built, starting with the liquid state, moving onto Single-Walled Carbon Nanotubes (SWCNTs) and focusing finally on the solvation of SWCNTs and modelling SWCNT-solvent systems.

- Chapter 3 focuses on the experimental and computational techniques used in the research before detailing the theory behind two complementary techniques used in this thesis. First, neutron diffraction with isotopic substitution (NDIS) which is the experimental method by which the structure of liquids and solutions was probed; and secondly the Monte Carlo modelling method of Empirical Potential Structure Refinement (EPSR) which was used to simulate the system in question and interrogate it to extract structural information.

- Chapter 4 presents NDIS experiments performed on the pure NMP solvent and analysis via Monte Carlo simulations using the EPSR method. Findings pertaining to the the liquid structure of NMP are reported.

- Chapter 5 presents two separate neutron scattering study into the structures of each of the solvents, DMF and DMA. Three-dimensional models of their structure is constructed in EPSR to obtain an unprecedentedly detailed spatial and orientational picture of their
liquid structure, from which molecular level structural information is accessed.

- Chapter 6 investigates structure and ordering in a SWCNT solution, also through neutron scattering of the solution and Monte Carlo modelling. This is the first atomistically-resolved measurement of local ordering in a concentrated nanoparticle solution – a benchmark measurement in this field.

- Finally, Chapter 7 summarises the results and concludes the thesis. Areas in which the work herein could be expanded in the future are suggested and discussed.
Chapter 2

Background and Literature

2.1 Introduction

This chapter covers the background and literature upon which the work in this thesis is built. The chapter comprises four main sections.

Section 2.2 focuses on liquids, introducing the liquid state and describing structure in liquids, addressing in particular the task of measuring and quantifying structure and the methods by which this is typically achieved.

Section 2.3 then outlines interactions occurring in liquids.

Section 2.4 introduces Single-Walled Carbon Nanotubes (SWCNTs). Their geometry and electronic properties are given, as well as their potential applications and the current challenges hindering their scalable use. The methods of Liquid Phase Exfoliation (LPE) and dissolution via reductive charging are then described. These routes yield dispersions and/or solutions of SWCNTs. The effectiveness of these techniques is critically dependent on the choice of solvent, so the section ends with a literature digest of the solvents found to be superior for these purposes.

Section 2.5 concerns modelling the solubility of SWCNTs, first describing DLVO and Oosawa-Manning theories, the underlying assumptions of these models and their invalidity in describing nanoparticle dispersions. A digest of the relevant literature surrounding SWCNT–solvent systems is then provided.
2.2 On Liquids and Liquid Structure

2.2.1 The Liquid State

The liquid state is intermediate in nature between the solid and gas states. In a solid, particles are packed closely, as shown in Figure 2.1, having a definite shape and volume. Gases are free to diffuse to completely fill the space within which they are contained, thus having no fixed shape. The solid and gas states are commonly approximated using the ideal crystal theory and the ideal gas model, respectively. In an ideal crystal, structure is arranged in what is known as a periodic lattice, comprising a unit cell, that is the smallest repeating motif, as shown in Figure 2.2(a). By repetitive translation of the unit cell, the three dimensional structure is built. Gases, on the other hand, are very well separated with no regular arrangement. They can be modelled using the ideal gas law, given by \( pV = nRT \), where \( p \) is the pressure, \( V \) is the volume, \( n \) is the number of moles of the substance, \( R \) is the gas constant and \( T \) is the temperature in Kelvin. Forces are assumed to act on atoms (or particles) only during perfectly elastic collisions of negligible duration.

\[
pV = nRT
\]

**Figure 2.1:** A schematic diagram showing the difference in levels of structure between a crystal, a liquid, and a gas.

In a liquid, particles are closely packed but are able to flow freely, occupying the shape of their container. Developing an equation that describes how a liquid’s behaviour changes with \( pV \), or \( T \) is therefore more challenging, though approximations do exist (e.g. van der Waals equation of state coupled with Maxwell’s construction). The intrinsically disordered arrangement of atoms in liquids, and their translational motions, invalidate
the repeating unit cell approach used in solids. In parallel, assuming an absence of interactions, as in the gas model, is also inappropriate as these interaction forces are of great relevance in liquids. These forces are in fact responsible for the observed deviations from the ideal gas law and are therefore key to the macroscopic properties of the bulk system comprising them. The problem is further complicated by the fact that diffusive motion in even the simplest of atomic liquids is dependent on the cooperative behaviour of neighbouring atoms. An adequate description of liquids thus necessitates knowledge of the interplay and intricate balance between all of these factors.

2.2.2 Structure in Liquids

Structural characterisation of liquids is a complex task. For crystals, the least squares method, used to fit the position of atoms in a repeating unit cell to diffracted intensities, provides a simplified yet effective route to structure determination. In liquids, on the other hand, atoms are continually moving around from one place to another, so there is no “structure” as such in the crystallographic sense. Liquids have no three-dimensional long-range ordering and structural correlations in liquids act only over 1-2 nm length scales. Even finding a repeating pattern is challenging for it will depend on the distance, the direction one looks from a central molecule, and the orientation of nearby atoms or molecules.

![Figure 2.2](image.png)

**Figure 2.2:** A schematic diagram showing the difference in levels of structure between a crystal and a liquid. (a) In the crystal, structure is defined using the simplest repeating unit i.e. the unit cell. (b) In a liquid, structure quantification involves delineating the volume by the concentric circles lying at radial distances of $r_{\text{min}}$ and $r_{\text{min}} + \Delta r$ from the central atom.
There is however a residual local structure that arises from the fact that no two atoms can occupy the same space. Each atom is surrounded by its own space, creating local arrangements of atoms which are continually changing as the atoms and molecules in a liquid diffuse around. By viewing the average structure of liquids as the time or space averaged sum of the most likely ‘inherent’ structural arrangements, an experimental glimpse at the local structure of liquids can be obtained. The method used for liquid structure quantification is based on “atom counting”.

For an atomic liquid, one can imagine sitting on an atom, looking out in all directions, and counting the number of atoms in some specified volume element, as illustrated in Figure 2.2(b). The elements are delineated by concentric circles of some radial distance, \( r \). As the radial distance from the central atom is increased, a histogram of the average number of atoms found in each volume element is computed. A typical histogram is shown in Figure 2.3(a). Repeating this, with a different atom used as the central atom, will give a slightly different histogram each time.

![Figure 2.3](image) **Figure 2.3:** (a) What a typical histogram of the number of atoms at a given distances from a reference central atom might look like. (b) The measured distribution which would be obtained when repeating the process for every atom in the liquid.
Finally, after having done so for all atoms, the results of all histograms are averaged. The resulting plot, given in Figure 2.3(b), gives the probability of finding an atom at a given distance from any chosen reference atom. The values of the measured distribution are then normalised by dividing by the distribution that would be found if the atoms were ideally distributed in the system. For a system with atomic number density, \( \rho \), this ideal distribution is given by:

\[
\text{Ideal Distribution} = \frac{4}{3} \pi \rho (r_{\text{max}}^3 - r_{\text{min}}^3),
\]

so the radial distribution function (RDF), \( g(r) \), in Figure 2.4, can be determined as:

\[
g(r) = \frac{\text{Measured Distribution}}{\text{Ideal Distribution}}.
\]

The \( g(r) \) function has two important characteristics. Firstly, \( g(r) = 0 \) at low radial distances, reflecting the repulsive nature of the atoms in that region. Secondly, as \( r \) increases to larger radial distances, \( g(r) \) tends to 1 as the arrangement of atoms becomes more random and so the measured distribution tends towards the ideal atomic distribution. A typical \( g(r) \) function is shown Figure 2.4, showing a series of peaks and maxima associated with neighbouring shells of atoms. The radial distance, \( r \), at the trough of each peak defines the upper limit of the “coordination shell”.

**Figure 2.4:** Schematic illustration of the radial distribution function, \( g(r) \), which quantifies correlations between atom pairs, its dependence on \( r \), and coordination shells.
The local structure of liquids is governed by specific interactions which exist between neighbouring atoms or molecules, typically revealed by close, sharp or intense features in the intermolecular RDFs, $g_{ij}(r)$s, which reflect the probability of finding atoms of type $j$ as a function of the distance, $r$, from an atom of type $i$. A complete set of these $g_{ij}(r)$s can be obtained from simulations – these will be discussed in more detail in Chapter 3.

2.2.3 Liquid Structure as Probed Experimentally

Diffraction is perhaps the most powerful experimental method for liquid structure determination, and is the main source of our experimental knowledge of static structure in liquids. Diffraction involves measurements of the way that the radiation interacts with a sample, measuring the scattering cross-section as a function of momentum transfer between the radiation and the sample, to provide information about the distribution of atom pair distances in the liquid. The theoretical basis is discussed in more detail in Chapter 3.

The most extensively studied liquid is water, yet, despite the huge amount of research that has been carried out to understand the properties of water, there is still no universally accepted structural model for water and some of its anomalous properties remain unexplained[14–16].

Besides water, little is known about the structure of most liquids despite their obvious importance. Advances in neutron scattering techniques over the last decade have paved the way for structural investigations of liquids and by combination with molecular modelling, the structures of a range of atomic, molecular and ionic liquids have been successfully deduced[17–27]. For example, the structure of liquid benzene was only reported in 2010 through neutron diffraction experiments combined with computer simulations[22]. In contrast to previously reported computationally-derived structures, diffraction data revealed a full spatial and orientational picture of benzene. Nearest neighbour coordination shells contain approximately 12 molecules was revealed. Despite the isotropy of the first solvation shell through radial distribution analysis, multidimensional analysis showed complex local orientational order in the liquid. At smaller separations (less than 5 Å), a preference for parallel displaced geometry of nearest neighbours was revealed, while at larger separations, the favoured geometry
was perpendicular with a benzene molecule directing two hydrogen atoms toward its neighbour’s aromatic C–C bonds. The findings allowed key questions concerning the nature of aromatic $\pi - \pi$ interactions in benzene to be addressed.

Of most relevance to the work herein are molecular liquids. In the case of simple cyclic and aromatic hydrocarbons, such as toluene, cyclohexane, cyclohexene, methylcyclohexane, pyridine and naphthalene\[22, 24, 25\], the findings have typically revealed two structural motifs: parallel approaches (at slightly closer distances) and perpendicular approaches. The parallel approaches at smaller separations are understood to result from aromatic ring interactions, since the highest proportion is found for benzene and naphthalene\[22, 25\]. Non-aromatic systems, such as cyclohexane and cyclohexene\[24\], have even lower proportion of parallel-arranged nearest neighbours. Introducing a methyl group, as is the case for toluene\[22\] and methylcyclohexane\[24\], also reduces the incidence of parallel arrangement. Adding a nitrogen heteroatom to the benzene ring, as in the case of pyridine\[25\], does not significantly alter the proportion of parallel approaches.

Neutron scattering in conjunction with molecular modelling have also been used to examine inter-molecular approaches in concentrated solvent mixtures and solutions\[8, 12, 28–33\].
2.3 On Interactions Within Liquids

The physical properties of liquids are all related to the strength of interactions between the molecules. These are known as *intermolecular* interactions and they exist between molecules. Unlike *intramolecular* interactions, such as covalent bonding, which occur between atoms within a molecule. Intermolecular forces are longer-ranged and characterised by an inverse dependence on the intermolecular distance, as opposed to the much faster exponential decay of the interactions due to wave-function overlap as in quantum mechanics. Based on their physical origin, these long-range interactions can be divided into electrostatic interactions, and van der Waals interactions (comprising Keesom, induction and dispersion interactions). While electrostatic and Keesom interactions can be described by classical mechanics, induction and dispersion interactions require quantum-theoretical considerations. In what follows, a brief description of these intermolecular interactions is given. An exhaustive and comprehensive account of these forces and interactions can be found elsewhere[34, 35].

2.3.1 The Electrostatic Interaction

The Coulomb force is the electrostatic force between any two charges. An electric field, \( E \), at a distance \( r \) away from some charge, \( Q_1 \), acting on another charge, \( Q_2 \), gives rise to the Coulomb force, given by \( F(r) \propto \frac{Q_1 Q_2}{r^2} \). Depending on the sign of the charges, i.e. positive or negative, the Coulomb force can be either attractive or repulsive. The Coulomb interaction follows an inverse square force-law and is of long-range. It is very strong though it is weakened in media of high \( \varepsilon \).

2.3.2 Ion-Dipole Interaction

Differences in the electronegativities of constituent atoms in a molecule cause uneven charge distribution across the molecule and lead to a molecule possessing a net dipole moment. These molecules are termed polar, or can sometimes be dipolar if they possess a permanent dipole moment. The dipole moment for two opposite charges a distance \( l \) apart, is given by \( \mu = q \cdot l \), in units of coulomb metres (C \( \cdot m \)) or Debye (D). Water, which
2.3. On Interactions Within Liquids

Figure 2.5: (a) The difference in electronegativities of oxygen and hydrogen atoms in water leading to a dipole moment (b) A schematic showing a charge $Q$ at a distance $r$ from the centre of a polar molecule with some dipole moment, $u$. $E_Q$ are the fields the ion and $E_u$ is the field of the dipole acting on the charge.

has $\mu = 1.84 \, D$, is an example of dipole: oxygen is more electronegative than hydrogen so the side of the molecule with the oxygen atom has a partial negative charge, as shown in Figure 2.5(b).

2.3.3 van der Waals (vdW) Interactions

A dipole possesses an electrostatic self energy, given as the sum of the energies of the two charges $\pm q$ at infinity, plus the Coulomb energy of bringing the two charges together to form it. This self energy is dependent on the dielectric constant of the medium, $\varepsilon$. Thus, the solubility of polar molecules in different solvents is expected to increase with their value of $\varepsilon$. However, while this is generally the case, exceptions exist since in some cases large energy terms arising from non-electrostatic solute-solvent interactions can dominate. These are known collectively as van der Waals interactions and are described in the following.
2.3. On Interactions Within Liquids

Dipole-Dipole Interactions (Keesom)

When two polar molecules are near each other, a dipole-dipole interaction can exist between them that is similar to the interaction between two magnets. The two dipoles will arrange themselves in either an anti-parallel arrangement or a head-to-tail, as shown in Figure 2.5(c). Since most polar molecules are anisotropic in shape (i.e. longer along the direction of the dipole), the centres of two such shaped molecules can come significantly close together when they align inline, thereby making the anti-parallel interaction more favourable. This statistically favoured orientational arrangement thus leads to an overall net attraction.

The interactions of (freely-rotating) dipoles in a bulk solution is given by a Boltzmann-averaged dipole/dipole interaction, termed the Keesom (or orientational) interaction, after Willem H. Keesom who first developed its mathematical description in 1921[36]. Dipole–dipole interactions have a huge impact on living organisms as they influence most processes of protein formation, from folding to binding[37, 38]. Though the dipole-dipole interaction is not as strong as charge-charge or ion-dipole interactions, in systems where molecules possess a large dipole moment, dipole-dipole interactions can cause strong mutual alignment of molecules and lead to short-range associations in the liquid.

Dipole–Induced Dipole Interaction (Induction)

In some instances, the dipole of a molecule possessing a permanent dipole moment can induce a dipole moment in a neighbouring molecule. The apolar molecule experiences an “induction” of the permanent dipole. The induced dipole moment scales with its electronic polarisability, α. This dipole–induced-dipole energy of interaction is often termed the induction interaction, or in some cases the Debye interaction, after Peter Debye. Induction interactions are always attractive and although induction forces are extremely small compared to dipole–dipole interactions, they cannot be ignored. Induction interactions are of huge importance when studying solutions of dipolar or ionic compounds in nonpolar solvents, particularly on introducing an ion into the neighbourhood of an uncharged, apolar molecule, as it will distort the molecule’s electron cloud.
Dispersion Interactions

Dispersion forces, also called London forces after Fritz London who first coined the attractive effect in 1930, are universal for all atoms and molecules. Even though dispersion is the weakest intermolecular force, it alone is responsible for the aggregation of molecules which possess neither free charges nor dipole moments. Dispersion is quantum mechanical in nature. Its origin can be understood simply by considering an uncharged nonpolar atom, comprising a positively charged nucleus around which electrons circulate at high frequencies. On average, the (time-average) dipole moment of this atom is zero, but the positions of electrons around the nuclear protons can give rise an instantaneous dipole, with a finite dipole moment. The electric field of this dipole can polarise a nearby atom, inducing a dipole moment in it. Since attractive orientations have higher probabilities than repulsive ones, this leads to a net attractive force.

The dispersion force is thus dependent on the electronic polarisability, $\alpha$, of molecules too. Since $\alpha$ is related to the molar refraction and the index of refraction[39], liquids with a large index of refraction typically have stronger dispersion forces. For instance, solvents with high polarisability are often good solvators of anions which also possess higher polarisabilities. Due to the greater polarisability of p-electrons, very strong dispersion forces exist between molecules with conjugated p-electron systems such as aromatic hydrocarbons; the crucial role of intermolecular dispersion interactions in reactions between aromatic moieties has recently been experimentally demonstrated[22, 25].

Combined vdW interaction

Together, Keesom, induction, and dispersion interactions are refereed to as the van der Waal interaction, given by:

$$U_{vdW} = U_{Keesom} + U_{Induction} + U_{Dispersion}$$

$$= -\frac{C_{Keesom}}{r^6} + -\frac{C_{Induction}}{r^6} + -\frac{C_{Dispersion}}{r^6}$$

$$= -\frac{C_{vdW}}{r^6}.$$
In simulations of atoms or molecules, these vdW interactions between pairs of atoms or molecules are approximated through interatomic potentials. Several types of potentials of increasing complexities exist; more details on these can be found here[34]. One commonly used potential is the Lennard-Jones (LJ) potential, which will be described in greater detail in Chapter 3.

2.3.4 Hydrogen Bonding

The moments of certain bonds, such as O\textsuperscript{−}–H\textsuperscript{+}, N\textsuperscript{−}–H\textsuperscript{+} and F\textsuperscript{−}–H\textsuperscript{+} for example, are very large, and since the electron-depleted H atom is small, electronegative atoms can get quite close to these highly polar X–H\textsuperscript{+} groups and experience a strong field. This results in what is known as a hydrogen bond (h-bond) – a strong type of directional dipole-dipole interaction.

Originally believed to be predominantly electrostatic[40] with only small charge transfer and polarisation contributions, the h-bond is now commonly accepted as a complex phenomenon that is partially electrostatic and partially covalent[41]. H-bonding is typically mediated by a relatively strong force of attraction between molecules, which can often orient neighbouring molecules in solid, liquid and gaseous states. In bulk water, for example, h-bonding leads to molecules being connected in a 3D network. Considerable energy is required to break h-bonds, which explains the exceptionally high boiling points of compounds like water, or hydrogen fluoride (HF), compared to other small molecules with a similar molecular weight.

Just as covalent bonds can vary in strength, the h-bond can be strong and weak. Weak h-bonding has been a subject of much research and scrutiny over recent years. The debate stems largely from the various definitions given for a hydrogen bonds, which has been extensively studied and documented since the early twentieth century. The original definition was given by Linus Pauling in 1939 as:

“Under certain conditions, an atom of hydrogen is attracted by rather strong forces to two atoms instead of only one, so that it may be considered to be acting as a bond between them” [42]
– L. Pauling (1939)
which, 20 years later, was altered, in light of experimental data and relevant theoretical interpretations, to:

“A hydrogen bond is said to exist when (1) there is evidence of a bond, and (2) there is evidence that this bond sterically involves a hydrogen atom already bonded to another atom”[43]
– Pimentel and McClellan (1960).

In 1993, the definition was generalised to

“Any cohesive interaction where H carries a positive charge and the acceptor atom a negative charge (partial or full), and the charge on H is more positive than the D atom” [44]
– Steiner and Saenger (1993)

as a result of neutron diffraction experiments that found that C–H donors could participate in the coordination of water molecules in the same way, and with the same functionality, as OH and NH [44].

The abundance of research over the decades and lack of consensus regarding the terminology and the fundamentals of the h-bonding interaction drove the International Union of Pure and Applied Chemistry (IUPAC) federation to attempt to unify the language and terminology by which h-bonds are defined [41]. Using crystallographic data, the physical forces that drive h-bonding were analysed broadly according to their relevance and magnitude and the geometric characterisation of the hydrogen bond focused bond distances, angles and energies characteristic of h-bonding.

In their most recent report, IUPAC defined a hydrogen bond as:

“An attractive interaction between a H atom from a molecular fragment D–H, in which D is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation” [41]
– IUPAC (2011)
and gave a list of criteria for a H-bond, D–H - - - A (as illustrated in Figure 2.6), as follows:

- The forces involved in the formation of a hydrogen bond include those of an electrostatic origin, those arising from charge transfer between the donor and acceptor leading to partial covalent bond formation between H and A, and those originating from dispersion.

- The atoms D and H are covalently bonded to one another and the D–H bond is polarised, the H - - - A bond strength increasing with the increase in electronegativity of D.

- The D–H - - - A angle, $\alpha$, tends toward 180° and should preferably be above 110°. The closer the angle is to 180°, the stronger is the hydrogen bond and the shorter is the H - - - A distance.

- The length of the D–H bond usually increases on hydrogen bond formation (characterised by bond stretching). The greater the lengthening of the D–H bond, the stronger the H - - - A bond.

Figure 2.6: Schematic of a hydrogen bond between donor (D) and acceptor (A) groups.

The IUPAC efforts clearly demonstrate the importance and intricacy of this topic. Today, a growing body of experimental and theoretical evidence confirms that weak hydrogen bonds like C–H - - - O play distinctive roles in structural chemistry and biology, particularly in determining molecular and supramolecular architectures[45].
2.4 On Single-Walled Carbon Nanotubes (SWCNTs)

2.4.1 History of SWCNTs

Historically, carbon was known to exist in three macroscopic forms: graphite, diamond and amorphous carbon (non-crystalline) carbon. “Nano” forms of carbon only became recognised as a new branch of carbonaceous materials after the Nobel prize winning discovery of buckminsterfullerene ($C_{60}$) in 1985 by Harry Kroto et al.\[46\]. The discovery was rapidly followed by advancements in fullerene synthesis, which later led to the discovery of single-walled carbon nanotubes (SWCNTs). Although there are claims of earlier reports of a tubular carbon material, the identification of carbon nanotubes is attributed to Iijima et al.\[47\]. While long postulated, pristine graphene layers were not synthesised until 2004, when physicists Andre Geim and Konstantin Novoselov managed to removed some flakes from a lump of bulk graphite with sticky tape. By repeatedly separating the graphite fragments, the pair created virtually defect-free flakes which were just one atom thick.

Geim and Novoselov’s Nobel prize winning and pioneering work formed a rich field in the study of 2D materials\[48, 49\]. Fascination with nanomaterials as a whole stems from the remarkable physical properties and the potential applications that these properties offer for the future. Despite the numerous forms of nano carbon, this project is only concerned with SWCNTs. As such, in what follows, focus will be chiefly on the structure and property of this carbon allotrope.

2.4.2 Geometry of SWCNTs

The simplest way to picture the structure of a SWCNT is to imagine a sheet of graphene rolled into a tube. Graphene is an infinite sheet of $sp^2$ hybridised carbon atoms which forms a planar, two dimensional (2D) structure. This sheet can be described as a 2D crystal, with a hexagonal lattice consisting of two triangular sub-lattices as shown in Figure 2.7(a). When wrapped along one if its lattice vectors, a seamless cylinder forms. The angle of the wrapping dictates what is known as the chirality of the
2.4. On Single-Walled Carbon Nanotubes (SWCNTs)

SWCNT, and the circumferential wrapping length defines its **diameter**. These are the defining characteristics of SWCNTs, from which the **unit cell** can then be determined.

**Chirality**

A SWCNT can be specified by the chiral vector, $C_h$:

$$C_h = n\mathbf{a}_1 + m\mathbf{a}_2 = (n,m)$$  \hspace{1cm} (2.6)

described by indices $(n,m)$ that denote the number of unit vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ in the honeycomb lattice contained in the vector, as shown in Figure 2.7(a). These unit vectors, $\mathbf{a}_1$ and $\mathbf{a}_2$ are defined as:

$$\mathbf{a}_{1,2} = \left( \frac{3}{2}a_{c-c}, \pm \frac{\sqrt{3}}{2}a_{c-c} \right) = \left( \frac{\sqrt{3}}{2}, \pm \frac{1}{2} \right) a$$  \hspace{1cm} (2.7)

where $a_{c-c}$ is the carbon nearest-neighbour distance and $a = \|\mathbf{a}_1\| = \|\mathbf{a}_2\| = \sqrt{3}a_{c-c}$.

Also labelled on Figure 2.7(a) is the chiral angle, $\theta_C$, between $C_h$ and the unit vector direction, which describes the spiral symmetry (i.e. the angle the hexagons make with respect to the nanotube’s longitudinal axis). $\theta_C$ is given by:

$$\theta_C = \arctan \left[ \frac{\frac{3\sqrt{3}}{2}m a_{c-c}}{\frac{3}{2}a_{c-c}^2(2n+m)} \right] = \arctan \left[ \frac{\sqrt{3}m}{m+2n} \right].$$  \hspace{1cm} (2.8)

Due to the symmetry of the honeycomb lattice, $\theta_C$ is confined to $0^\circ \leq \theta_C \leq 30^\circ$. Accordingly, nanotubes are classified as either axially achiral or chiral. Chiral nanotubes have a chiral angle, $\theta_C$, between 0 and $30^\circ$. Achiral SWCNTs have $\theta_C = 0^\circ$ or $30^\circ$. Achiral SWCNTs are further classified into **armchair** SWCNTs if they have $n = m$ and a chiral angle of $\theta_C = 30^\circ$, or **zigzag** SWCNTs if they have indices $(n,0)$ and a chiral angle of $\theta_C = 0^\circ$. Examples of both types of nanotubes are shown in Figure 2.7(b).
2.4. On Single-Walled Carbon Nanotubes (SWCNTs)

Figure 2.7: (a) A carbon nanotube’s unrolled honeycomb lattice. A portion of a graphene sheet can be rolled seamlessly to form a SWCNT, by connecting site O with A, and site B with B’, in this case the rectangle OABB being the unit cell of the nanotube. The chiral vector, $C_h$, is defined by the vectors OA and OB. $T$ is the translational vector of the (4,2) nanotube which would be constructed here. (b) Schematic showing the various configurations of carbon nanotubes, from left to right: an achiral armchair SWCNT, an achiral zigzag SWCNT, and a chiral SWCNT.
2.4. On Single-Walled Carbon Nanotubes (SWCNTs)

**Diameter**

The diameter of a nanotube is defined using, \( \mathbf{C}_h \), as:

\[
d_{\text{swcnt}} = \frac{\| \mathbf{C}_h \|}{\pi}
\]  
(2.9)

which, when substituting in the magnitude of \( \mathbf{C}_h \), yields the expression:

\[
d_{\text{swcnt}} = \frac{\sqrt{3}a_{c-c}}{\pi} \sqrt{n^2 + m^2 + nm}.
\]  
(2.10)

As well as its \((n,m)\) indices, a nanotube can be equivalently specified using \(d_t\) and \(\theta_C\).

**Unit Cell**

The unit cell of the nanotube is defined as the area delineated by \( \mathbf{C}_h \) and the translational vector, \( \mathbf{T} \), along the shortest repeat distance along the nanotube axis, OB, as seen in Figure 2.6(a). \( \mathbf{T} \) is defined as:

\[
\mathbf{T} = t_1 \mathbf{a}_1 + t_2 \mathbf{a}_2 \equiv (t_1, t_2),
\]  
(2.11)

where the coefficients \(t_1\) and \(t_2\) can be related to the indices, \((n,m)\), by:

\[
t_1 = \frac{2m + n}{d_R}, \quad t_2 = -\frac{2n + m}{d_R}.
\]

\(d_R\) is the greatest common divisor of \((2n + m)\) and \((2m + n)\). \( \mathbf{T} \) is orthogonal to the chiral vector. The magnitude of \( \mathbf{T} \) is given by:

\[
T = \| \mathbf{T} \| = \frac{\sqrt{3} \| \mathbf{C}_h \|}{d_R} = \frac{3a_{c-c}}{d_R} \sqrt{n^2 + m^2 + nm}.
\]  
(2.12)

The number of hexagons \(N\) in the unit cell can then be evaluated by dividing the area of the cell, \( \mathbf{C}_h \times \mathbf{T} \), by the area of a hexagon, \( \mathbf{a}_1 \times \mathbf{a}_2 \), given by:

\[
N = \frac{2(m^2 + n^2 + nm)}{d_R},
\]  
(2.13)

There are 2 carbon atoms per graphene unit cell, so for a unit cell of a SWCNT, there will be \(2N\) carbon atoms present (since the unit cell area of a nanotube is \(N\) times larger than that for a graphene layer[50]).
Table 2.1: Summary of structural properties for single-walled carbon nanotubes, showing relevant quantities and corresponding formulae.
2.4.3 Electronic Properties

Each carbon atom in a SWCNT has four valence electrons – three of these are involved in $sp^2$ hybridisation forming the C-C $\sigma$-bonds, and the fourth electron occupies a $p_z$ orbital in the form of a delocalised $\pi$ system. The $z$-axis is defined perpendicular to the rolled graphene sheet, with the $\pi$ system parallel. In-plane covalent $\sigma$ bonding and $\sigma^*$ anti-bonding determine the binding energy and elastic properties of a SWCNT, while out-of-plane orbitals that are unable to couple to the $\sigma$ states due to their opposite symmetry, interact with each other and create delocalised $\pi$ bonding and $\pi^*$ anti-bonding orbitals. The $\sigma$ electrons are responsible for the strong in-plane covalent bonding between the carbon atoms within the sheets, while the $\pi$ states are responsible for the weak interaction between carbon nanotubes.

The electronic band structure of SWCNTs is estimated from graphene’s, which is most widely described using the nearest-neighbour tight-binding model\cite{51}. Graphene is a semi-metal or zero-gap semiconductor whose valence and conduction bands touch and are degenerate at six $K$ points – positions that define the corners of the first Brillouin zone. As a 2D graphene sheet is rolled up to form a 1D tube, periodic boundary conditions are imposed by the chiral vector $C_h$ (described in Section 2.4.2 and seen in Figure 2.7). The consequent radial confinement yields allowed quantised states (or 1D sub-bands) which can be enumerated, as follows:

$$C_h \cdot k = 2\pi q$$  \hspace{1cm} (2.14)

Differences in electronic character arise as a result of these sub-bands, or ‘cutting lines’, across the Brillouin zone. If one of the sub-bands (or cutting lines) pass through a $K$ point, the energy density will contain a zero-energy band-gap and the rolled nanotube will have metallic character. Otherwise, the rolling gives rise to semiconducting SWCNT.

An illustrative example is shown in Figure 2.8, displaying the allowed sub-bands for two achiral zigzag tubes, (9,0) and (10,0). Notice that the (9,0) sub-bands contain a $K$ point while the (10,0) sub-bands don’t. In general, if $n - m$ is a multiple of 3 then the allowed $k$ states or lines intersect the $K$ and $K'$ points and the nanotube is metallic. Resultantly,
2.4. On Single-Walled Carbon Nanotubes (SWCNTs)

if \( n - m \) is not a multiple of 3 (including 0), and \( k \) states miss the \( K \) and \( K' \) points, the tube is semiconducting with a band-gap. As a consequence, 1/3 of SWCNTs are metallic and 2/3 are semiconducting.

![Diagram](image.png)

**Figure 2.8:** Schematic exemplifying the quantised 1D sub-bands for the metallic (9,0) nanotube and a semiconducting (10,0) single-walled carbon nanotube. The first Brillouion zone is defined by the white hexagon and the black dots in the corners represent the K points. Adapted with permission from [52]; Copyright 2018 American Chemical Society.

2.4.4 Applications and Challenges

**Applications**

The diverse properties of SWCNTs have enabled an array of applications. For example, metallic SWCNTs demonstrate good thermal stability, conductivity and current capacity, which have proven useful in integrated circuits[53] as well as transparent conducting films [54]. Their thermal stability has also made them useful for field emission devices[55, 56], as their high aspect ratio provides optimal geometrical field enhancement. On the other hand, the bandgaps of semiconducting SWCNTs have made them useful for photovoltaics (e.g. solar cells)[57], light emitting devices[58] and transistor devices[59, 60]. The high optical absorption across all wavelengths also make SWCNTs an ideal material for next generation optoelectronic and photonic devices[61].

Additionally, SWCNTs have exceptional mechanical strength and high thermal/electrical conductivities that make them useful in multifunctional high performance nanocomposites[62]. The intrinsic stiffness, strength and toughness of SWCNTs allow reinforcement of matrices in a classic shear-lag, Rule of Mixtures fashion to create high performance materials.
Coupled with the (di)electric, thermal, and optical properties of SWCNTs, the composites are often multifunctional.[62–65].

Finally, their high surface area (combined with electronic properties) make SWCNTs promising candidates as catalyst supports[66], preservatives[67], as well as novel energy storage devices such as lithium-ion batteries and electrochemical super-capacitors[68–71].

Challenges

Despite the wide range of potential applications, the practical application of carbon nanomaterials is limited by various challenges. First and foremost are those challenges associated with synthesis of SWCNTs. Synthesis typically leads to a mixture of diameters, lengths and helicities, leading to mixed electronic properties. Though the bulk synthesis of single chirality SWCNTs is yet to be demonstrated, post-synthetic sorting strategies have been developed[72, 73], but are difficult to scale. Research has been further impeded by the intrinsic chemistry of as-synthesised SWCNTs. Defects such as bends, vacancies, sp$^3$ sites, bond rotations and atomic substitution can arise in SWCNTs during synthesis, or post-synthesis processing, which have been shown to affect the thermoelectric properties of SWCNTs[74] and decrease their mechanical properties[75, 76]. Furthermore, various impurities, both inorganic and carbonaceous, are found in SWCNT samples, whose nature and extent are usually dictated by their synthesis route. Purification routes have been developed for the removal of these impurities, including acidic[77], gas phase[78] and electrochemical purification[79].

Another major challenge relates to the poor solubility of SWCNTs. This is due to the strong van der Waals forces acting between them that causes them aggregate into large ropes and/or bundles that can span tens of nanometers in diameter and have micrometer lengths. These bundles have inferior mechanical properties (due to weak parallel slippage akin to sliding sheets of graphite) and dramatically altered (opto)electronic properties. For this reason, and since desirable properties are associated with isolated, individual nanotubes, which are rarely available to experimentalists, the disentanglement of SWCNTs from bundles is necessary. Separating
2.4. On Single-Walled Carbon Nanotubes (SWCNTs)

SWCNTs is a non-trivial task, making this issue a serious hurdle to real applications.

2.4.5 Dispersion of SWCNTs

The homogeneous dispersion of SWCNTs is an essential first step to take advantage of the unique properties of individualised SWCNTs. After dispersion in a solvent, SWCNTs can be sheared parallel to the in-plane direction (or expanded perpendicular to the in-plane direction, i.e. by intercalation) in a scalable top-down method known as Liquid Phase Exfoliation (LPE). Dispersions and LPE have been a very active area of research for more than one decade.

As SWCNTs are insoluble or at best extremely poorly soluble in all solvents apart from chlorosulfonic acid\cite{80}, various dispersant methods have been developed to apply shear to the SWCNTs in the liquid to separate the bundles, through low shear ball-milling/shear-mixing or high shear ultrasonication, such as covalent \cite{77,81–83} and the addition of a stabilising agent (e.g. the use of surfactant\cite{84}, or DNA\cite{85}), macromolecules\cite{86,87} and acid doping\cite{88}), all of which have been successful in producing highly exfoliated systems of dispersed nanotubes. SWCNTs have been also dispersed and stabilised with the aid of specific solvents, without any additional stabilising agents. In all cases, these LPE dispersion methods lead to a significant fraction of the SWCNTs remaining in (smaller) bundles and aggregates. These remaining aggregates may then be separated using such as ultracentrifugation\cite{89} or chromatography\cite{90}, separating the dispersion consisting of a small fraction of individualised nanotubes and the bundles.

Both ultrasonication and centrifugation have low yields and are not easily scalable. Indeed, ultrasonication is itself a difficult technique to scale, limiting the industrial application of sonicated dispersions of SWCNTs. Also importantly, these shear separation techniques are known to cause significant damage to the material, (particularly sonication), reducing aspect ratios for example and introducing vacancies into the sp\(^2\) framework\cite{91}, well known to be detrimental to both mechanical and electronic properties.
2.4.6 Charging SWCNTs

Charging SWCNTs is an alternative approach that gives much higher concentrations of truly dispersed SWCNTs. By increasing the separation of the SWCNTs, charging reduces attractive vdW interactions between the tubes. It is worth noting however that the overall bonding in the lattice is increased since electrostatic interactions gluing the ions (SWCNTs and metals) are stronger than vdW interactions. The charging facilitates dissolution, purification, separation, chemical modification, and assembly. All stable alkali metals have been shown to be capable of forming nanotubide intercalants[92].

Charging is typically achieved chemically either i) by direct metal intercalation (wherein the metal is added as a plasma, a liquid, a vapour or eutectic mixtures thereof), or ii) via solvated reductant routes (such as Birch reductions or single electron transfer agents in coordinating solvents). Birch reduction routes do not require the low pressures and high temperatures that are typically needed for direct metal intercalation. Alternative routes to the reduction of carbon nanomaterials do exist, for example electrochemical charging[93].

Of most relevance to the work within this thesis are negatively charged SWCNTs, termed nanotubides, or nanotubide salts[79, 94]. These are the product of SWCNT reduction. Reduced SWCNTs have been shown to exhibit nematic liquid crystal behaviour when dispersed with a crown ether solution[95]. Unlike metastable dispersions, nanotubide salts have been found to spontaneously dissolve in solvents to form true solutions (i.e. thermodynamically stable). This is unlike a dispersant phase, where the free energy of the aggregated state (i.e. SWCNT bundle and unassociated bulk solvent) is lower than that of the dispersion.

The spontaneous dissolution of nanotubides was first achieved by Penicaud et al. in 2005[96]. In 2012, Fogden et al. again demonstrated solvation of carbon nanotubes and subsequent spontaneous dissolution in DMF. This route has achieved high SWCNT dispersion concentrations[95, 97, 98] now being used for the manufacture of macroscopic materials, such as fibres and sheets[95]. The benefits of spontaneous dissolution as a method for liquid exfoliation are clear: the dissolution process is simple
to implement, it is intrinsically scalable, and it results in stable solutions
of pristine nanotubes with well-defined functional properties.

In this work, nanotubide salts were formed using Birch reduction
via liquid ammonia. Liquid ammonia is an ionising solvent which can
dissolve an alkali metal to form a strong reducing agent solution, with the
formed solvated electrons capable of reducing nanotubes. The experimental
method for preparation of the nanotubide salt via the ammoniation scheme
is shown in Figure 2.9 and proceeds as follows. First, a metal (in this
case, sodium) is added to a pre-weighed amount of SWCNT powder in a
reaction tube under argon atmosphere. Liquid ammonia is condensed onto
the mixture and the initially colourless liquid ammonia turns blue, due
to the dissolution of the metal and the concomitant $1s > 2p$ transition of
solvated electrons[80]. Without stirring or agitation, the SWCNT powder
swells and the solution gradually changes from blue to clear to black, as
the nanotubes accept the solvated electrons, spontaneously de-bundle, and
dissolve into the liquid ammonia.

**Figure 2.9:** Liquid ammonia reduction of SWCNTs. The process scheme
includes first the reduction of SWCNTs, their solvation in ammonia, and the
subsequent dissolution in sodium-ammonia solutions. The process scheme
is illustrated by photographs of relevant phases. Re-used with permission
from [79]; Copyright 2018 American Chemical Society.
2.4.7 Suitable Solvents for SWCNT Solubilisation

The effectiveness of LPE is critically dependent on the quality of the dispersions and therefore on the choice of solvent[99, 100]. Metastable dispersions have been demonstrated in a range of common solvents, and several systematic investigations of solvent success reported in the literature[79, 101–107]. On the whole though, a few solvents have been much more effective than others at forming stable dispersions of SWCNTs. Amongst those, amides including N-methyl-2-pyrrolidone (NMP) and dimethylformamide (DMF) have been most commonly used. NMP, in particular, has been unrivalled. Dispersion and exfoliation of nanotubes has been in structural analogues of NMP too, such as N-benzylpiperidine (NBenP) and N-cyclohexyl-2-pyrrolidone (CHP)[108].

In the case of nanotubides, solvents are often the same as those used for pristine SWCNTs, and also include NMP and DMF. Dimethyl sulfoxide (DMSO) too is routinely used as a dispersant solvent, but questions have been raised about its stability with nanotubides as it has been proposed that methylation of the SWCNT at the expense of charge is a contributing factor for solubility[109]. Though less commonly used, DMA has also proven an ability to disperse nanotubes with exceptionally high stabilities[103, 110].
2.5 Understanding SWCNTs in Solution

2.5.1 Dissolution at the Nanoscale

Understanding interactions between nanoparticles in liquid media is crucial and our lack of knowledge of these is an underlying problem in the processing of all low-dimensional nanomaterials, for they play a critical role in dispersion, dissolution, exfoliation – steps that are crucial for the production of individualised nanospecies with which desirable properties are associated. Traditionally, interactions of micron-sized particles are approximated by Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (discussed in the next section), which treats colloid stability in terms of a balance of attractive van der Waals forces and repulsive electrostatic forces. However, the structural uniqueness and discreteness of nanoparticles add an element of complexity compared to micron scale particles, that even adaptations of these classical theories have had little general applicability for nanoparticle systems. Essential distinctions between nanoparticles and microparticles result from their size difference of one to five orders of magnitude. Figure 2.10 attempts to illustrate this distinction. The crystallinity of a nanoparticle’s core diversifies the possible shapes they can have, and unlike small ions or larger particles/colloids, nanoparticles comprise structural elements (such as adsorbed or functionalised species) that are of comparable size to that of the surrounding media. This size similarity gives rise to ion-specific effects, enhanced nanoparticle anisometry, and collective effects at the molecular, atomic and nanoscale, all of which lead to strongly coupled dynamics.

Figure 2.10: Schematic of hydrated ions, a nanoparticle, and a micron size particle, illustrating the structural uniqueness and discreteness of NPs. Obtained from [5] and used with permission from AAAS.
While DLVO theory can provide an adequate description for particles sized 50 nm and larger[112, 113], many deviations arise as the particles become smaller. These deviations had actually been noted since the 1970s, for example when it was reported that classical treatment of inter-particle forces incorrectly predicts coagulation in nanoscale silica. Since then, various other studies [1–4] have established that stability of nanoparticle dispersions under different media conditions is indeed atypical, unusual and distinct to colloidal stability in micron-scale systems. For example, while ionic strength of species is widely used to disperse or drive the crystallisation of the suspended particles via electrostatics, a lack of a correlation was observed between charge (or ionic strength) and stability of dispersions in the cases of 4 nm capped zinc oxide nanoparticles[114] and 2.3 nm capped gold nanoparticles [115]. These non-classical findings were in direct contrast to the body of knowledge accumulated for micro-particles and were rationalised by proposals of preferential absorption of solvent at the nanoparticle interface, specific packing of the interfacial layer, steric effects of the surface layer, and necessitated the incorporation of additional terms such as osmotic and elastic potentials to the total potential[2, 116, 117].

Furthermore, in the case of gold nanoparticles for example, non-classical behaviour was observed in phase transitions. Reversible recrystallisation from an disordered solid to a highly ordered superlattice occurred upon heating[118], contrary to what is expected according to classical thermodynamics (i.e. an increase in degree of ordering upon cooling).

The problem lies in the inconsistency built into the theory, which separates forces between particles into electrostatic and van der Waals forces, handled by a nonlinear Poisson-Boltzmann (PB) description[119] and a linear Lifschitz theory[120], respectively. Although the linearised PB equation of point-like ions though has been demonstrated to be reliable down to distances of about 5 nm[3], it is known to neglect ion correlations and excluded volume of ions[121, 122] and polarisation effects[123], known to play a fundamental role in interesting phenomena such as like-charge attraction[124] and be of huge relevance in the presence of dielectric discontinuities and multivalent ions[125]. Though there have been many improvements to DLVO theory, such as ion fluctuation forces[126] and
the charge regulation in the double layer[127], the theory remained unchallenged for over half a century.

More recently, it was noted that local solvent ordering effects become increasingly important upon reduced particle dimensions. Crucially, in this regime, the solvent can no longer be considered as a uniform density continuum described by a single dielectric constant as approximated in DLVO. Advanced neutron scattering methods used to measure the arrangement of the solvating ammonia molecules around fulleride ions [7], for example, found that the solvent’s coordination shells were up to four times the density of the bulk solvent. In the case of fulleride dispersions, the polar moment of the solvating ammonia molecules did not point toward the fulleride anions, but rather tangentially with only one hydrogen atom per ammonia molecule directed to the fullerides[7, 8]. This counterintuitive arrangement enables the ammonia molecules within the solvation shells to maintain the hydrogen-bonding arrangement found in bulk ammonia[8]. Dense solvation shells have been measured for a range of other nanoparticles in different solvents too[6]. In aqueous solutions of NaCl and KCl salts for example, the structure of water was found to be modified by the metal ions, while hydrogen bonding between water molecules remained intact[9]. Other hydrated ion structure investigations have found that cation hydration is templated in solvation shells of water oxygen and hydrogen correlations out to four layers from the ions[12]. Molecular ordering has also been reported in ionic liquid assemblies, such as the layer found at sapphire surfaces for example[10]. More recently, atomistic simulations of metal oxide nanoparticles in water[13] found highly ordered layers of water were found at the interface. The structure of water was found to be strongly influenced by the crystal structure and morphology of the nanoparticles. Other studies on the water solvation of silver nanoparticles have also reported modification of the structure of water by the silver particles[11]. Many factors associated with the local solvent ordering, such as steric effects, hydrogen bonding, and charge-screening have therefore been shown to be intrinsically interlinked, re-emphasizing the ineffectiveness of classical models, such as DVLO and OM for understanding nanoparticle solutions.
These atomistically resolved measurements, coupled with atomic simulations of interactions, have been crucial in shedding light on the mechanisms for nanoscale dissolution and as these tools evolve, it is becoming possible to accurately examine nanoscale interactions. This is the crux of the second part of this thesis (Chapter 6) which explores these phenomena that have been rarely studied, particularly in the case of one-dimensional carbon nanotubes.

2.5.2 DLVO and Polyelectrolyte Theories

The Electrical Double Layer

Classical DLVO theory predicts that short-range van der Waals attractions overcome the highly screened electrostatic repulsion between like-charged colloids, thus inducing their coagulation. The solubility of nanoparticles (including SWCNTs and nanotubides) is typically modelled using adaptations of DLVO colloid theory, whereby coagulation or agglomeration is avoided through the formation of an “electric double-layer” which surrounds their charged surface. The electric double layer comprises two parallel layers of charge surrounding a charged particle’s surface, as shown in Figure 2.11. A *Stern layer* comprises counter-ions that are attracted and closely attached to the surface of the nanotube. This layer electrically screens the surface charge. The second layer is an adjacent film of the dispersion medium (i.e. the solvent) known as the *diffuse layer*, or the Gouy-Chapman layer, containing loosely-bound “free ions”. These layers result in a charge field which dissipates at increasing distances from the colloid, as in the schematic in Figure 2.11.

For two nanotubes, the repulsive potential is of the general form:

\[
V_{\text{electrostatic}}(r) = Ce^{-\kappa r}
\]

where \( r \) is the distance between two nanotubes, \( C \) is a constant which depends on the the zeta potential, \( \zeta \), and geometric properties, and \( \kappa^{-1} \) is the Debye length, \( \lambda_D \), given by:

\[
\lambda_D = \left( \frac{\varepsilon_0 \varepsilon_r k_B T}{2N_A e^2 I} \right)^{\frac{1}{2}}
\]
2.5. Understanding SWCNTs in Solution

where, \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon_r \) is the dielectric constant, \( k_B \) is the Boltzmann’s constant, \( T \) is the Temperature, \( N_A \) is Avogadro’s Number, \( e \) is the elementary charge and \( I \) is the ionic strength of the electrolyte, given by the sum of the product of the molar concentration of ions and their respective charge (i.e. \( \frac{1}{2} \sum^n c_i z_i^2 \)), taken over all ions in the solution. For a 1:1 electrolyte such as sodium chloride, where each ion is singly-charged, the ionic strength is equal to the concentration. \( V_{\text{electrostatic}} \) is usually obtained using the mean-field Poisson-Boltzmann (PB) formalism[119].

![Diagram](image)

**Figure 2.11:** A schematic diagram showing an electric double layer formation in a liquid at contact with a negatively-charged particle. The electrical potential within the electric double layer has the maximum value on the particle surface (i.e. the Stern layer). The potential drops with increasing distance from the surface, approaching zero at the boundary.

The attractive vdW potential, \( V_{\text{vdW}}(r) \), was shown by McLachlan to be proportional to the Hamaker constant, \( A \), defined as:

\[
A = \frac{3I}{16\sqrt{2} (n_{\text{solute}}^2 + n_{\text{solvent}}^2)^2} \left( n_{\text{solute}}^2 - n_{\text{solvent}}^2 \right)^2
\]

and \( n \) is the refractive index. From the equations above, one can appreciate that as the refractive indices of the solute and the solvent approach one another, \( V(r) \) approaches zero. For this reason, matching these so-called ‘solubility parameters’ would mean zero attractive potential, no solute
aggregation and thus lead to solubilisation. This is the basis of “like dissolves like” rule.

The Oosawa-Manning (OM) model

When the colloid is a polyelectrolyte, and it is placed in a solvent, the DLVO model can be expanded by incorporating polyelectrolyte counter-ion condensation as modelled by Oosawa and Manning[128, 129]. In the OM model, a polyelectrolyte in solution would dissociate into a polyion and solvated counter-ions. Post dissociation, the charge on the polyion replaces the potential difference from colloid/electrolyte interactions (as modelled in DVLO theory). At high concentrations of charge, counter-ions from the electrolyte condense onto (the Helmholtz layer of) the polyelectrolyte. The condensation will occur until the distances between the unscreened charges on the polyion decreases to match the separation of two like-charges in the solvent from purely thermal effects. This distance is known as the Bjerrum length, \( l_B \), given by:

\[
l_B = \frac{e^2}{4\pi \varepsilon_{\text{solvent}} \varepsilon_0 k_B T} \quad (2.17)
\]

where \( e \) is the elementary charge, \( \varepsilon_{\text{solvent}} \) is the solvent dielectric constant, \( \varepsilon_0 \) is the permittivity of free space, \( k_B \) is the Boltzmann constant, and \( T \) is the absolute temperature. The Bjerrum length can be decreased by increasing temperature or selecting a solvent with a higher dielectric constant, and is related to the Debye length via:

\[
\lambda_D = \frac{1}{\sqrt{8\pi l_B I}}. \quad (2.18)
\]

In water at room temperature, \( l_B = 0.7 \) nm, that is a few molecular lengths, so mean-field theories can be used to describe the diffuse part of the double layer at low salt concentrations when the Debye length greatly exceeds the Bjerrum length. It is only under this condition, i.e. \( \lambda_D \gg l_B \), that it is justified to use a mean-field theory for the diffuse part of the double layer.
Application of DLVO to SWCNTs

The application of DLVO/OM theory to charged carbon nanomaterials and solutions thereof was pioneered by Penicaud[96, 97]. Though the one-dimensional character of SWCNTs allows them to be considered as “rigid” polyelectrolytes, charge is found to be delocalised over a $\pi$-cloud rather than localised on specific groups. This translates into a continuum of various possible locations along the surface onto which counter-ions can condense. It is also worth noting that SWCNTs do not act as infinitely thin chains, and diameter effects are known to play an important factor for nanotubide dissolution [94, 130]. Thus, they are instead treated as surfaces with uniform charge density. Condensation thus occurs when the distance between unshielded charges on the nanotube surface is smaller than the distance within the solvent at which the interaction of like charges is comparable to $kT$ – the so-called Bjerrum length, $l_B$.

More recently, to better understand the mechanisms of induced colloidal stability, a theoretical framework which combines coarse-grained Molecular Dynamics simulations with DLVO theory and Langmuir isotherm was developed[131]. The framework was used to describe the adsorption density as a function of surfactant concentration and the curvature of SWCNTs (and graphene[132, 133]). Using a modified DLVO theory of colloidal stability, the authors successfully modelled the surface electric potential, the intertube potential energy profile, and the energy barrier height.

2.5.3 The Breakdown of DLVO-OM

The main key assumptions of DLVO theory that are often applicable at macro- and micro- dimensions but no longer valid when particles reach nanoscale size are summarised here:

Treating the intervening liquid medium simply as a structureless continuum: In any system where the dimensions of the nanoparticle are comparable to the dimensions of solvent molecules or solvated ions, nanoparticles and the surrounding medium must be treated as two distinct and discrete entities. Media outside and inside of the nanoparticle can no longer be assumed as uniform continua either. Interfacial layers between a nanoparticle and the surrounding medium
can often have a thickness comparable to, or sometimes even greater than, the diameter of the nanoparticle’s cores, which means local atomic polarisability must be taken into account as opposed to a classical continuous dielectric function.

**Finite size consequences at nanoscale dimensions:** Though modelling counter-ions as point charges is usually appropriate for simple (small) cations, nano-species cannot be treated as point particles. As nanoparticle diameters reach 1 nm for example, it becomes comparable to or smaller than the Bjerrum length, at which separation the energy of electrostatic interactions between ions is equal to the thermal energy, \( k_B T \), in the media. Furthermore, DLVO and OM models also fail to address the steric effects of bulky counter-ions, where condensation to the Helmholtz layer can be sterically hindered, leading to notable consequences on the system[95].

**Additivity of particle interactions:** DLVO-based models assume that the total potential is a sum of multiple independent repulsive and attractive components as in DLVO theory, that is, \( V(r) = V_{vdW} + V_{electrostatic} + V' \) where \( V' \) represents other interactions. This is referred to as the additivity approximation, which fails to capture non-additive nature of the “solvation” force. It also fails as the size of the particles and the distances between them reach nanoscale dimensions. The problem is exacerbated when systems comprise metals of high polarisabilities that increasing the coupling between different interactions.

### 2.5.4 Thermodynamic Considerations

**Gibbs Free Energy**

In general, a substance is said to be soluble in a given solvent if the Gibbs free energy of mixing, \( \Delta G_{mix} \), for the solute-solvent mixture is negative. At constant temperature and pressure, all systems tend towards the minimum possible Gibbs free energy. \( \Delta G_{mix} \) has both enthalpic and entropic components, given by:

\[
\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}
\]
where:

- $\Delta H_{\text{mix}}$ is the enthalpy of mixing, given by:

$$
\Delta H = \Delta U + p \Delta V
$$

comprising a system’s internal energy, $\Delta U$, plus the amount of work required to accommodate the system by displacing the environment in order to establish the required pressure, $p$, and change in volume $\Delta V$.

The total enthalpy of a system cannot be measured directly: only a change in enthalpy relative to a defined reference point carries any physical meaning, e.g. $\Delta H$ is negative in exothermic (heat-releasing) processes and positive in endothermic (heat-absorbing) reactions.

- $T$ is the temperature; and

- $\Delta S_{\text{mix}}$ is the entropy of mixing per unit volume, and is defined as:

$$
\Delta S = k_B \ln \Omega
$$

where $\Omega$ is the number of a system’s possible microscopic configurations (or micro-state), and $k_B$ is the Boltzmann constant.

A negative $\Delta G_{\text{mix}}$ typically necessitates a large and positive $\Delta S_{\text{mix}}$. However, due to their large size and considerable rigidity, SWCNTs act as rigid rods, that consequently do not gain much translational or rotational freedom upon dissolution (unlike for example flexible polymers), and thus have relatively small $\Delta S$. In most cases, $\Delta S_{\text{mix}}$ is too small (or not large enough) to compensate for the often unfavourable enthalpic mixing contribution, which is reason why SWCNTs are not soluble. For this reason, the entropy term cannot be relied upon to minimise $\Delta G_{\text{mix}}$. Thus, for nanotubes to be soluble in a given solvent, $\Delta H_{\text{mix}}$, needs to be small or negative.
Hildebrand and Hansen Solubility Parameter

The concept of the solubility parameter was first proposed by Hildebrand[134], which defined a single solubility parameter, $\delta$, in terms of the total cohesive energy density of a solvent:

$$\delta = \sqrt{\frac{E}{V_m}} \quad (2.22)$$

where $E$ is the energy of vaporisation and $V_m$ is the molar volume of the solvent. $\delta$ provided a simple qualitative measure of solubility behaviour based on the principle of “like-dissolves-like”, implying that polar substances can readily mix with other polar substances, and similarly for apolar ones, but polar and apolar would separate and tend to stay isolated from one another. Of course, this theory is not applicable universally and our understanding of this so-called hydrophobic effect is still lacking today, despite it being a fundamental physical process and its importance as the primary building block of much of chemistry, as it dictates which solvent can dissolve which solutes.

The solubility parameters are related to the enthalpy term, $\Delta H_{mix}$, by:

$$\Delta H_{mix} = \chi \phi (1 - \phi) \frac{kT}{\nu_0} \quad (2.23)$$

where $\phi$ is the nanotube volume fraction, $\nu_0$ is the solvent molecular volume, and $\chi$ is the Flory-Huggins parameter, given by:

$$\chi \approx \frac{\nu_0}{kT} (\delta_{solute} - \delta_{solvent})^2. \quad (2.24)$$

From Eq.’s (2.23) and (2.24), the Hildebrand–Scratchard expression:

$$\Delta H_{mix} \approx (\delta_{solute} - \delta_{solvent})^2 \phi (1 - \phi) \quad (2.25)$$

can be derived, where $\delta_{solute}^H$ and $\delta_{solvent}^H$ are known as the Hildebrand solubility parameters. It is clear from Eq. (2.23) that the smaller $\chi$ is, the smaller the enthalpy of mixing per unit volume of solvent (and therefore the more favourable mixing is). Thus, the magnitude and sign of $\chi$, which is dependent on the Hildebrand solubility parameters $\delta_{solute}$ and $\delta_{solvent}$, can be predictive of solubility.

Charles Hansen improved Hildebrand’s theory by partitioning the the
total internal cohesive solvent forces into dispersive, polar, and hydrogen bonding interactions\cite{135}, represented by three parameters are $\delta_D$, $\delta_P$ and $\delta_H$, that satisfy the relationship:

\[(\delta_{\text{Hildebrand}})^2 = \delta_P^2 + \delta_D^2 + \delta_H^2, \tag{2.26}\]

where the $\delta_P$ parameter accounts for permanent dipole-permanent dipole forces, the $\delta_D$ parameter accounts for non-specific intermolecular interactions related to dispersion forces, and $\delta_H$ accounts for specific intermolecular interactions such charge-transfer interactions, electron interactions, and hydrogen bonding. The solubility of a molecule X in a solvent Y in the Hansen formalism is correlated with an “interaction distance” between their respective sets of Hansen parameters. Minimisation of this distance is equivalent to minimising the free energy penalty for substituting molecule X with one of Y. In order to minimise $\Delta H_{\text{mix}}$, a solute and a solvent with similar Hansen parameters are required. Values for the Hansen parameters of many solvents are known in the literature\cite{135}.

While Hildebrand solubility parameters were only applicable for nonpolar systems, Hansen solubility parameters allowed more precise exploration of the nature of the exfoliation process as they were used as a framework for interpreting intermolecular force components in terms of their contributions to the cohesive energy of materials and their solutions. However, Hansen parameters are still not efficient for predicting good solvents\cite{101–103, 105, 106}. The approach has only been partially successful; for example, there are solvents (e.g. pyridine) that exhibits worse exfoliation ability for graphene than other solvent, despite having closer Hansen solubility parameters values to that of graphene\cite{99}. Today, Hansen parameters are mainly used for polymer solutes, that is, molecular solutes which unlike nanomaterials are particularly distinctive in their interaction with solvents.

**Surface Energy**

Since solvent-SWCNT interactions are localised at well-defined nanotube surfaces, it was proposed that it would be more suitable to use the surface energy rather than the cohesive energy in these systems. Since the surface energy is related to the cohesive energy density through the
2.5. Understanding SWCNTs in Solution

Surface tension [136, 137], Coleman et al. developed a new set of solubility parameters, implicating that surface energy is a fundamental parameter determining the interaction of nanotubes with solvents. A thermodynamic analysis of the SWCNT–solvent system led to the consideration that the enthalpy of mixing is minimised when the nanotube surface energy matches that of the solvent. Successful solvents of SWCNTs, they concluded, have a surface energy close to the values of nanotube/graphite surface energy, estimated to be 70 mJ/m$^2$ [105, 138, 139]. However again, the theory was only partially successful, as there are a set of solvents with similar surface energies to amide solvents that do not solvate SWCNTs. Clearly, there is at least an extra parameter that needs to be considered together with the surface energy theory when choosing a solvent for SWCNT solubilisation. Arguably also, bundles of SWCNTs should not occur for a true solution, and their presence implies that the dispersion mechanism remains unclear.

2.5.5 SWCNT-Solvent Systems in the Literature

A full understanding of the mechanisms that lead to the dispersion or dissolution of SWCNTs is still lacking. Though some attempts have been made, detailed interpretation of the results is often difficult since different experiments have led to contradictory conclusions. In order to obtain a microscopic picture of the undergoing process, research has recently turned to computer simulations as convenient tool to explore the solvation process. Here, a literature digest of these solvent-SWCNTs simulations is given.

SWCNTs in Water (2001)

An atomistic picture of the structure of the SWCNT–water interface has been provided through Molecular Dynamics simulations [140]. The system was modelled in the micro-canonical (NVE) ensemble. The carbon nanotube represents an infinitely long tube, and end-effects induced by the caps were neglected. By examination of the water radial density profile and water orientation, the structural properties of the SWCNT water interface were studied. A cavity in the bulk water was created to accommodate the nanotube and the water molecules stood off from the nanotube at a distance of approximately 3.2 Å, as shown in Figure 2.12.
The orientation of the water molecules at the interface was inferred from the orientation of the dipole moment of water, and showed a preference for angles of $94.95^\circ$, indicating that the dipole moment in water is nearly tangential to the SWCNT plane. The water’s hydrogen bonding structure in the vicinity of the SWCNT was also modified: the average number of hydrogen bonds in the bulk was found to be 3.75 and decreased to 2.89 at the SWCNT-water interface.

In other SWCNT-water system investigations, the structure of confined water has also been shown to be dependent on the diameter of the SWCNTs\cite{141}. Isosteric heat of adsorption, density profiles along the pore axis and across the pore radii, order parameter across the pore radii, and x-ray diffraction studies are performed, to find layered structures when the internal diameter of the nanotubes is commensurate to the establishment of a hydrogen-bonded network. At room temperature, radial density profiles indicate a pronounced layered structure when water is confined within (12,12), (10,10) and (8,8). A high degree of confinement for water adsorbed within (8,8) and (10,10) SWCNTs induces a disorder-to-order phase transition to cubic or octagonal water nanotubes at 298 and 248 K, respectively. In (6,6) SWCNTs, water forms one-dimensional hydrogen-bonded chains where each water molecule accepts a hydrogen from the preceding molecule and donates a hydrogen to a following molecule along the chain.
SWCNTs in Toluene (2004)

Unlike water, toluene is non-polar and so the insolubility of SWCNTs in a non-polar is of interest. An achiral (10,10) armchair SWCNT modelled in toluene solvent using classical molecular dynamics simulations, again in the micro-canonical (NVE) ensemble. The results showed that toluene molecules form two solvation shells around the SWCNT, the first well-defined and a second that is more-diffuse. In the first solvation shell, the toluene molecules oriented themselves in such a way that the benzene-ring portion is closer to the nanotube axis (and the methyl-group part further away).

Furthermore, the SWCNT solvation energy in toluene were calculated. The resulted showed the important role of the configurational entropy of the solvent in the solvation of SWCNTs. The total energy change associated with the introduction of a SWCNT into the toluene was found to be negative, suggesting SWCNTs should be soluble in this solvent. However, interactions between SWCNTs and toluene molecules resulted in major reorganisation of the toluene molecules, and the associated conformation was found to decrease the configurational entropy of the toluene. From the solvation entropy for SWCNT in toluene, the authors calculated the solvation Gibbs free energy which was found to be small and positive, suggesting that suspension of SWCNTs in toluene is not stable (which is consistent with experimental observations).

SWCNTs in NMP (2008)

In exploring the kinetic mechanisms of carbon-nanotube dispersion aggregation in NMP, molecular dynamics simulations by MacKernan et al. revealed a number of features governing the effective NMP-mediated interactions of pairs of SWCNTs. The simulations showed that pairs of SWCNTs (i.e bundled SWCNTs) are more stable than pairs of isolated tubes[142], which implied that once in the form of a bundle, SWCNTs will essentially never spontaneously separate without the introduction of some external energy, or by significant alteration of the SWCNT’s electronic character.
2.5. Understanding SWCNTs in Solution

SWCNTs in Benzene (2010)

The structure and dynamics of benzene inside and outside of armchair \((n,n)\) SWCNTs have also been studied via molecular dynamics simulations[143]. The \(\pi\)-interaction with aromatic compounds plays a significant role in enabling non-covalent sidewall functionalization of SWCNTs, which has important implication in a variety of systems requiring immobilisation of molecules. In this simulation, one rigid SWCNT was immersed in liquid benzene consisting molecules. Five different SWCNTs, i.e., \(n = 7, 8, 9, 10\) and 12 were simulated. Ends of the nanotubes were terminated with hydrogen atoms, and modelled by the Lennard-Jones parameters. Benzene molecules were found to form a cylindrical solvation shell on the outside of the nanotubes, as shown in Figure 2.13. Benzene molecules were oriented such that their molecular planes lie parallel to the nanotube surface, in doing so forming a solute-solvent \(\pi\)-stacked structure. Benzene molecules inside the nanotube had ring orientations that were generally parallel to the nanotube wall for \(n = 9–12\), but became perpendicular to the nanotube axis at \(n = 8\), and slanted at \(n = 7\).

Figure 2.13: Snapshot of the configuration of benzene molecules inside and outside of an achiral (8,8) single-walled carbon nanotube. Obtained from[143].
Chapter 3

Neutron Diffraction and Computational Modelling

3.1 Introduction

This chapter covers the theory behind the powerful technique of Neutron Diffraction which was used to measure the structure of the solvents and solution studied in this thesis. Section 3.2 begins with the fundamentals of diffraction, describing how it can be used as a tool to access structural information at the atomic scale. Section 3.3 describes the neutron scattering theory. Section 3.4 then outlines the experimental details, from instrumentation to techniques used. The chapter also explains the theory behind the computational modelling technique used in the analysis of the neutron data, which was performed via Empirical Potential Structure Refinement (EPSR) method, based on the Metropolis Monte-Carlo (MMC) algorithm. Section 3.5 outlines MMC theory and the fundamentals of the EPSR technique. Note that it is not aim of this chapter to provide a comprehensive report on scattering techniques and computational modelling tools, but to provide relevant information relating to the techniques used throughout. More information can be found here[144–148].
3.2 Basics of Diffraction

3.2.1 Wave Interference and Bragg’s Law

When two or more waves interact or interfere in the same region of space, the resultant amplitude measured at that region is given by the sum of the amplitudes of all the waves passing that point. This phenomenon is known as superposition and comprises two extremes cases: The two waves can either be in phase, in which case the resultant total wave has an amplitude equal to the sum of the amplitudes of the two original waves, or the waves are completely out of phase, in which case there is no (or zero) resultant wave. These two cases are known as constructive and destructive interference, respectively, and it is through this process that a diffraction pattern arises.

At the heart of wave interference or diffraction is Bragg’s law, which is given by:

\[ n\lambda = 2dsin\theta \]

(3.1)

where \( \lambda \) is the wavelength, \( d \) is the separation between scattering planes and \( \theta \) the scattering angle. \( n \) is an integer which gives the order of the reflection. Bragg’s law thus describes the condition on the angle of scattering for constructive interference to be maximal. The condition is illustrated in Figure 3.1, for an incoming and reflected waves with wave-vectors, \( k_i \) and \( k_f \), respectively. By measuring the angles \( \theta \) at which constructive interference occurs, the scattering planes’ separation length, \( d \), can be found using Bragg’s law and the path lengths equations whereby the length of the opposite side of the dotted triangle can be obtained as \( l_2 = dsin\theta \). Thus, by measuring the angles at which constructive interference with a known wavelength (\( \lambda \)) occurs, a diffraction pattern is obtained.

3.2.2 Reciprocal Space and the Fourier Transform

What is actually measured in a diffraction experiment is the data in reciprocal space, commonly referred to as \( Q \)-space. However, the atoms’ nuclei from which the radiation is scattered are in real space. These two spaces are related by a Fourier Transform, a particular integral transform
3.2. On Liquids and Liquid Structure

Figure 3.1: Schematic showing Bragg diffraction geometry. Two incident waves scatter off consecutive scattering planes, with the path difference shown in . A signal will only be measured if the path length (highlighted in green) is an integer number of wavelengths, which it is in this case.

which allows the function measured in the experiment to be converted into a description of the sample, more specifically in terms of the plane spacings, \(d\), introduced above.

Reciprocal space can be understood by considering Young’s double slit experiment, as in Figure 3.2. Light is shone onto a plate comprising two slits that are at distance \(d\) apart. Waves then emanate from the slits and, via superposition of the waves, a pattern is formed at a screen with maxima and minima as described in section 3.2.1. On inspection of this pattern, the separation between the maxima is found to be \(2\pi/d\). In other words, an inverse (or reciprocal) proportionality exists between the separation of the slits (or the radiation source) and the separation of the peaks. This key finding led to the concept of a diffraction pattern being in reciprocal space, such that \(Q = 2\pi/d\).
3.2.3 The Scattering Vector

Having established the inverse relationship between the separation of the slits and the separation of the peaks, the scattering vector in reciprocal space, $Q$, can now be written in terms of the wave-vectors, $k_i$ and $k_f$. Consider a scattering event comprising an incoming wave-vector, $k_i$, being scattered by a nucleus and a final wave-vector $k_f$, as in Figure 3.3. By the principle of conservation of momentum,

$$\hbar Q = \hbar k_i - \hbar k_f$$

(3.2)

where $Q$ is the scattering vector, defined as the difference between the incident and scattered wave vectors:

$$Q = |Q| = |k_i - k_f|.$$

(3.3)

The diffraction condition is shown in the Figure 3.3 in terms of an expanded scattering triangle. In this case, the magnitudes of $k_i$ and $k_f$ are equal: the process is therefore elastic. In this elastic regime, in which
|k_f| = |k_i|, the scattering atom is assumed to be at a fixed position and the incident and scattered waves have the same kinetic energy, the magnitude of Q can be written, The planes are perpendicular to Q, and the spacing between the planes, d, is given by:

\[ d = \frac{2\pi}{|Q|} \]  (3.4)

By combining Eq.’s (3.1) and (3.4), as:

\[ Q = |Q| = \frac{4\pi}{\lambda} \sin\theta, \]  (3.5)

where 2\theta is the scattering angle and \( \lambda \) is the neutron wavelength incident onto the sample.
3.2.4 Small-Angle and Wide-Angle Diffraction

Since a direct proportionality exists between $\sin \theta$ and $Q$ in Eq. (3.5), it follows that an inverse relationship must exist between $\sin \theta$ the separation of scattering planes, $d$. Since $\sin \theta$ ranges between $[-1,1]$ in periods of $2\pi$, $2\theta$ has a maximum value of $\pi$, and thus $\theta$ has a maximum of $\frac{\pi}{2}$. Using Bragg’s law, it is clear that for a constant $n\lambda$, lower values of $\sin \theta$ correspond to larger values for $d$. Thus, to probe larger length scales, small-angle scattering (SAS) techniques covering lower values of $2\theta$ are used, that is, the angular range up to $1^\circ$ are used, providing information on the structure of large-scale structures or large molecular assemblies. Applications vary from studies of polymers and biological molecules to nanoparticles and micro-emulsions, most of which aim to extract information about the size, shape and/or orientation of some component of the sample.

In contrast to SAS, the wide-angle scattering (WAS) regime, typically covering $2\theta$ range of 5-60$^\circ$, probes smaller scale features, which have smaller values for $d$ and larger values of $\sin \theta$. In terms of the scattering geometry, WAS is very similar to SAS, only the distance from sample to the detector is shorter and thus diffraction maxima at larger angles are observed. WAS often involves the analysis of Bragg peaks scattered to wide angles. Typically, crystalline structures are characterised by sharp Bragg peaks, whereas amorphous systems yield broad(er) ones.

3.2.5 Probes and Sample Interaction

The actual scale of how small or how wide these angle measurements are is defined by the wavelength ($\lambda$) of the radiation being used as a probe. An important constraint on diffraction is that the characteristic wavelength of the probe be of the order of, or on a similar scale to, the structural features being studied. Commonly used probes include electromagnetic waves (like x-rays), or matter waves (like neutrons or electrons). The sensitivity of a probe is governed by its interaction with the sample. The elementary scatterers of x-rays are electrons, as the interaction of an x-ray with the sample occurs be via the electron cloud of the atom. The size of the measured signal in an x-ray diffraction experiment is thus proportional to the number of electrons around the atom, i.e. the atomic number, $Z$. In
the case of neutrons, however, the interaction is with the nucleus, mediated via the strong nuclear force, so in contrast to x-rays the scattering is not dependent on the atomic number but on the scattering length, $b$, which varies by atom and by isotopes of atoms. This means that there is no need for an atomic form factor to describe the shape of the electron cloud of the atom, and the neutron scattering power of an atom does not fall off with the scattering angle as it does for x-rays. This important difference in sample interaction is why neutron scattering has been able to make seminal contributions to structural studies of hydrogen-containing molecules via isotopic substitution. More details about the neutron scattering length is given in the following section.
3.3 Neutron Diffraction Theory

3.3.1 The Neutron

A neutron moving at velocity $v$ can be ascribed a wavelength, $\lambda$, defined by the de-Broglie relation, $\lambda = \frac{h}{mv}$, where $h$ is the Planck constant and $m$ is the mass of the neutron (mass = 1u, approximately $1.6605 \times 10^{-27}$ kg). Typical thermal neutrons have a wavelength of about 15 nm (or 1.5 Å), comparable with interatomic spacings; and a speed of $\sim 2000$ m/s, hence a kinetic energy comparable with that of atoms in a solid, for example. Neutrons carry no charge and compared with x-rays, they are weakly interacting, so they cause no radiation damage to a sample, or at most disturbances to a sample’s properties so small that could be approximated as small fluctuations from the equilibrium state. Indeed, this weak interaction with matter aids and simplifies the interpretation of the scattering. While weakly interacting, neutrons are largely penetrating, in contrast to x-rays and electrons.

3.3.2 Scattering Geometry

In a scattering experiment, incident neutrons are scattered by the sample into a finite element of solid angle $d\Omega$ in the direction $(\theta, \phi)$, as shown in Figure 3.4. The sample is a collection of $N$ atoms or scattering centres. To specify the geometry of the scattering process we use polar coordinates, taking the direction of the incident neutrons as the polar axis. Let the direction of the scattered neutrons be $\theta, \phi$.

The number of neutrons scattered in a given direction as a function of their energy $E'$ can be given by the partial differential cross-section, given by:

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{\Phi d\Omega dE}{\text{Neutrons scattered per second into } d\Omega \text{ with final energy between } E' \text{ and } E' + dE'}$$

(3.6)
given in units of [time$^{-1}$ energy], divided by [area$^{-1}$ time$^{-1}$], and thus has [area] dimensions as expected from a cross-sectional quantity.
3.3. Neutron Diffraction Theory

Figure 3.4: The geometry of a scattering experiment. Neutrons incident onto a sample (represented by grey cube) are scattered into a finite element of solid angle $d\Omega$ in the direction $(\theta, \phi)$.

Without inclusion of the scattered neutron’s energies, a simple count all the neutrons scattered into the solid angle $d\Omega$ in the direction $(\theta, \phi)$ can be given by the differential cross-section as:

$$
\left( \frac{d\sigma}{d\Omega} \right)_{tot} = \frac{R_{total}}{\Phi d\Omega}
$$

where, $R_{total}$ is the scattering rate, that is, the number of neutrons scattered per second into $d\Omega$ in the direction $(\theta, \phi)$, and $\Phi$ is the neutron flux incident onto a sample, given in units of $s^{-1} m^{-2}$.

The total differential cross-section, $\left( \frac{d\sigma}{d\Omega} \right)_{tot}$, can be expressed in terms of the partial-differential cross-section, $\frac{d^2\sigma}{d\Omega dE'}$, as:

$$
\frac{d\sigma}{d\Omega} = \int_0^\infty \frac{d^2\sigma}{d\Omega dE'} \ dE',
$$

and similarly, the total scattering cross-section, $\sigma$, in terms of the differential cross-section $\frac{d\sigma}{d\Omega}$, as:

$$
\sigma_{total} = \int_{all \ directions} \frac{d\sigma}{d\Omega} 2\pi \sin \theta \ d\theta
$$
3.3.3 Scattering by a Single Nucleus

We consider first the simple case of scattering by a single nucleus. If waves of any kind are scattered by an object small compared to the wavelength of the waves, then they can be approximated as spherically symmetric waves. Since the wavelength of thermal neutrons is much larger than the range of the nuclear force, the incident ($i$) and scattered ($f$) wave-functions of the neutron can be approximated to spherically symmetric S-waves[149], such that:

$$\psi_i = e^{ikz},$$  \hspace{1cm} (3.10)

$$\psi_f = -\frac{b}{r}e^{ikr},$$  \hspace{1cm} (3.11)

where $k$ is the magnitude of the wave-vector $\mathbf{k}$, $z$ is the position of the incident wave on an axis in the direction of $\mathbf{k}$, $r$ is the distance of the scattered wave at position, $r$, from the fixed nucleus (the origin). Because of the $\frac{1}{r}$ factor, the intensity (which is the square of the amplitude of the wave-function) decreases with the inverse square of the distance from the source, consistent with the inverse square law of all wave motions.

$b$ is the scattering length which measures the strength of the scattering interaction and is dependent only on the nucleus from which it is scattered. Using the scattering length, $b$, a hypothetical area which represents the effective scattering area presented by a nucleus to an incident neutron, known as the scattering cross-section, $\sigma$, can be defined as

$$\sigma = 4\pi b^2$$  \hspace{1cm} (3.12)

where the $4\pi$ factor originates from the integration over all the scattering angles (i.e. over a sphere). $\sigma$ makes it easier to visualise the size of the signal from different atoms and isotopes of atoms. Positive scattering lengths correspond to repulsive nuclei potentials, and vice-versa. Since the strength of the neutron-nucleus interaction is dependent on $b$, and independent of the atomic number, the response from light atoms is much higher than it is for x-rays, allowing neutrons to distinguish between atoms of comparable atomic number.
3.3. Neutron Diffraction Theory

The cross-section \( \frac{d\sigma}{d\Omega} \) for scattering from a single fixed nucleus can be calculated using Eq. (3.7). First, the number of neutrons passing through the area \( dS \) per second is \( v dS |\psi_f|^2 \) which, using Eq. (3.11), reduces to \( v b^2 d\Omega \). Then, the flux of incident neutrons is calculated as \( \Phi = v |\psi_i|^2 = v \). Thus, \( \frac{d\sigma}{d\Omega} \) can be given as:

\[
\left( \frac{d\sigma}{d\Omega} \right)_{\text{tot}} = \frac{v b^2 d\Omega}{\Phi d\Omega} = b^2.
\]

(3.13)

### 3.3.4 Scattering from a system of particles

For scattering by a general system of particles, a general expression for the cross-section \( \frac{d^2\sigma}{d\Omega dE'} \) seen in Eq. (3.8) for a specific transition of the scattering system from one of its quantum states to another can be derived using Fermi’s golden rule derivation (which for scattering processes is equivalent to the Born approximation). Both of these approximations are based on first-order perturbation theory. The justification for the use of the golden rule is that, when combined with the pseudo-potential, it gives the required result of isotropic scattering for a single fixed nucleus. The full derivation is given elsewhere, e.g.[149], and arrives at the following:

\[
\frac{d^2\sigma}{d\Omega dE'} = \frac{k_f}{k_i} \frac{1}{2\pi h} \sum_{j,j'} b_j b_{j'} \int_{-\infty}^{\infty} \langle \exp \{ -i\kappa \cdot R_{j'}(0) \} \exp \{ -i\kappa \cdot R_j(0) \} \rangle \times \exp(-i\omega t) dt
\]

(3.14)

where \( h \) is Planck’s constant, \( k_i \) and \( k_f \) are the wave-vectors of the incident and scattered neutrons, respectively, and the \( b \) terms are the scattering lengths of a pair of nuclei, \( j \) and \( j' \), and the the summation is over this pair of nuclei.

The measured intensity, \( I(Q) \), in a neutron scattering experiment is then calculated from the partial differential cross-section, as:

\[
I(Q) = \Phi \frac{d^2\sigma}{d\Omega dE'} d\Omega dE'
\]

(3.15)

given in units of counts per unit solid angle per second.
3.3.5 The Time-Dependent Pair-Correlation function

In 1954, van Hove combined Eq.’s (3.14) and (3.15) to express the intensity in a neutron scattering experiment as:

\[
I(Q, \epsilon) = \frac{1}{h} \frac{k'}{k} \sum_{j,j'} b_j b_{j'} \int_{-\infty}^{+\infty} \langle e^{-iQr_j(0)} e^{-i\epsilon t} e^{iQr_j(t)} \rangle e^{-i\epsilon t} dt \tag{3.16}
\]

where the summation is over a pair of nuclei, which at time \( t = 0 \) are at positions \( r_j(0) \) and \( r_j(t) \), respectively\[150\]. The angular brackets denote an average over all possible starting times for observations of the system (equivalent to an average over all the possible thermodynamic states of the sample). The energy change of a neutron is written as \( E - E' = h\epsilon \).

For diffraction, \( t = 0 \) and the ergodic principle is assumed; that is that the time-averaged local structure can be approximated from the average of many of these static frames. For zero energy transfer scattering (i.e. elastic scattering), \( Q \) is as defined in Eq. (3.5). The property usually measured in a neutron diffraction experiment is therefore the elastic differential-cross section \((\frac{d\sigma}{d\Omega})_{\text{elastic}} = \left| \frac{d^2\sigma}{d\Omega dE} \right|_{E=0} \).

By introducing the Dirac delta function, the sum over atomic sites in Eq. (3.15) can be re-written, and the van Hove’s neutron-scattering law can be expressed in terms of the time-dependent pair-correlation function, \( G(r, t) \), as:

\[
I(Q, \epsilon) = \frac{N}{h} \frac{k'}{k} \sum_{j,j'} b_j b_{j'} \int_{-\infty}^{+\infty} G(r, t) e^{-iQr} e^{-i\epsilon t} d^3r dt \tag{3.17}
\]

where \( N \) is the number of atoms in the sample.

\( G(r, t) \) describes how the correlation between two particles evolves with time. Because it is obtained by summing the delta functions over all possible pairs of atoms, it is equivalent to the probability of an atom being at the origin of a coordinate system at time zero and an atom being at position \( r \) at time \( t \).
3.3.6 Self and Distinct Scattering

Since the sum over the scattering lengths in Eq. (3.16) is over all atoms, it therefore comprises not only $b_\alpha b_\alpha$ and $b_\beta b_\beta$ combinations (i.e. self scattering), but also also calculations of $b_\alpha b_\beta$ combinations (i.e. distinct scattering). The differential cross-section for total diffraction is therefore written in terms of these two contributions as follows:

$$\left( \frac{d\sigma}{d\Omega} \right)_{total} = I(Q) + \langle \vec{b}^2 \rangle - i(Q)$$

where $\langle \vec{b}^2 \rangle$ is the self-scattering and $i(Q)$ is the distinct scattering. The self scattering arises from correlations between an atom and itself and for diffraction in the static approximation, it is a $Q$-independent constant. The distinct scattering arises from interference between two distinctly different atoms. It is this term which contains details about interference and from which information about interatomic distances, and therefore the structure, can be determined.

3.3.7 Coherent and Incoherent Scattering

Every element, and every isotope of each element, has two different scattering lengths: a coherent scattering length, $b_{coh}$ and an incoherent scattering length, $b_{inc}$, which are given by:

$$b_{coh} = \langle b \rangle,$$

$$b_{inc} = \left( \langle b^2 \rangle - \langle b \rangle^2 \right)^{\frac{1}{2}}.$$

The coherent term arises from correlations between the positions of the nuclei $j$ at time zero and nucleus $i$ at time $t$. Occasionally $i$ and $j$ are the same nucleus but in general they are not, as the total number of nuclei is very large. Thus, interference effects arise which are known as the coherent scattering of a sample, providing the structural information. The incoherent scattering depends only on the correlations between the same nucleus at different times. Incoherent scattering does not give rise to interference effects, it merely provides a measure of the diffusion of atoms.
In diffraction measurements, coherent scattering is measured but the incoherent scattering adds a structureless background to the signal. Some atoms, or alloys, such as isotope of titanium, zirconium and niobium, can be mixed to give a net coherent scattering length of zero. The signal from these materials is therefore dominated by incoherent scattering. These are known as null-scatterers, as their composition ensures that they do not contribute any coherent neutron scattering to the measured signal. They are used to make sample holders (cans) for neutron diffraction experiments.

### 3.3.8 The Neutron Correlation Function

A neutron correlation function, $T(r)$, may be obtained from the distinct scattering by a Fourier transformation, given as:

$$T(r) = T^0(r) + \frac{2}{\pi} \int_0^\infty Q_i(Q) \sin(rQ)dQ,$$

where $T^0(r)$ is the average density contribution to the correlation function, given by:

$$T^0(r) = 4\pi g^0 \left( \sum_\alpha c_\alpha b_\alpha \right)^2,$$

where $g^0$ is the average atomic number density in the sample, $c_\alpha$ is the atomic fraction for element $\alpha$, and the summation is over all species elements in the sample. For example, for H$_2$O, $l = \text{H}, \text{O}$. $\bar{b}_\alpha$ is the coherent scattering length for element $\alpha$.

The total neutron correlation function, $T(r)$, is a weighted sum of partial correlation functions, given by:

$$T(r) = \sum_\alpha \sum_\beta c_\alpha \bar{b}_\alpha \bar{b}_\beta t_{\alpha\beta}(r)$$

where $\bar{b}_\beta$ is the scattering length of element $\beta$, and each partial function, $t_{\alpha\beta}(r)$, is related to a generalised van Hove distinct correlation function by:

$$t_{\alpha\beta}(r) = 4\pi r G_{\alpha\beta}(r, 0)$$

such that the correlation function measured is related to the van Hove correlation function as seen in Eq. (3.17) at time $t = 0.$
3.3.9 Pair Correlation Functions and Structure Factors

In real space, it is conventional to use the pair correlation function, \( g(r) \), instead of neutron correlation function, \( T(r) \). As briefly described in Section 2.2, \( g(r) \) represents real space correlations between pairs of atoms as a function of their separation, \( r \), and is therefore an simpler function to visualise. It is defined in terms of the density function, \( \rho(r) \), given by:

\[
\rho(r) = \rho_0 g(r). \tag{3.25}
\]

where \( \rho_0 \) is the bulk number density of the sample.

\( T(r) \) and \( g(r) \) are related by:

\[
g(r) = \frac{T(r)}{4\pi r} \tag{3.26}
\]

In reciprocal space, it is also conventional to use partial structure factors, \( S_{\alpha\beta}(Q) \)s, that contain information about correlations between the atomic species. These are related to the atomic distances in real space, i.e. the \( g_{\alpha\beta}(r) \), via a Fourier transformation:

\[
S_{\alpha\beta}(Q) = 1 + \frac{4\pi \rho_0}{Q} \int_{0}^{\infty} r [g_{\alpha\beta}(r) - 1] \sin(Qr)dr. \tag{3.27}
\]

The sum of these partials, weighted by their scattering lengths and atomic fractions, is then represented by the total structure, \( F(Q) \), is given by:

\[
F(Q) = \sum_{\alpha \leq \beta} (2 - \delta_{\alpha\beta}) c_{\alpha} c_{\beta} l_{\alpha}^{coh} l_{\beta}^{coh} [S_{\alpha\beta}(Q) - 1], \tag{3.28}
\]

\( F(Q) \) is related to the total radial distribution function, \( G(r) \), also via a Fourier transformation, given by:

\[
G(r) = \frac{1}{(2\pi)^d} \int_{0}^{\infty} 4\pi Q^2 [F(Q)] \frac{\sin(Qr)}{Qr} dQ. \tag{3.29}
\]

The key aim of most structural studies of liquids is to extract \( g_{\alpha\beta}(r) \), the function representing real space correlations between atom pairs as a function of the separation, \( r \), between them.
3.3.10  Isotopic Substitution

The summative way in which interference from different pairs of atom types can be combined is experimentally significant as it allows major simplifications to be sought by isotopic substitution methods, which involve substituting atoms within a material with isotopes of different scattering lengths. Assuming the isotopic composition has no impact on structure\cite{151} and that the scattering lengths are sufficiently different, measurement of a range of isotopomers at the same molar ratio gives rise to a series of diffraction patterns, where different atomic correlations are more well represented in some patterns relative to others. By subtracting several datasets the number of atom types contributing to the interference may be reduced. With sufficient contrast of scattering lengths, the $S_{\alpha\beta}(Q)$s (and thus the $g_{\alpha\beta}(r)$s) for different atom pairs may be extracted.

Since scattering lengths are dependent on the average of the spin states of the individual nuclei, they do not vary consistently across the periodic table. For the work in thesis, full advantage is taken of the difference between the scattering lengths of hydrogen ($b_{coh}^H = -3.74$ fm) and deuterium ($b_{coh}^D = +6.67$ fm). When augmented with H/D isotopic substitution, neutron diffraction is a very powerful probe of the position of hydrogen atoms, and thus a powerful experimental tool for structural investigation of hydrogen-containing samples, such as the solvents studied herein.

Though this approach might seem very powerful for the characterisation of structure in disordered materials, the combination of many data sets decreases the signal-to-noise ratio. Furthermore, the range of available isotopes with significantly different scattering lengths is limited, and is typically very expensive. As such, computer simulations are employed in order to extract a full set of correlations; these are described in Section 3.5.
3.4 The Neutron Diffraction Experiment

All neutron sources are based on nuclear reactions that free neutrons bound in nuclei; these can be created in reactors or by accelerators.

3.4.1 Neutron Sources

Nuclear Reactors

In a nuclear reactor, fission of \( ^{235}\text{U} \)-enriched fuel elements is used to produce a constant flux of neutrons that covers a range of wavelengths. The method is based on James Chadwick’s experiment for which he was awarded the Nobel Prize in Physics in 1935, wherein a beryllium target is bombarded by \( \alpha \) particles to produce neutrons via the reaction:

\[
^9\text{Be} + \alpha \rightarrow C \rightarrow ^{12}\text{C} + ^1\text{n}
\] (3.30)

Using monochromators or velocity selectors, a range of wavelengths can then be selected accordingly with the appropriate diffraction technique.

Neutron Spallation

At neutron spallation sources, beams of protons are accelerated to high energies and then bombarded onto a heavy metal target. The interaction between the protons and the nuclei in the target leads to an excitation of the nuclei, causing a cascade that leads to high-energy particles, such as neutrons, being ejected from the nuclei. Spallation sources can be either continuous or pulsed. In continuous spallation sources, such as the SINQ in Switzerland, a constant beam of neutrons is produced via the spallation process, which later needs to be monochromated or pulsed. At pulsed neutron sources, such as the SNS in the USA or ISIS in the UK, the protons initiating spallation arrive in packets. This leads to the ejected neutrons to be of a pulsed nature, allowing for the time-of-flight of neutrons to be measured. Consequently, their wavelength can be calculated using the de Broglie relationship:

\[
\lambda = \frac{h}{mv} = \frac{ht}{mL}
\] (3.31)

where \( t \) is the time-of-flight and \( L \) is the path-length (both of which are instrument calibrated). By measuring both the scattering angle, \( 2\theta \), and
the time-of-flight, $t$, rather than the scattering angle alone, pulsed neutron sources can simultaneously access a range of different wavelengths without necessitating any monochromation.

### 3.4.2 Instrumentation

In order to achieve maximum real-space resolution, neutron data require large $Q_{\text{max}}$ values, which necessitates short wavelength neutrons (as per Eq. (3.5)). These are available at high-energy sources, where dedicated instruments are built.

The neutron scattering experiments presented in this thesis were all collected using the NIMROD (Near- and InterMediate Range Order Diffractometer) instrument the ISIS spallation neutron source, based at the Rutherford Appleton Laboratory in the UK. NIMROD, shown in Figure 3.5, was purposefully optimised for structural studies of hydrogen-containing materials, particularly liquids. It makes use of high energy neutrons ($1 \text{ meV} < E < 30,000 \text{ meV}$), delivered by a hybrid liquid water and liquid hydrogen neutron moderator assembly, whose wavelengths range between 0.05-10 Å. The instrument uses the short-wavelength (fast) neutrons to access high-$Q$ regions and achieve high structural resolution, and the long-wavelength (slow) neutrons to access low-$Q$ regions and probe longer length-scale correlations.

**Figure 3.5:** Diagram of the NIMROD instrument giving an overview of the main components from which it is constructed. Obtained from [152]. Permission granted from AIP Publishing.

Detection of neutrons requires the neutron to be captured by a nucleus within the detector. NIMROD uses silver- and lithium-doped
3.4. The Neutron Diffraction Experiment

ZnS scintillation detectors, with a wide-angle detector bank covering a scattering angle range between $3.5^\circ$ and $40^\circ$ and a low angle detector bank covering a scattering angle range from $0.5^\circ$ to $2.2^\circ$.[152] This detection angle (and wavelength) range corresponds to an approximate $Q$-range of $0.02 \, \text{Å}^{-1} < Q < 50 \, \text{Å}^{-1}$.

3.4.3 Experimental Details

To enable the extraction of intermolecular structural correlations (or partial pair distribution functions), a series of diffraction experiments are carried out. As discussed in Section 3.3.10, measurement of several isotopomeric samples allows for multiple diffraction patterns of a specific system to be measured. Samples are contained in cells and loaded onto the sample changer. Scattering data from the empty sample cells, empty instrument, and a Vanadium standard are also collected beforehand so appropriate corrections could be made to the measured diffraction data.

More specific details for each experiment are given in each of the Results chapters 4, 5 and 6.

3.4.4 Correction and Calibration of Raw Data

In a neutron scattering experiment, only a small fraction of the neutron beam incident onto the sample is scattered; the rest is transmitted through the sample as shown in Figure 3.6, potentially undergoing attenuation (i.e. absorption of the neutron by the sample) or multiple scattering (events when the radiation is scattered twice or more before it leaves the sample).

In the analysis of solid samples, whose atomic structure can be assumed to be constant, the static approximation is applied, under which the contributions due to attenuation, multiple scattering and inelastic scattering area are assumed to be negligible. The work presented in this thesis deals with liquid samples, so the raw\textsuperscript{1} diffraction data must be corrected for these contributions before yielding the structure factor. These must be accounted for when merging the data from the detectors.

\textsuperscript{1}The raw data is measured as the number of counts per $\mu$s recorded by each detector: 1 count equals 1 detected neutron.
To ensure these necessary corrections can be made, diffraction measurements must be taken from:

1. the empty instrument;
2. the empty cells;
3. a vanadium standard cell; and
4. each sample-containing cell.

The correction procedure is performed using Gudrun routines[153], based upon the widely used ATLAS package[154], and involves the following steps:

- Correction of all datasets for detector dead-time, that is the time in between two events during which nothing is recorded. By grouping detectors and comparing the standard deviations within their groups, weakly-counting detectors (with very low standard deviation) or those yielding noisy data (those with large standard deviation) are removed. Each dataset is then normalised to remove the effect of varying incident neutron flux levels.

- Correction of all datasets for effects due to attenuation. This involves subtraction of multiple scattering from datasets for both cells and sample containing cells (which can be estimated using theory outlined here[155]), as well as making absorption corrections according to Soper and Egelstaff[156].

- Normalisation of datasets for cells and datasets of sample containing cells to the vanadium standard, in order to covert to an absolute scale of barns atom$^{-1}$sr$^{-1}$. The scattering from vanadium is almost entirely nuclear spin incoherent and differential cross section can be quite accurately determine, so it is used for instrument calibration.

- Extracting the scattering from the sample only, by subtraction of corrected and calibrated scattering from its cell.

- Correction for self self-scattering background and inelasticity effects. The self scattering background typically manifests itself as unphysical peaks at low $r$, that are further complicated by truncation ripples introduced after Fourier transformation due to the finite nature of
$Q_{max}$. Inelastic self-scattering is corrected for using the Placzek corrections. For light atoms, the Placzek correction is not suitable but an alternative correction has been developed by Soper[156], using a dynamical scattering law modelled on a harmonic oscillator.

Figure 3.6: Exemplar events occurring during a scattering experiment.
3.5 Empirical Potential Structure Refinement

3.5.1 Computational Modelling and Simulations

A range of computational methods exist, known collectively as computer simulations, which have been instrumental in the development of liquid state theory in general. Simulations are used to generate models that present theoretical or simplified versions of real-world systems. By and large, their usefulness rests on the fact that a model comprising only a few hundred or a few thousand atoms is often adequate to simulate a whole macroscopic system. The two main algorithms that are most-commonly used to study liquids are stochastic Monte Carlo (MC) and deterministic Molecular Dynamics (MD). MC methods use a probability ensemble to generate a set of configurations for the system being studied, making them useful for calculation of static properties. On the other hand, MD simulations track the trajectories of particles with time allowing access to dynamic information in a system and the thus study of time-dependent processes.

The Empirical Potential Structure Refinement (EPSR) method employed in this thesis uses the Metropolis Monte Carlo algorithm. EPSR was specifically designed for the study molecular liquids and has been used successfully to deduce a variety of solvent and solution structures. In brief, EPSR analyses neutron scattering (and/or x-ray) data by building a three-dimensional simulation box which represents the system, and then refines the positions of atoms in order to match the data. Once agreement is achieved, the box is then interrogated to extract information pertaining to the position and orientation of atoms in the system.

3.5.2 Constructing an EPSR Simulation Box

A system of $N$ molecules is set up such that each molecule is randomly placed in a box of predefined side lengths. The simulation box represents a periodic repeatable unit of the liquid’s structure. The size of the box determines the range over which structure may be modelled. It is typically prepared such that the distances over which the intermolecular potentials operate are less than half the box dimension. The initial configuration is
setup with the correct temperature and number composition. In this way, the atomic number density of the simulation is constrained.

Each molecule/atom/particle is replicated periodically in space such that all replicas contain the same number of particles and behave identically. Traditional implementation of periodic boundary conditions is used, so that if a particle leaves one side of the box, it will re-enter on the opposite side (see Figure 3.7). This way, a constant number of particles is maintained throughout the simulation and boundary effects are overcome.

![Figure 3.7: A diagram illustrating periodic boundary conditions and the minimum image convention. The green spheres represent atoms in a simulation box. As an atom leaves the box in the direction of the arrow, its periodic image in the adjacent box enter the box from the opposite side.](image)

In EPSR, molecules are defined through a constraint on the distances between first and second neighbour atoms. Bond angles are constrained by creating appropriate length bonds between first and third atoms. Similarly, bond dihedrals are maintained by creating bonds between the first and fourth atoms.
3.5.3 Interatomic Potentials

The accuracy of a produced structural model is limited by the accuracy of the pairwise potentials (between molecules) which describe intermolecular interactions. In EPSR, a reference potential \( U_{\text{ref}} \), is defined at the outset and used on its own in order to build a model of the system of interest. The reference potential, \( U_{\text{Ref}} \), is given as:

\[
U_{\text{ref}} = U_{\text{intra}} + U_{\text{inter}},
\]

(3.32)
calculated from the pairwise addition of inter- and intra-molecular contributions over all atom pairs.

The inter-molecular potential, \( U_{\text{inter}} \), between two particles \( i \) and \( j \) of type \( \alpha \) and \( \beta \) is given by a sum of 12-6 Lennard-Jones (LJ) and Coulombic potentials as:

\[
U_{\text{inter}}(r_{ij}) = U_{\text{LJ}} + U_{\text{Coulomb}}
\]

(3.33)
\[
= 4\varepsilon \left[ \left( \frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^{6} \right] + \frac{q_{\alpha} q_{\beta}}{4\pi\varepsilon_{0} r_{ij}}.
\]

(3.34)

Lorentz-Berthelot mixing rules are used to calculate molecular parameters, such that:

\[
\varepsilon_{\alpha\beta} = (\varepsilon_{\alpha} \varepsilon_{\beta})^{\frac{1}{2}},
\]

(3.35)
\[
\sigma_{\alpha\beta} = \frac{1}{2}(\sigma_{\alpha} + \sigma_{\beta}).
\]

(3.36)

where \( \varepsilon \) is Lennard-Jones well-depth parameter, \( \sigma \) is the finite distance at which the inter-particle potential is zero, and \( q \) is the partial charge.

Typically, parameter values for \( \sigma \) and \( \varepsilon \) are obtained from the literature and inputted for different atom types at the outset. Common chemical structure optimisation software, or force-field databases such as AMBER[157, 158], GROMOS[159], OPLS[160] are used.

The form of the potential is shown in Figure 3.8. LJ forces are short range and fall off quickly with increasing \( r \). Coulombic forces are long range and fall off as \( r^{-2} \). The parameters in the potential
3.5. Empirical Potential Structure Refinement

Figure 3.8: The Lennard-Jones Potential, $U_{LJ}$, as a function of the radial distance, $r$. The core diameter, $\sigma$, is defined as the radial distance where $U = 0$, and the potential minimum (or Lennard-Jones well-depth) is given by $\varepsilon$.

are related to intermolecular interactions within the system. The “12 term” represents the short range repulsive interaction between two atoms due to the Pauli Exclusion Principle, which reproduces the repulsions between molecules with closely overlapping electron clouds. The “6 term” represents vDW attractions between atoms (as mentioned in Section 2.2.4) which arise due to dispersive or London forces, as described in Section 2.2.4. For liquids containing polar molecules, there are also attractive and repulsive interactions between regions of positive and negative charge termed Coulomb charge interactions. Truncation terms are used by EPSR to reduce potentials to zero for distances greater than half the box dimensions. Both the Coulombic and non-Coulombic potentials are truncated by multiplying by a truncation factor, as detailed by Soper et al.[161].

As well as the intermolecular potential, EPSR uses an intra-molecular potential, $U_{intra}$, is defined as:

$$U_{intra}(r_{ij}) = C \sum_i \sum_{\alpha \beta \neq \alpha} \frac{(r_{\alpha \beta i} - d_{\alpha \beta})^2}{2w_{\alpha \beta}^2}$$  \hspace{1cm} (3.37)

where $r_{\alpha \beta i}$ is the actual separation of the atoms $i$ and $j$ and $d_{\alpha \beta}$ is their average separation (the equilibrium bond distance). A broadening function,
3.5. Empirical Potential Structure Refinement

\[ w_{\alpha}^{2} = \frac{d_{\alpha}^{\beta}}{\sqrt{\mu_{\alpha}^{\beta}}} \], is used to avoid the need to specify and refine individual Debye-Waller factors for each intramolecular distance, thus accounting for thermal fluctuations over the molecule. \( C \) is a user-defined constant through which one can tune the intramolecular disorder.

### 3.5.4 Running the Simulation

The initial reference potentials generate a starting configuration of molecules. The probability of a configuration, \( g \), is given by:

\[ P_{g} \propto \exp \left( -\frac{U_{g}}{k_{B}T} \right) . \quad (3.38) \]

where \( U \) the potential energy, \( k_{B} \) the Boltzmann constant and \( T \) is the temperature. The dependence on temperature and potential energy enables simulations to reproduce the balance of intermolecular interactions and thermal energy present in the system.

The molecules are moved individually in steps. There are four types of small random moves: whole molecule translations, whole molecule rotations, molecular side-chain rotations and atomic translations. A move is either accepted or discarded according to the Metropolis condition[162]:

- if the movement leads to a reduction in \( U \) (i.e. \( \Delta U \) is negative), it is accepted;
- if the movement increases \( U \) (i.e. \( \Delta U \) is positive), it is accepted with probability \( \text{pf} \frac{P_{g}}{P_{f}} = \exp \left( -\Delta U \frac{k_{B}}{k_{B}T} \right) \).

The condition ensures that the system proceeds along a Markov chain and visits a large volume of the available phase space. By minimising the energy of the system (rather than goodness of fit, as in reverse Monte Carlo), it is less likely for the simulation to get stuck in a local energy minimum.

Random moves are made and the procedure is iterated, changing the system configuration, as exemplified in Figure 3.9, until the simulation reaches equilibrium. Using Eq. (3.28), a structure factor, \( D(Q) \), is calculated from the data, and another simulated structure factor, \( F(Q) \), is calculated from the simple EPSR model produced. By modification of potentials between the constituent atoms, the model is driven towards the experimental data. The process is shown in Figure 3.10.
Figure 3.9: An illustrative example of Monte Carlo modeling of a system, showing [right] the progress in the system’s configuration and [left] the simulated (dotted line) and experimental (solid line) radial distribution functions against the radial distance, $r$. Figure adapted from [163], with permission from IOP.
Figure 3.10: Flow diagram showing steps involved in Data Correction and EPSR simulation. A structure factor, $D(Q)$, is extracted from the data, and another simulated structure factor, $F(Q)$, is calculated from the simple EPSR model produced. By modification of potentials between the constituent atoms, the model is driven towards the experimental data. When a satisfactory agreement is reached between $D(Q)$ and $F(Q)$, structural information can be extracted from the simulation.
3.5.5 The Empirical Potential

The total energy in EPSR is comprised of the reference potential, and an empirical potential. When the empirical potential (EP) is switched on, an extra term \( U_{EP} \) is added to the total energy, such that:

\[
U_{Total} = U_{Ref} + U_{EP}.
\]  
(3.39)

In EPSR, the EP takes the form of a series of power exponential functions:

\[
U_{EP}(r) = kT \sum_i C_i p_n(r, \sigma_r)
\]  
(3.40)

where \( C_i \) are real coefficients, \( \sigma_r \) is a width function that is defined by the user (0.01 Å for all work in this thesis) and \( p_n(r, \sigma) \) is given by:

\[
p_n(r, \sigma) = \frac{1}{4\pi \rho \sigma^3(n + 2)!} \left( \frac{r}{\sigma} \right)^n e^{\frac{-r}{\sigma}}.
\]  
(3.41)

For very large values of \( n \), the function approaches a Gaussian centred on \( r = n\sigma \). It is therefore a very natural function to represent an intermolecular potential which tends to vary rapidly with \( r \) at shorter distances and becomes more slowly varying at longer distances. Advantageously also, \( p_n(r, \sigma) \) has an exact three-dimensional Fourier transform in \( Q \)-space so coefficients can be estimated from the difference between the \( Q \)-space data and simulation, by fitting a series of the form:

\[
U_{EP}(Q) = \sum_i C_i P_n(Q, \sigma_r)
\]  
(3.42)

to the data in \( Q \)-space. The extracted coefficients, \( C_i \), are then used in Eq. (3.40) to produce a new empirical potential.

These difference coefficients are accumulated are used to form new versions of EP, as shown in the smaller loop in Figure 3.10. The process is repeated a large number of times until the difference coefficients approach zero as the simulation approaches the supplied data; i.e. structural convergence is reached.
3.5.6 The Case for EPSR

Though it is difficult to quantify the certainty with which the simulated model might represent the true structure of the system being studied, the use of the diffraction data, and scattering lengths contrasts, achieved through isotopic substitution, essentially act to constrain the EPSR model. Furthermore, though the arrival at a unique solution is not truly possible since the pairwise data could be reproduced by numerous different arrangements within the simulation box, it can be argued from a statistical thermodynamics viewpoint that, for models comprising a large number of particles, the probability of any particular solution significantly greatly different from the most likely (most probable) or ‘correct’ solution is small.

The true interactions within liquids cannot always be accurately described by the interatomic pair potentials described in Section 3.5.3. The Lennard-Jones reference potential itself, for instance, has its limitations. For example, Coulomb partial charges are centred on nuclei in EPSR and so might not be a true description of the actual distribution of charge on a molecule. This is of particular relevance in cases where permanent dipole-permanent dipole interactions (such as hydrogen bonds) may exist as it weakens descriptions of these directional interactions[43]. Secondly, the truncation of Coulombic interactions at a distance that is less than half the box is not ideal as Coulombic interactions could in theory be much longer ranged, especially for non-uniform arrangements of polar species. Furthermore, the pairwise additivity of all of these interactions is not strictly valid as the effect of induced dipoles effect is often dependent on structure and ordering of molecules in the vicinity[164]. Although more complex force fields exist for such purposes, using them to construct structural model remains computationally prohibitive at present. Of course, EPSR does attempt to address – and successfully avoids – many of these limitations. For example, inaccuracies of the starting forcefield are corrected by the additional empirical potentials (EPs). Not only do these EPs provide a better representation of an intermolecular potential, but also smooth the statistical noise and artefacts of the measurement which would otherwise be transferred to the built model[161]. The rapid variation of the EPs at low $r$ also allows the inadequacies of the reference force fields to be overcome, enabling better fitting than in classical Monte Carlo simulations.
Furthermore, through isotopic substitution, EPSR can isolate partial structure factors (PSFs) using pair separations from the simulated model and substitute for those unavailable from experiment, thus estimating all PSFs in a system. Thus, during iterations of the model under the Metropolis condition, the accuracy of the structure (and equivalently the estimates of the partial PSFs) improves. This symbiotic relationship is facilitated by an impressive association between the way in which the diffraction data are separated into PSFs and the process by which the EPs are derived.
Chapter 4

Results I: The Liquid Structure of NMP

4.1 Introduction

This chapter presents neutron scattering data from the solvent N-methyl-2-pyrrolidone (NMP). Besides being widely used in industry, NMP is exceptionally successful in maintaining dispersions of nanomaterials, and has even been shown to dissolve these species to form true solutions. NMP has long been recognised as a very important but unusual solvent, particularly in the dissolution of carbon nanotubes where it has been unrivalled, yet the origin of its atypical behaviour is unclear. Here, its liquid structure, which ultimately dictates its solvent properties, is studied using state-of-the-art neutron scattering techniques. The data are analysed through Monte Carlo simulations using the Empirical Potential Structure refinement (EPSR) method. A three-dimensional model of NMP is constructed to obtain a detailed spatial and orientational picture of NMP, giving unprecedented molecular level structural information about the solvent.

4.2 About NMP

NMP (C₅H₉NO), shown in Figure 4.1, is a strongly polar (μ = 4.09 D) aprotic solvent that is a liquid at room temperature. It is used in petrochemical processing as an extraction medium[165], due to its relatively low volatility and affinity for aromatic hydrocarbons. It is
also commonly used for the surface treatment of textiles, resins and plastics[166–169], and in the pharmaceutical industry for drug extraction and crystallisation. It has been reported to increase the solubility and permeability of several drugs, by simultaneously acting as a cosolvent and a complexing agent[170, 171]. In recent years, owing to its widespread adoption as a solvent for nanomaterials processing, the number of scientific papers involving the use of NMP has significantly increased[172]: NMP has been found to be an exceptional solvent for maintaining dispersions of nanomaterials, including graphene[173], single-walled carbon nanotubes (SWCNTs)[174], and a range of other layered materials[99] following their energetic separation from one another. NMP has even been shown to dissolve these species[96, 175–177] when they are negatively charged, i.e. to form true solutions spontaneously upon contact without any external agitation.

Figure 4.1: The molecular structure of the N-methyl-2-pyrrolidone (NMP) with structural formula C$_5$H$_9$NO, alongside a ball and stick schematic. [Key: Green: Carbon; Red: Oxygen; Purple: Nitrogen; Grey: Hydrogen].

Several efforts have been made to understand the success of NMP for these processes compared with other solvents, and its ability to dissolve both ionic and neutral species. The most common approaches have typically involved the comparison of a range of empirical parameters (for example, Hansen and Hildebrand solubility parameters[106, 107]) with related nanomaterial properties, or matching surface energy arguments between solvents and disposed nanomaterials[105, 108, 139]. But it has been shown that this principle cannot be applied universally. The failure of these empirical models suggests that considering macroscopic solution thermodynamics alone is inadequate in the search for good solvents.
4.3 Experimental Details

Neutron diffraction data of liquid NMP were collected on the Near and InterMediate Range Order Diffractometer (NIMROD) instrument at the ISIS spallation neutron source (Harwell, UK). Data were collected from three samples:

(1) a hydrogenated sample (C₅H₉NO);

(2) a deuterated sample (C₅D₉NO); and

(3) a 1:1 mixture of (1) and (2).

Each sample was contained in flat-plate null scattering Ti₀.₆₈Zr₀.₃₂ alloy cells of internal dimensions 35 mm x 35 mm x 1 mm, after the cells were cleaned with deionised water, acetone and isopropanol, and heated in a vacuum oven for 4 hours. Standard TiZr cell seals which give a net coherent scattering length of zero were used – the effectiveness of which was tested by weighing the loaded cells before and after drying in the vacuum oven. Once loaded onto the sample changer, the temperature was maintained at 21°C using appropriate sample environment equipment (in this case, a built-in refrigerator).

Scattering data were collected over the range 0.02 Å⁻¹ < Q < 50 Å⁻¹. Data from the empty sample cells, empty instrument, and a Vanadium standard were also collected beforehand so appropriate corrections (as detailed in Section 3.4.4) could be made to the measured (raw) data. The scattering from vanadium is almost entirely nuclear spin incoherent and so is used for instrument calibration as its differential cross section can be quite accurately determined. Particular attention was paid to correction of inelasticity effects, especially for the samples containing hydrogen. Inelasticity effects were removed from the total differential scattering cross-section using an iterative method as developed by Soper[178].
4.4 Details of EPSR Simulation Runs

Structure refinement was initialised using an equilibrated box containing 1000 NMP molecules in a cubic box and side length 40 Å with an atomic density of 0.10008 Å⁻¹ at 298 K. The labels assigned to atomic sites on the NMP molecule are shown in Table 4.1, along with atom-entered OPLS force-field parameters which were used to seed the EPSR model.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Atom numbering</th>
<th>Atom</th>
<th>$\varepsilon$ / kJ mol⁻¹</th>
<th>$\sigma$ / Å</th>
<th>$q$ / e</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMP</td>
<td>C1</td>
<td></td>
<td>0.43932</td>
<td>3.7500</td>
<td>0.2614</td>
</tr>
<tr>
<td></td>
<td>H1</td>
<td></td>
<td>0.12552</td>
<td>2.5000</td>
<td>0.0589</td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td></td>
<td>0.27614</td>
<td>3.5000</td>
<td>-0.1179</td>
</tr>
<tr>
<td></td>
<td>C3</td>
<td></td>
<td>0.27614</td>
<td>3.5000</td>
<td>-0.0696</td>
</tr>
<tr>
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<td>N</td>
<td></td>
<td>0.71128</td>
<td>3.2500</td>
<td>-0.0769</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td></td>
<td>0.87864</td>
<td>2.9600</td>
<td>-0.3480</td>
</tr>
<tr>
<td></td>
<td>C4</td>
<td></td>
<td>0.27614</td>
<td>3.5000</td>
<td>-0.0613</td>
</tr>
<tr>
<td></td>
<td>H2</td>
<td></td>
<td>0.12552</td>
<td>2.5000</td>
<td>0.0589</td>
</tr>
</tbody>
</table>

Table 4.1: Reference seed potentials and atom nomenclature for all of the labelled atoms in the EPSR model of liquid NMP, showing Lennard-Jones well-depth, $\varepsilon$, core diameter, $\sigma$, and Coulomb charge, $q$. The arrow indicates the polar moment of the molecule[179].

Using the seed potentials, standard Metropolis Monte Carlo steps were used to bring the simulation to equilibrium. Traditional implementation of periodic boundary condition and the minimum image convention were used. Once equilibrated, structure refinement was initialised. During this process, the interatomic site-site potentials are iteratively refined to drive the simulated structure toward agreement with the experimental data. This was achieved through modification of an additional empirical potential, based on the difference between measured and simulated structure factors, as explained in Section 3.5.5. This allowed molecular and electronic information known a priori to be built into the refinement procedure. Once a agreement is achieved, the simulation was allowed to proceed without further perturbation of the potentials. Ensemble average structural information was then accumulated.
Table 4.2 shows the final parameters extracted at the end of simulation, show minimal changes to the potentials with which the EPSR model was seeded (see Table 4.1).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Atom</th>
<th>$\epsilon$ / kJ mol$^{-1}$</th>
<th>$\sigma$ / Å</th>
<th>$q$ / e</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMP</td>
<td>C1</td>
<td>0.439319998</td>
<td>3.7500</td>
<td>0.261400014</td>
</tr>
<tr>
<td></td>
<td>H1</td>
<td>0.125520006</td>
<td>2.5000</td>
<td>0.0588999987</td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td>0.276140004</td>
<td>3.5000</td>
<td>– 0.117849998</td>
</tr>
<tr>
<td></td>
<td>C3</td>
<td>0.276140004</td>
<td>3.5000</td>
<td>– 0.0696000010</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>0.711279988</td>
<td>3.2500</td>
<td>– 0.0768999979</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>0.878639996</td>
<td>2.9600</td>
<td>– 0.347999990</td>
</tr>
<tr>
<td></td>
<td>C4</td>
<td>0.276140004</td>
<td>3.5000</td>
<td>– 0.0612999983</td>
</tr>
<tr>
<td></td>
<td>H2</td>
<td>0.125520006</td>
<td>2.5000</td>
<td>– 0.0588999987</td>
</tr>
</tbody>
</table>

Table 4.2: Final LJ potentials (extracted from simulation) and atom nomenclature for all of the atoms in the EPSR model of liquid NMP.
4.5 Results and Analysis

4.5.1 Data Fitting

A few important considerations before and during the data fitting are noted. First, during the correction of the raw data, a tweak factor was needed in order to adjust the container scattering, as the attenuation correction was over-subtracting the data. Over-subtraction was occurring when performing inelasticity corrections (as detailed in Section 3.4.4) too, so each set of raw data required slightly different treatment. In some cases, for the hydrogenated dataset (h-NMP) for example, manual subtraction of artefacts at low-$Q$ was performed. Performing inelasticity corrections proved a challenging task. A peak or “bump” was found at around 0.2 Å$^{-1}$ in the hydrogenated sample which was due to known inelasticity effects. As a result, the low $Q$ data (i.e. below 0.2 Å$^{-1}$) were discarded.

During the data fitting, one problem encountered related to the setup of inter-torsional angles, i.e. dihedrals, whose inclusion was necessary to ensure non-planarity of the NMP molecule. The complication arose as their inclusion would, in some cases, restrict bending motion of some bonds. It was found that the defined dihedrals were working against each other in some configurations. To solve this, the dihedral temperature was varied, altering the rigidity of the molecule during refinement which was found to have a big impact on the fitting. Decreasing the bonds’ vibrational temperature and thereby making the bonds stiffer, also helped restricting some of the molecule’s vibrational freedom, and establishing the required molecular configuration.

The experimental data and EPSR-refined model fits obtained for the three interference differential cross-sections (or structure factors), $F(Q)$, are shown in Figure 4.2(a). The $F(Q)$ plots show the data up to 20 Å. Evidently, the differences between these functions are negligible, and a very good agreement is achieved between the experimental data and the EPSR-derived model. Small discrepancies can be seen between the experimental data and empirical model at low values of $Q$, mainly in the hydrogenated sample. These correspond to unphysical short-range interatomic correlations and are due to imperfect corrections of the inelastic scattering contribution from the hydrogen.
The total radial distribution functions, $f(r)$, obtained by direct Fourier transformation of the $F(Q)$ functions, are shown in Figure 4.2(b). For clarity, these are presented up to 8 Å only. These $f(r)$ functions provide a good indication of the quality of the intramolecular fits, which is evidently very good. Judging by the quality of the fits, the reference potentials used in the EPSR model clearly provide a sensible starting point for the data fitting. Such close agreement seen in both $Q$- and $r$-space distribution functions indicates that the model is reliable and appropriate to extract structural information about NMP.

To illustrate the influence of EPSR on the achieved fits, fits to the deuterated data before and after switching on the empirical potential are plotted in Figure 4.3 and demonstrate clearly the role that EPSR plays in driving the molecular simulation towards agreement with the data.
4.5. Results and Analysis

Figure 4.2: (a) The experimentally derived total structure factors, $F(Q)$, [green rectangles] and EPSR-refined fits [black line] for neutron diffraction data collected for NMP. (b) Total radial distribution functions, $f(r)$, [green rectangles], obtained by Fourier transformation of the $F(Q)$ functions, and EPSR-refined fits [black lines].
Figure 4.3: The experimentally measured data [purple dots] vs. the simulated model fits in EPSR without [black lines] and with potential refinement [blue lines] for the deuterated NMP sample, C₅D₉NO in (a) Q-space and (b) r-space. The functions show clearly the role EPSR plays in driving the molecular simulation towards agreement with the data.
4.5.2 Radial Distribution Functions in NMP

Analysis of the EPSR ensemble enables the extraction of individual site-site radial distribution functions (RDFs). This was done for all atomic pair correlations in the system. Selected correlations between the atom types that make up the NMP molecule are plotted in Figure 4.4. Table 4.3 provides the coordination numbers (CN), $N_{\alpha\beta}(r)$, of species $\beta$ from species $\alpha$ at a distance $r$, calculated using:

$$N_{\alpha\beta}(r) = \int_0^r g_{\alpha\beta}(r) \rho_\beta \cdot 4\pi r^2 dr.$$  \hspace{1cm} (4.1)

ESPR also permits the extraction of the site-site radial distribution function (RDF) between the centres of geometry for NMP. This $g_{NMP-NMP}(r)$ function is plotted in Figure 4.5. The peaks in this function are well-resolved, suggesting well-defined local order in relative distance. Three distinct coordination shells can be identified which are localised at distances of 6.0, 10.6 and 15.7 Å. The integral of the $g_{NMP-NMP}(r)$ up to the first minimum gives the total number of molecules in the solvation shell (coordination number) as ~13.3. This coordination number is greater than that found for most aromatic molecules which vary between 12.4 and 12.8 (NMP > toluene > cyclohexane/cyclohexene > methylcyclohexane)[24], and closer to tightly packed molecules in the structurally simple and tightly packed benzene (13.4).

Intermolecular site-site radial distribution functions (RDFs) between selected atom types are given in Figure 4.6. These plot the correlation between nitrogen atoms, N–N, oxygen atoms, O–O, as well as the correlations between oxygen with the ring hydrogen and methyl hydrogen atoms, which are of relevance when investigating hydrogen bonding later.
4.5. Results and Analysis

Figure 4.4: EPSR-derived site-site intermolecular partial distribution functions for NMP at room temperature: C1-C1, C2-C2, C3-C3, C4-C4, N-N, N-H1, N-H2, O-O, H1-O, O-H2, H1-H1 and H2-H2.
### Table 4.3: Relevant coordination numbers (CNs) obtained by integration of the indicated partial distribution functions.

<table>
<thead>
<tr>
<th>Correlation</th>
<th>$r_{\text{min}}$ (Å)</th>
<th>$r_{\text{max}}$ (Å)</th>
<th>CN (atoms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-H$_{\text{ring}}$</td>
<td>2.47</td>
<td>6.35</td>
<td>2.9</td>
</tr>
<tr>
<td>C1-H$_{\text{Me}}$</td>
<td>2.47</td>
<td>6.26</td>
<td>2.9</td>
</tr>
<tr>
<td>C2-H$_{\text{ring}}$</td>
<td>2.48</td>
<td>4.01</td>
<td>0.9</td>
</tr>
<tr>
<td>C2-H$_{\text{Me}}$</td>
<td>2.47</td>
<td>3.95</td>
<td>0.9</td>
</tr>
<tr>
<td>N-N</td>
<td>3.31</td>
<td>8.05</td>
<td>4.5</td>
</tr>
<tr>
<td>N-O</td>
<td>2.72</td>
<td>4.97</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>4.97</td>
<td>6.05</td>
<td>1.1</td>
</tr>
<tr>
<td>N-H$_{\text{ring}}$</td>
<td>2.39</td>
<td>4.89</td>
<td>1.5</td>
</tr>
<tr>
<td>N-H$_{\text{Me}}$</td>
<td>2.37</td>
<td>6.39</td>
<td>3.1</td>
</tr>
<tr>
<td>O-O</td>
<td>2.49</td>
<td>4.17</td>
<td>1.0</td>
</tr>
<tr>
<td>O-H$_{\text{ring}}$</td>
<td>2.11</td>
<td>3.46</td>
<td>0.8</td>
</tr>
<tr>
<td>O-H$_{\text{Me}}$</td>
<td>2.11</td>
<td>3.50</td>
<td>0.9</td>
</tr>
</tbody>
</table>

**Figure 4.5:** The NMP-NMP $g(r)$ at room temperature, plotted up to 20 Å, showing three well-defined coordination shells localised at distances of 6.0, 10.6 and 15.7 Å.
Figure 4.6: Relevant site-site radial distribution functions, $g(r)$s, of pure liquid NMP. $H_{\text{ring}}$ and $H_{\text{Me}}$ are the ring hydrogen atoms and the methyl hydrogen atoms, respectively, as shown in labeling scheme for the molecule. Inset: The NMP-NMP $g(r)$, identical to that shown in Figure 4.6, plotted again for comparison.
4.5.3 Positional Arrangement of NMP Molecules

Since site-site RDF’s only give a one-dimensional representation of the liquid, using them to visualise spatial and orientational structure in three dimensions is difficult. Instead, spherical density functions (SDFs) can be constructed to aid this visualisation. SDFs present a three-dimensional map of the density of neighbouring molecule centres around an oriented central molecule, as a function of angular distance and position. As opposed to 1-dimensional histogram binning (as in the case of the site-site RDFs), SDFs are calculated from spatial probability densities of molecules around other molecules and amounts to performing three-dimensional histogram binning. SDFs therefore shows regions of space around a central molecule that are most likely to be occupied within a specified distance range. In this way, the arrangement of solvent molecules within this first shell for example can be explored further.

Here, a central NMP molecule’s orientation was fixed by defining two axes: an $x$-axis from atom C3 to C1, and a $y$-axis from N to C4. The $z$-axis is then formed from their cross product, effectively fixing the specified atoms as a point of reference for the central molecule. Figure 4.7 shows the nearest neighbour NMP-NMP spatial density function, that is, $g_{\text{NMP-NMP}}(r, \phi)$. A top and a side view of the isosurface are given for lucidity, chosen to enclose the most probable regions at the 30% occupancy level within the first coordination shell, i.e. up to 8 Å. A close to six-lobed symmetric distribution of molecules is observed for the five-membered ring. A continuous band circumscribing the NMP molecule by encircling the oxygen atom and encompassing regions above and below the ring is found. There is a preference for dominant lobes to occupy the middle of the C-C bonds, analogous to benzene[22] and methylcyclohexane[24]. The lobe approaching the oxygen atom is directly aligned with this atom and at a slightly larger distance. Whilst the six-fold symmetry of the most probable positions in methylcyclohexane was found to be slightly disrupted by the presence of methyl group, the structure of NMP appear to be significantly less disrupted by the presence of the methyl group. The lobe approaching the oxygen atom is found to be directly aligned with this atom and at a slightly larger distance, which is best seen in the side view.
4.5. Results and Analysis

Figure 4.7: Spatial probability densities showing the 30\% most probable positions of NMP molecules in the distance range 2-8 Å around a central NMP molecule. For a condensed view of the molecule, the three methyl hydrogens are grouped as one. Plotted using Aten[180].

4.5.4 Orientation in the First Solvation Shell

To examine the orientations of these nearest neighbours in more detail, the radial distribution function (aRDF) for the angle between the normal to the ring plane in NMP can be calculated. The aRDF, $g(r, \theta)$, is the RDF plotted as a function of the angle between the $z$-axes of the central and surrounding molecules, and defined in the range $0^\circ \leq \theta \leq 90^\circ$ as:

$$g(r, \theta) = \frac{\Delta n(r, \theta) \rho}{\frac{2}{3} \pi \left((r + \Delta r)^3 - r^3\right) \sin \theta \cdot \Delta \theta \cdot \rho} \quad (4.2)$$

where $n(r, \theta)$ is the number of molecules in the distance range $r + \Delta r$ and angle range, $\theta + \Delta \theta$; $\rho$ is the bulk number density and the $\frac{1}{\sin \theta}$ factor corrects for the $\theta$-dependence of the solid angle when integrating over the azimuthal angle.

The aRDF for NMP, $g(r, \theta)$, where $\theta$ is the angle between the normal to the ring planes, is shown in Figure 4.9, with the coordinate axes reference frame which was used in the calculation of this aRDF given in Figure 4.8. The $g(r, \theta)$ has been normalised so it is equal to 1 at long $r$. The aRDF exhibits clear peaks within distance range of the first coordination shell, i.e. up to 8 Å. Two most probable orientations exist at two distinct distance
ranges. At shorter distances, between 3 and 5 Å, two distinct peaks exist at $0^\circ$ and $180^\circ$, indicative of ring-parallel nearest neighbour molecules.

At the longer distance range, that is, between 5 and 8 Å, there is a preference for perpendicular nearest neighbours, i.e. $\theta \approx 90^\circ$. Similar preference for ring perpendicular arrangements of molecules at longer distances within the first coordination shell have been previously reported for a variety of related liquids[22, 24, 181].

To supplement the contrasting populations of molecules in the two distances ranges seen in the aRDF, further SDFs of neighbouring molecules at the shorter and longer distance ranges have also been calculated. These are plotted in Figure 4.10. The isosurface, shown in Figure 4.11(a) (top view), shows very clearly the preference for NMP molecules to occupy positions parallel to the ring at the shorter distance range. On closer inspection, however, the isosurface is found to be marginally offset, towards the oxygen atom, as seen in Figure 4.11(a) (side view). The favoured
nearest neighbour geometry is parallel displaced, similar to aromatic benzene\cite{22, 182, 183}.

**Figure 4.9:** Angular radial distribution function (aRDF) for NMP ring center–ring centre, $g(r, \theta)$, where $\theta$ is the angle between the normal to the ring planes (see inset), showing preference for both parallel and perpendicular at different distance ranges.
4.5. Results and Analysis

4.5.5 Orientational Ordering due to Dipole Moment

Further quantitative analysis of the cumulative coordination numbers in the aRDF allow us to calculate the percentages of molecules which sit parallel or perpendicular in each of the distance ranges. These indicate that a notable population of molecules (4.4%) in the first shell are oriented close to completely parallel at very close distances i.e. below 5.4 Å. Though a small proportion, this value is greater than that found for similar cyclic hydrocarbons (between 2.3 and 3.2%)[24] and close to the value of that for benzene (4.6%). One interpretation is that the polar groups in NMP enhance this parallel stacking and overcome, what would normally be, the disrupting influence of the methyl group on local order.

**Figure 4.10**: Spatial probability densities for liquid NMP. The functions show the top 30% for NMP molecules in the two distance ranges, (a) 3-5 Å and (b) 5-8 Å, surrounding a central NMP species.
This hypothesis can be explored by determining whether there is any correlation of the two different populations of nearest-neighbour orientations with the dipole moment of the NMP molecule, which lies very close to the direction of C=O bond, as indicated by the arrow on the molecule labelling schematic in Table 4.1. The molecular dipole was calculated in ORCA v4.0.1 though MP2 calculations using a def2-SVP basis set. Initial molecular geometries were calculated from MM2 Force Field relaxed structures in ChemBio3D (v.14.0.0.117). Molecular dipoles were calculated in ORCA v4.0.1 though MP2 method has been shown to be of comparable accuracy to most hybrid functionals[184].

Choosing an angle, \( \theta \), between the C–O bonds of neighbouring molecules allows the identification of any orientational preference relative to the C=O bonds on neighbouring molecules. This aRDF is shown in Figure 4.11. The inset illustrates the chosen angle \( \theta \) and the reference frames used. Again, within the first solvation shell, two distinct signatures are found, at distances that correspond to the parallel and perpendicular approaches, revealing two populations (with peaks at 4.1 Å and 5.8 Å) of favourable configurations within the first nearest neighbour zone.

At the shorter distances (3 to 5 Å), where NMP molecules are found stack in parallel, the data reveal pronounced preference for the C=O bonds of these molecules to align anti-parallel to one another. Strikingly, for distances corresponding to the perpendicular molecules (5 to 8 Å), the opposite arrangement of C=O bonds is found, that is, the polar moments in neighbouring perpendicular molecules align in parallel. This ordered series of first anti-parallel and then parallel orientations of the C=O bonds is not limited to the first solvation shell, but is actually repeated in the second solvation shell, extending up until 13.5 Å, with peaks at 8.1 Å and 10.7 Å, demonstrating the existence of polar ordered trimers in the liquid.

It is worth noting that in methylcyclohexane, which has negligible polar moment, these parallel arrangements of nearest neighbour molecules are absent[24]. It thus appears while the methyl group is sufficient to disrupt this arrangement in methylcyclohexane, this is overcome by the polar moment of the NMP molecule.
Figure 4.11: Angular radial distribution function (aRDF), similar to that in Figure 4.9, but with the $x$-axis defined along C=O bond so that the angle $\theta$ is defined as in inset, to show orientational preference of similarly aligned molecules.
4.5.6 Extent of Hydrogen Bonding in NMP

In recent years, the liquid structure of NMP liquid structure was probed using x-ray scattering and complementary molecular dynamics simulations[185], without refinement to the x-ray data. The authors reported a “part-preservation” of a methyl-carbonyl hydrogen bond network which was originally reported in NMP’s crystal structure[186]. In the following, the extent to which this hydrogen bonding is present in liquid NMP can be explored.

First, intermolecular correlations between the carbonyl oxygen and the methyl hydrogen atoms (H$_{\text{ring}}$ and H$_{\text{Me}}$) are studied. The O–H$_{\text{ring}}$ and O–H$_{\text{Me}}$ RDFs shown in Figure 4.6 both show a first maximum at 2.7 Å. As per the recently published IUPAC definition of a hydrogen bond[41], directionality is a key criterion and defining characteristic of a hydrogen bond. In a hydrogen bond, intermolecular angle X–H - - - - Y is generally linear (or 180°), with a recommended lower limit of 110° for this angle.

In light of this, a histogram of the intermolecular bond angles between the four atoms constituting the potentially hydrogen bond donating and accepting groups, C1-O - - - H$_{\text{Me}}$-C4, was computed. The data was then converted to a probability function shown in Figure 4.12. As expected, angles below 90° are highly sterically constrained due to the presence of the rest of the molecule. The probability distribution shows no indication of a strongly preferred direction (i.e. one that is centred around 180°).

However, despite the lack of strong directionality, weak O–H$_{\text{Me}}$ hydrogen bonds have been observed in a variety of systems[45]. In fact, this weak (or non-conventional) hydrogen bond has been the subject of intense debate over recent years, as a growing body of experimental and theoretical evidence now confirms that hydrogen bonds like C–H - - - O play distinctive roles in structural chemistry and biology. In fact, the C–H - - - O bond has emerged as the archetype of the weak hydrogen bond[45, 187]. As such, the findings can point to weak hydrogen bonding interactions in NMP which, though might not dominate the local structure of the solvent, do nevertheless occur and are another contributing factor enabling a greater range of solvent-solute approaches.
4.6 Discussion

In this chapter, the liquid structure of NMP solvent was investigated using neutron scattering with hydrogen-deuterium substitution in conjunction with EPSR simulations. The combination of experimental techniques and computational analysis allowed us to conduct a full spatial and orientational study of the solvent’s structure.

The findings reveal a variety of structural features. Parallel approaches at shorter distances result from anti-parallel alignment of dipoles. However, counterintuitively, at further distances but within the nearest neighbour shell where the molecules are arranged perpendicularly, the dipoles align in parallel. Compared with several related solvents (mentioned in Section 4.2), NMP has a relatively large population of parallel approaches, similar only to benzene, despite its non-aromaticity and the presence of the normally structure-reducing methyl group. This is direct contrast to these related solvents where parallel approaches form a minor proportion and the relative population of perpendicular arrangements is far greater.

Figure 4.12: Probability density function showing the most probable angles for the intermolecular bond angle C1–OMe–O investigated herein. The pdf shows a wide range of conformation angles.
Moreover, NMP exhibits dense intermolecular packing. Despite having a methyl group, which significantly reduces the structure of toluene and methylcyclohexane compared with benzene and pyridine, respectively, NMP has a greater packing structure than any related solvent apart from the structurally simple benzene. It was shown that this packing does not occur from hydrogen bonding or ring interactions but from the dipole-dipole interactions between neighbouring atoms.

The polar order in NMP was found to extend beyond its first solvation shell, showing evidence of trimers reaching into the nanometer range. This intricate liquid structure distinguishes NMP from related solvents and explains its success in solvating both charged and uncharged species. The combination of structural features, together with its strong polar moment, elucidate its effectiveness a dissolving charged nanomaterials, in contrast to benzene for example. On the other hand, its unrivalled effectiveness in dispersing uncharged species, such as SWCNTs[108], graphene[188] and other 2D materials[176, 189], can also be understood by considering the high degree of order found in the liquid. The order allows NMP to reduce the relative entropic cost accompanying the introduction of a solute, enabling coordination to itself in different configurations, thus maintaining intra-solvent bonding within and across solvation shells[6], which implicates an inherent order and therefore an already low configurational entropy. For dissolution to occur, the free energy of the solution must be lower than the combined free energy of the solvent and solute. Since pure NMP is highly structured, the entropic ‘cost’ of solvent-solute ordering, is relatively low given its already low configurational entropy. This is in contrast to toluene, for example, where recent thermodynamic calculations have shown that despite a favourable enthalpic gain, solute coordination is associated with an entropic cost that is too big[190]. As a result, despite a large enthalpic gain upon charged nanocarbon dissolution[139], NMP serves to reduce the overall entropic cost accompanying the introduction of the solute which explains its success in solvating uncharged species. In the same vein, the findings also explain NMP’s reorganisational adaptability near surfaces – such as enhanced ordering in vicinity of graphene for example[191, 192]. This extent of solvent ordering near the surface layer was recently shown to play a very important role in determining the thermodynamics of solute-solvent aggregation, and will be the focus of the investigation of
carbon nanotube solutions in Chapter 6.

For charged nanomaterials, the additional enthalpic gain upon solvent coordination leads to spontaneous dissolution at high concentrations\cite{7, 94, 98, 176, 193}. Whilst $\Delta H_{\text{mix}}$ has been proposed to be the principal determining factor in the stability of uncharged solvent-SWCNT systems\cite{105, 139}, the results herein provide a complementary explanation for the system’s thermodynamic stability; i.e. the minimal overall change of NMP’s order upon solute coordination. Interestingly, upon the addition of NaI salt to a NMP/SCWNT dispersion, the SCWNTs eventually crash out\cite{194}, confirming the thermodynamic dissolution of the SWCNTs and further implicating the complex balance of the different NMP–solute interactions.

These results emphasise the importance of versatility for intermolecular bond formation for effective solubilisation. In summary, our findings reveal a balance of interactions in liquid NMP that are unusually well-developed, and dissimilar to related solvents. This intrinsic order can enable a range of local solvent-solution interactions and can serve to reduce the entropic cost accompanying on introduction of a solute, rationalising NMP’s ability to coordinate to and solvate a variety solute species, even in the absence of charge.
Chapter 5

Results II: The Liquid Structures of DMF and DMA

5.1 Introduction

This chapter presents results from neutron scattering experiments on the liquid structures of the two common solvents: dimethylformamide (DMF) and dimethylacetamide (DMA). Besides their prevalence in organic and inorganic chemical synthesis, DMF and DMA have found a wide range of applications in industry, and like NMP, they are also very effective solvents for the dispersion of a wide range of low-dimensional materials. Yet, their liquid structures, which ultimately dictates their solvation properties, has not been established. Here, neutron diffraction augmented with isotopic substitution was combined with EPSR molecular modelling to probe their liquid structure. A description of the local spatial and orientational structure of both solvents is revealed.

5.2 About DMF and DMA

DMF and DMA, shown in Figure 5.1, are polar aprotic solvents with an impressive combination of physicochemical properties. Both have relatively high boiling points (153 and 165 °C) and sizeable permanent dipole moments ($\mu = 3.9$ and $3.7$ Debye at room temperature, respectively). DMF and DMA have found a wide range of applications in industry. For example, DMF is commonly used as spinning solvent for fibres and a processing solvent for leather production[195]. Its miscibility in all proportions with
water, alcohols, ethers, ketones, esters as well as with chlorinated and aromatic hydrocarbons, which has led to its use as an effective component in paint removers[196] as well as an aromatic compound extractor in petroleum refining[197]. DMA, on the other hand, is widely used in polymer processing[198] and as a reaction medium in the production of textiles and plasticisers[199]. It has also proven to be indispensable solvents in the pharmaceutical industry, where they are used to accelerate nucleophilic substitution reactions[200–202].

![Figure 5.1: The molecular structures of [left] dimethylformamide (DMF) and [right] dimethylacetamide (DMA).](image)

More recently, the number of scientific papers involving the use of DMF and DMA has significantly increased[172], owing to their widespread adoption as a solvent for nanomaterials processing[132, 203–205]. DMF is one of the most effective solvents for these purposes, particularly for graphene and single-walled carbon nanotubes[101, 104, 107, 139, 206, 207]. Albeit less prevalent, DMA has also recently proven an ability to form nanomaterials suspensions[205, 208], with exceptionally high stabilities[103].

The related properties of the two liquids are not so surprising perhaps for DMF and DMA are structurally closely related. Both are carboxamides (or amino carbonyls) with the general structure $R_1\text{-C(=O)-NR}_2R_3$ where $R_2$ and $R_3$ are methyl groups. They differ only in their $R_1$ group: while DMF has a hydrogen atom, DMA has a methyl group. As acyclic amides, their resonance structure develops a partial double bond character, as seen in Figure 5.2., with $\pi$-electron delocalisation over the N-C=O entities. This delocalisation ordinarily drives acidic compounds into planarity, but the configuration of the CNC'C" molecular fragment in both compounds has
5.2. About DMF and DMA

Figure 5.2: The resonance structures of dimethylformamide (DMF) and dimethylacetamide (DMA).

been a subject of significant debate. In the case of DMF, solid state studies have reported skeletal planarity[209] whilst electron and x-ray diffraction studies in the gas[210] and liquid[209, 211, 212] phase have yielded pyramidal structures. This planarity, or lack thereof, has also been a subject of many ab initio and Density Functional Theory (DFT) calculations. Earlier calculations have reported an equilibrium structure of DMF with a planar nitrogen bond configuration[213], in contrast to experimental findings from studies in the gas and liquid phases. However, more recently, ab initio vibrational calculations have revealed equilibrium structures of five DMF dimers which showed DMF equilibrating to, again contrastingly, non-planar configurations[214].

In the case of DMA, the literature is much less abundant. Only a few theoretical calculations exist that have predicted both planar and slightly non-planar equilibrium structures[215–217]. These mixed results are not surprising for the question of whether a molecule possesses an exactly planar equilibrium structure is difficult to tackle by both theory and experiments, and studies in different phases have often yielded contrasting results, even for the simple formamide[218, 219].
Another topic in the literature concerns hydrogen bonding in the solvent, particularly in the case of DMF. Formamide (FA) and N-methylformamide (NMF), of which DMF is a derivative, are both protic and can therefore act as both proton donors and acceptors via their N–H and C=O groups, respectively, consequently able to form C=O––H–N hydrogen bonds (h-bonds). Neutron diffraction studies have revealed the existence of this h-bonding network in the liquid structures of both FA and NMF’s. FA comprises a structure dominated by large cyclic clusters, with each molecule participating in exactly two h-bonds cooperatively arranged around the ring[220]. The preferred nearest neighbour orientation of two molecules is such that the C–N bonds of neighbouring molecules sit anti-parallel, forming strong directional C=O––H–N bonds at 1.95 Å[221]. As for its derivative, N-methylformamide (NMF), the findings point to very stable dimers and “linear” trimers leading to a chain-like structure stabilised by weak h-bonds. Interestingly, however, the intensity of these C=O––H–N h-bonds has been found to be greater in NMF than in FA[222].

In contrast to FA and NMF, DMF is aprotic. The added methyl-group and concomitant lack of a labile hydrogen makes DMF unable to donate hydrogen. As such, the formation of strong h-bonds is less likely[45]. However, reports of h-bonding in DMF do exist. For example, Raman and Infrared spectroscopy studies of liquid DMF by Fini et al. have reported h-bonds between the weakly donating carbonyl hydrogen and methyl hydrogen atoms[223]. This h-bonding network was again reported by x-ray diffraction studies and supported by complementary Molecular Orbital calculations[211, 212]. H-bonding was also reported in more recent studies using Fourier-transform infrared spectroscopy and molecular simulations[224, 225].

The literature for DMA is mostly limited to studies where the solvent is mixed with another species, where hydrogen bonding has been reported[226–228], but no reports of hydrogen bonding were found for the pure solvent.
5.3 Experimental Details

Neutron diffraction data was collected on the Near and InterMediate Range Order Diffractometer (NIMROD) instrument at the ISIS spallation neutron source (Harwell, UK). Measurements of three isotopomeric samples were taken for each solvent.

The DMF samples were:

1. a hydrogenated sample (C$_3$H$_7$NO);
2. a deuterated sample (C$_3$D$_7$NO); and
3. a 1:1 mixture of (1) and (2).

The DMA samples were:

1. a hydrogenated sample (C$_4$H$_9$NO);
2. a deuterated sample (C$_4$D$_9$NO); and
3. a 1:1 mixture of (1) and (2).

Each sample was contained in a flat-plate null scattering Ti$_{0.68}$Zr$_{0.32}$ alloy cells of internal dimensions 35 mm x 35 mm x 1 mm, after the cells were cleaned with deionised water, acetone and isopropanol, and heated in a vacuum oven. Standard TiZr cell seals were used. Tests for leakage were performed by weighing the loaded cells before and after dying in the vacuum oven, and before and after running the experiment. The alloy composition ensures that the cell does not contribute any coherent neutron scattering to the measured signal. Once loaded onto the sample changer, the temperature was maintained at 21°C using appropriate sample environment equipment (in this case, a built-in refrigerator).

Scattering data from the empty sample cells, empty instrument, and a Vanadium standard were also collected beforehand so appropriate corrections could be made to the measured diffraction data. The scattering from vanadium is almost entirely nuclear spin incoherent and so is ideal for instrument calibration as its differential cross section can be accurately determined.
5.4 Details of EPSR Simulations

The EPSR simulations for both DMF and DMA were initiated by constructing a cubic box for each of the liquids containing 500 molecules at the atomic number densities 0.09330 Å⁻¹ for DMF and 0.09750 Å⁻¹ for DMA. The seed parameters used for the EPSR simulations were obtained for the atom-centred OPLS/AA force field[160, 229]. These are summarised in Tables 5.1 and 5.2, along with the labels assigned to atomic sites for each of the molecules. Tables 5.3 and 5.4 list the parameters extracted at the end of the simulations, revealing minimal changes to the seed parameters.

**Table 5.1:** Reference seed potentials and atom numbering scheme for atoms in the EPSR model of liquid DMF.

<table>
<thead>
<tr>
<th>DMF Atom numbering</th>
<th>Atom</th>
<th>ε / kJ mol⁻¹</th>
<th>σ / Å</th>
<th>q / e</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C1</td>
<td>0.2759</td>
<td>3.50</td>
<td>-0.11</td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td>0.4389</td>
<td>3.75</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>0.7106</td>
<td>3.25</td>
<td>-0.14</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>0.8778</td>
<td>2.96</td>
<td>-0.50</td>
</tr>
<tr>
<td></td>
<td>HMe</td>
<td>0.1260</td>
<td>2.50</td>
<td>-0.06</td>
</tr>
<tr>
<td></td>
<td>H2</td>
<td>0.1260</td>
<td>2.50</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**Table 5.2:** Reference seed potentials and atom numbering scheme for atoms in the EPSR model of liquid DMA.

<table>
<thead>
<tr>
<th>DMA Atom numbering</th>
<th>Atom</th>
<th>ε / kJ mol⁻¹</th>
<th>σ / Å</th>
<th>q / e</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C1</td>
<td>0.2761</td>
<td>3.50</td>
<td>-0.11</td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td>0.4393</td>
<td>3.75</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>C3</td>
<td>0.2761</td>
<td>3.50</td>
<td>-0.18</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>0.7112</td>
<td>3.25</td>
<td>-0.14</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>0.8786</td>
<td>2.96</td>
<td>-0.50</td>
</tr>
<tr>
<td></td>
<td>HMe</td>
<td>0.6276</td>
<td>2.42</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>HC</td>
<td>0.6276</td>
<td>2.42</td>
<td>0.06</td>
</tr>
</tbody>
</table>
Table 5.3: Final seed potentials of liquid DMF, extracted as is from EPSR at the end of simulation.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$\varepsilon$ / kJ mol$^{-1}$</th>
<th>$\sigma$ / Å</th>
<th>$q$ / e</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.275999993</td>
<td>3.50</td>
<td>-0.109999999</td>
</tr>
<tr>
<td>C2</td>
<td>0.439000010</td>
<td>3.75</td>
<td>0.500000000</td>
</tr>
<tr>
<td>N</td>
<td>0.711000025</td>
<td>3.25</td>
<td>-0.140000001</td>
</tr>
<tr>
<td>O</td>
<td>0.878000021</td>
<td>2.96</td>
<td>-0.500000000</td>
</tr>
<tr>
<td>HMe</td>
<td>0.126000002</td>
<td>2.50</td>
<td>0.0599999987</td>
</tr>
<tr>
<td>H2</td>
<td>0.126000002</td>
<td>2.50</td>
<td>0.000000000</td>
</tr>
</tbody>
</table>

Table 5.4: Final seed potentials of liquid DMA, extracted as is from EPSR at the end of simulation.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$\varepsilon$ / kJ mol$^{-1}$</th>
<th>$\sigma$ / Å</th>
<th>$q$ / e</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.276140004</td>
<td>3.50</td>
<td>-0.109999999</td>
</tr>
<tr>
<td>C2</td>
<td>0.439319998</td>
<td>3.75</td>
<td>0.500000000</td>
</tr>
<tr>
<td>C3</td>
<td>0.276140004</td>
<td>3.50</td>
<td>-0.180000007</td>
</tr>
<tr>
<td>N</td>
<td>0.711279988</td>
<td>3.25</td>
<td>-0.140000001</td>
</tr>
<tr>
<td>O</td>
<td>0.878639996</td>
<td>2.96</td>
<td>-0.500000000</td>
</tr>
<tr>
<td>HMe</td>
<td>0.0627600029</td>
<td>2.42</td>
<td>0.060000000</td>
</tr>
<tr>
<td>HC</td>
<td>0.0627600029</td>
<td>2.42</td>
<td>0.0599999987</td>
</tr>
</tbody>
</table>
Two inter-torsional angles (dihedrals) were defined in DMF to reproduce the molecule’s skeletal planarity, as suggested by the majority of findings discussed in Section 5.2. For DMA, no dihedrals were defined from the outset. Instead, bonds and dihedrals were calculated using the semi-empirical quantum chemistry program MOPAC, using the PM5 model. This saw the molecule equilibrate to a puckered configuration with a slight deviation from planarity at the nitrogen (to which the energy of DMA has been shown to be relatively insensitive[217]) – a configuration that is in close agreement with the equilibrium structures found in the literature[216]. Hydrogen atoms of methyl groups attached to the nitrogen atom were allowed to freely rotate around the C-N axis in both DMF and DMA molecules.

Initially, for each simulation box, two sets of structure factors were set up, one with the empirical potential itself held to zero, and another after the empirical potential switched on. Checks were also performed on the EPSR method by using different seed potentials to investigate the influence of the choice of potential on the observed structure. An iterative procedure was used to drive the simulated structure towards the experimental data, achieved through application of perturbations to the intermolecular site-site potentials, as detailed in Chapter 3.
5.5 Results and Analysis

5.5.1 Data Fitting

First, the model of the experimental data which was constructed in EPSR is discussed. Figure 5.3 shows the total normalised structure factors, $F(Q)$s, and the EPSR-refined fits for DMF, along with the total radial distribution functions (RDF), $f(r)$s, in real space, and corresponding fits. The $f(r)$ functions are obtained by direct Fourier transformation of the $F(Q)$ functions. Even though the $Q$-range was measured experimentally from 0.125 to 50 Å$^{-1}$, the $F(Q)$ plots only show the data up to 10 Å in order to present salient features more clearly. Also for clarity, the RDFs are presented up to 6 Å. Evidently, good agreement is achieved between the data and the simulation. At small values of $Q$, and mainly in the hydrogenated DMF sample (h-DMF), there is little discrepancy between the experimental data and the simulated model. These are due to known effects of inelastic scattering correction in this region, which are most difficult to remove for the hydrogen containing isotopomer[178].

The same functions are plotted for DMA in Figure 5.4. Similar discrepancies are seen to the fits of the hydrogenated DMA in the same low $Q$ region which, when compared with the better fits achieved to the deuterated sample and the mixture samples in both cases, confirms its origin as incomplete inelasticity corrections due to the light hydrogen, and emphasises the difficulty in removing those.

The termination effects that the $f(r)$'s are subjected to, due to them being determined by direct Fourier transformation, deems them unsuitable for thorough intermolecular structure determination, but they provide a good indication of the quality of the intramolecular fits, which judging by Figures 5.4 and 5.5 are evidently good, especially for deuterated samples. Thus, the model can be reliably and confidently used to calculate intermolecular correlations.
5.5. Results and Analysis

Figure 5.3: (a) The experimentally measured total structure data (maroon triangles) and EPSR refined model fits (black lines) for neutron diffraction data collected for DMF. (b) Total radial distribution functions (maroon triangles) obtained by Fourier transformation of the total structure factors, and corresponding EPSR refined model fits (black lines).
5.5. Results and Analysis

Figure 5.4: (a) The experimentally measured total structure data (cyan triangles) and EPSR refined model fits (black lines) for neutron diffraction data collected for DMA. (b) Total radial distribution functions (cyan triangles) obtained by Fourier transformation of the total structure factors, and corresponding EPSR refined model fits (black lines).
5.5.2 Radial Distribution Function Analysis

Analysis of the EPSR ensemble enables the extraction of all radial distribution functions (RDFs) in each system. The RDF calculates the centre-of-mass radial distribution functions between all species in the system. The calculation amounts to 1-dimensional histogram binning, which averages the spatial probability density spherically. The first RDF calculated is that between the molecular centres of geometry for each of the molecules, i.e. $g_{\text{DMF-DMF}}(r)$ and $g_{\text{DMA-DMA}}(r)$. These are plotted alongside one another in Figure 5.5.

Both functions show similar trends. Three distinct intermolecular shells can be identified. For DMF, the shell maxima occur at 5.5, 9.9 and 14.7 Å. For DMA, these occur at 5.9, 10.5 and 15.8 Å, with the third peak appearing slightly broader (i.e. less structured) than that in DMF. Spatial correlation decays rapidly beyond $\sim 16$ Å for both solvents, appropriately with the absence of low-$Q$ peaks for either solvent (as evident in the structure factors in Figures 5.3 and 5.4).

![Figure 5.5](image)

**Figure 5.5:** Molecular centre–of-mass–centre-of-mass radial distribution functions for DMF and DMA, that is, $g_{\text{DMF-DMF}}(r)$ and $g_{\text{DMA-DMA}}(r)$. 
### Table 5.5: Distance ranges of the first three solvation shells of pure DMF, along with coordination numbers (CN).

<table>
<thead>
<tr>
<th>Solvation Shells</th>
<th>( r_{\text{min}} ) (Å)</th>
<th>( r_{\text{max}} ) (Å)</th>
<th>Peak (Å)</th>
<th>CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.4</td>
<td>7.4</td>
<td>5.5</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>7.4</td>
<td>12.3</td>
<td>9.9</td>
<td>47</td>
</tr>
<tr>
<td>3</td>
<td>12.3</td>
<td>16.9</td>
<td>14.7</td>
<td>99</td>
</tr>
</tbody>
</table>

### Table 5.6: Distance ranges of the first three solvation shells of pure DMA, along with coordination numbers (CN).

<table>
<thead>
<tr>
<th>Solvation Shells</th>
<th>( r_{\text{min}} ) (Å)</th>
<th>( r_{\text{max}} ) (Å)</th>
<th>Peak (Å)</th>
<th>CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.5</td>
<td>7.8</td>
<td>5.9</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>7.8</td>
<td>13.4</td>
<td>10.5</td>
<td>53</td>
</tr>
<tr>
<td>3</td>
<td>13.4</td>
<td>18.1</td>
<td>15.8</td>
<td>99</td>
</tr>
</tbody>
</table>

RDFs are normalised to reflect the number density of the surrounding species, so using the tail (second minimum) of each first peak, the first solvation shell can be defined. Consequently, coordination numbers, \( N(r) \), can be calculated using Eq. (4.1). The distances and coordination numbers for the three solvation shells of each solvent are summarised in Tables 5.5 and 5.6. On average, the total number of molecules in the first solvation shell (coordination number) is found to be 12.8 for DMF and 13.0 for DMA.

RDFs between all atomic species were also calculated and selected correlations are shown in Figure 5.6 and Figure 5.7 for DMF and DMA respectively.
Figure 5.6: Intermolecular (site-site) partial distribution functions, $g_{X-X}(r)$, for pure DMF at room temperature showing correlations between selected atoms.
Figure 5.7: Intermolecular (site-site) partial distribution functions, $g_{X-X}(r)$, for pure DMA at room temperature showing correlations between selected atoms.
5.5.3 Spherical Density Functions

Spherical density functions (SDFs) allow the visualisation of correlations as three-dimensional maps, showing regions of space around a central molecule (of fixed orientation) that are most likely to be occupied by the molecular centres of a neighbouring molecule in the liquid. In contrast to 1-dimensional histogram binning in the case of the RDFs, calculations of SDFs are based on 3-dimensional histogram binning into volume elements.

The SDF for DMF is plotted in Figure 5.8. The isosurface shows three main molecular lobes. First, a lobe which circles over the carbonyl hydrogen and oxygen atoms, shifted slightly away from the centre of the molecule, relating to the polar region of the molecule. Second, a small lobe positioned near the carbonyl-side of the molecule and pointing towards the carbon atom of the carbonyl group, oriented orthogonally to the first lobe with which it appears to associate. A third well-defined lobe at the opposite end of the DMF molecule is positioned near the methyl-groups, pointing towards the nitrogen atom.

![Figure 5.8: Spatial density function for DMF showing the 30% most likely molecular-centre–molecular-centre correlations, in the distances up to 7.4 Å (i.e. within their first solvation shell). [Key: Carbon (green), Nitrogen (purple), Oxygen (red), Hydrogen (white)]](image)
The SDF for DMA, plotted in Figure 5.9, appears less structured on the whole. Although the first lobe is similar to that in DMF, the second appears to fragment outwards into two smaller lobes, one pointing directly towards the methyl group and another to the C2–C3 bond. The third lobe appears to be shifted downwards, no longer symmetrically encompassing both methyl groups nor pointing directly towards the nitrogen atom.

**Figure 5.9:** Spatial density function for DMA. The isosurface shows the 30% most likely molecular-centre–molecular-centre correlations, in the distances up to 7.9 Å (i.e. within their first solvation shell). [Key: Carbon (green), Nitrogen (purple), Oxygen (red), Hydrogen (white)]
5.5.4 **Orientational Correlation Analysis**

Next, orientational ordering due to the dipole moment of each of the molecules is explored. In order to define the relevant axes, the directions of the dipole moments in both DMF and DMA need to be first calculated. Though DMF’s dipole moment could be obtained from the literature[230], no reports of DMA’s were found. As a result, these were instead calculated in ORCA v4.0.1 though MP2 calculations using a def2-SVP basis set. Initial molecular geometries were calculated from MM2 Force Field relaxed structures in ChemBio3D (v.14.0.0.117). The method has been shown to be of comparable accuracy to several hybrid functionals, and revealed a dipole moment for DMF in agreement with that recently calculated by [230]. The dipole moment for each molecule is shown in Figure 5.10.

![Figure 5.10: Dipole moment directions for (left) DMF and (right) DMA. Molecular dipoles were calculated though MP2 calculations using a def2-SVP basis set.](image)

By defining axes that lie along the dipole moment of the molecule, and calculating the an angle between the axes of a central and a surrounding molecule, orientation due to the polar moment can be explored by calculation of the angular RDF, $g(r, \theta)$, using:

$$g(r, \theta) = \frac{\Delta n(r, \theta) \rho}{\frac{2}{3\pi} \left( (r + \Delta r)^3 - r^3 \right) \sin\theta \cdot \Delta \theta \cdot \rho} \quad (5.1)$$

where $n(r, \theta)$ is the number of molecules in the distance range $r + \Delta r$ and angle range, $\theta + \Delta \theta$; $\rho$ is the bulk number density and the $\frac{1}{\sin\pi}$ factor corrects for the $\theta$-dependence of the solid angle when integrating over the azimuthal angle.
The aRDF for the DMF molecules is plotted in Figure 5.11. The N-O axis, which lies close to the direction of dipole moment direction in DMF molecule, was chosen as the principal axis for the calculation (see Figure 5.11(a), inset). The aRDF presents three peaks all within the first solvation shell (i.e. up to 7.4 Å). The first and sharpest peak occurs at 3.5 Å and shows preference for an anti-parallel arrangement of the N–O bonds in nearest neighbours, consistent with the orientation of the two dominant dimers out of the five recently found in recent molecular simulations[231]. However, at distances slightly further out, yet still within the first solvation shell, two other peaks at 4.4 and 6.2 Å indicate parallel alignment of the N–O bond in neighbouring DMF molecules at these distance ranges.

**Figure 5.11:** Angular radial distribution functions (aRDFs), $g(r, \theta)$s, for DMF where $\theta$ is the angle between the N-O axes of a central and a surrounding molecule.
For DMA, the $g(r, \theta)$ was calculated with the angle $\theta$ between the axes lying along the C2-O axis, i.e. the direction of the dipole moment (see Table 5.2 and Figure 5.10). The aRDF for DMA is shown in Figure 5.12. Again, two orientations exist at two distinct distance ranges: a peak also at 3.5 Å for the anti-parallel orientation and another at 5.5 Å for parallel (i.e. $\theta = 180$) orientations. It is worth noting that the peaks in DMA are broader and appear slightly less intense than in DMF, implicating a strong effect of polar ordering in DMF.

![Figure 5.12: Angular radial distribution functions (aRDFs), $g(r, \theta)$s, for DMA where $\theta$ is the angle between the C-O axes of a central and a surrounding molecule.](image-url)
5.5.5 Hydrogen Bonding

As discussed in the introduction, an important property of solvent structure is hydrogen bonding, which is also one of the prevalent issues in the literature relating to the structure of DMF, i.e. to what extent it might dictate or govern its structure. To investigate hydrogen bonding in DMF, the relevant intermolecular contacts between the carbonyl oxygen atom, O, and the donor groups, HMe–C1 and H2–C2, are studied first. Figure 5.13(a) shows the intermolecular site-site partial distribution functions between these atom types in DMF. Similar site-site RDF analysis was performed for DMA ensemble in order to establish the correlation between relevant contacts. Note that the x-axis starts from 1.5 Å instead of 0 in order to display more clearly notable features in the distribution function. As defined by Jeffrey [232], donor-acceptor distances of 2.2-2.5 Å are "strong, mostly covalent", 2.5-3.2 Å are "moderate, mostly electrostatic", and 3.2-4.0 Å are "weak, electrostatic". Both functions show peaks occurring at 3.6 Å. As such, an initial look at the O–C contacts in both DMF seems to point to a weak electrostatic correlation.

![Figure 5.13: EPSR-derived site-site intermolecular partial distribution functions showing (top) correlations in DMF between the oxygen atom with the methyl (HMe) and the carbonyl hydrogen (H2) atoms, and (bottom) correlations in DMA between the oxygen atom with the methyl (HMe) and the carbonyl hydrogen (HC) atoms in DMA.](image)
Table 5.7: Distance ranges of O-HX intermolecular correlations between potentially h-bonding sites in DMF and DMA.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Correlation</th>
<th>r_{min} (Å)</th>
<th>r_{max} (Å)</th>
<th>Peak (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>O–H_{Me}</td>
<td>2.1</td>
<td>3.3</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>O–H2</td>
<td>2.1</td>
<td>3.7</td>
<td>2.7</td>
</tr>
<tr>
<td>DMA</td>
<td>O–H_{Me}</td>
<td>2.1</td>
<td>3.3</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>O–H_{C}</td>
<td>2.1</td>
<td>3.4</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Quantitative analysis of these correlations in both solvents was then carried out, to determine the number of occurrences of these bonds in the box, using a cut off distance 2.7 Å. Figure 5.14(a) shows these data in terms of probability distributions of the number of bonds. For both the O–H_{Me} and O–H2 correlations in DMF, the average coordination number is less than 1, indicative of a poor association between atoms in the distance range. In contrast to DMF, the probabilistic analysis of the number of hydrogen atoms around the carbonyl oxygen in DMA, plotted in Figure 5.14(b), both show an average coordination number larger than 1, implicating a stronger h-bonding association in the case of both O–H_{C} and O–H_{Me} correlations.
5.5. Results and Analysis

(a) DMF

![Bar charts showing probability distributions for DMF.]

(b) DMA

![Bar charts showing probability distributions for DMA.]

**Figure 5.14:** Probability distributions of the number of hydrogen atoms, $H_{Me}$ and $H_2$ in DMF, and $H_{Me}$ and $H_C$ in DMA, within a bonding distance $< 2.7$ Å to the carbonyl oxygen atom in each molecule.
One criterion, or key defining characteristic, for a hydrogen bond, as per the recently published IUPAC definition\cite{41}, is its directionality. In a hydrogen bond, the intermolecular angle $X$-$H$-$Y$ is generally linear (or 180°), with a recommended lower limit of 110° for this angle. In light of this, the distribution of these angles in both DMF and DMA were studied. Histograms of the intermolecular bond angles between the three atoms constituting the potentially hydrogen bond donating and accepting groups in both solvents were then computed, that is $C_1$-$H_{Me}$-----O and $C_2$-$H_2$-----O in DMF, and $C_1$-$H_{Me}$-----O and $C_3$-$H_C$-----O in DMA, and the data were converted to a probability functions. These are shown in Figure 5.15 for DMF and Figure 5.16 for DMA.

**Figure 5.15:** Probability density function (pdf) showing the most probable angles for the intermolecular bond angle $C_1$-$H_{Me}$-----O and $C_2$-$H_2$-----O investigated for DMF.

In the case of DMF, the distribution appears to be centred around 120°, i.e. within the range (IUPAC lower limit being 110°) of that which is characteristic of hydrogen bonding. The distribution of angles was also calculated for DMA, for which a stronger association is found between the carbonyl oxygen and both hydrogen atoms. However, in the case of DMA, the probability distribution was computed at both distance ranges, first where the correlation peaks and second the end of the peak for
5.5. Results and Analysis

This was in order to assess whether directionality strength changes between the two distances. The probability distribution functions for both O–H\textsubscript{Me} and O–H\textsubscript{C} contacts are shown in Figures 5.16(a) and 5.16(b), and demonstrate a wide range of conformation angles, also centred around 120°. No real strong directionality is apparent, especially not at the shorter distance range, i.e. 2.7 Å. In the same vein, therefore, DMA seems to exhibit weak hydrogen bonding that is slightly stronger than DMF, given the higher coordination number results.

![Figure 5.16](image)

**Figure 5.16:** Probability density function (pdf) showing the most probable angles for the intermolecular bond angle C1–H\textsubscript{Me}-----O and C3–H\textsubscript{C}-----O investigated for DMA at two distance ranges, first the distance at which the peak occurs and then the peak maximum.
5.6 Discussion

In this chapter, the liquid structures of two solvent, DMF and DMA were investigated using neutron scattering augmented with isotopic substitution hydrogen and deuterium. The analysis of the data was carried out using EPSR molecular modelling. A very good agreement was achieved between the neutron data and the simulated model, with only small discrepancies at low $Q$ that stem from imperfect inelasticity corrections.

From the EPSR models, structural information pertaining to spatial and orientational correlations in each of the solvents were extracted. Individual site-site RDFs the atomic pair correlations in both systems showed differences between the two solvents, though centre-of-mass RDFs appeared very similar and showed similar trends in position and intensity. As expected of the smaller molecule, the solvation shells in DMF occurred at shorter distances and on average, the total number of molecules in the first solvation shell (coordination number) was calculated to be 12.8 for DMF and 13 for DMA. It is interesting to compare these coordination numbers to those found for related aromatic solvents (to which NMP was compared in Chapter 4), which varied between 12.4 and 12.8, revealing tighter packing molecules in these non-aromatic solvents. Spherical density functions for both solvents revealed a higher degree of ordering in DMF, while DMA’s isosurface appeared less structured on the whole. Differences were predominately at the carbonyl-group side of the molecule, as to be expected as this is the differentiating group between the two molecules. Orientational correlation functions implicated a strong effect of polar ordering in DMF than DMA too.

The last point of investigation related to hydrogen bonding in the solvents, a commonly discussed issue in the literature for DMF, less so for DMA. Distances, angles and directionality trends were analysed for the h-donating and h-accepting groups in both solvents, and quantitative analysis of coordination numbers was performed. The findings point to weak hydrogen bonding in both solvents. On average, however, and curiously, a stronger association between the hydrogen bonding donating and accepting groups was found in DMA, for which all previous analysis had indicated less local order. This hydrogen bond network provides another
route of molecular association, thereby allowing them to be involved in a
greater range of approaches upon introduction of a solute.

It is regrettable that there is lack of data comparing the solubility of
different species, uncharged or charged, in these solvents. Such study would
further enhance the scientific importance of this research and elucidate the
underlying and interlinked physical phenomena.
Chapter 6

Results III: Structure and Ordering in Solutions of Single-Walled Carbon Nanotubes

6.1 Introduction

As discussed in Chapters 1 and 2, understanding interactions between nanoparticles and between nanoparticles and surrounding solvent molecules is crucial, as our lack of knowledge of these is currently an underlying problem in the processing and controlled manipulation of all nanomaterials. Studies exploring these interactions and phenomena for solvated nanoparticles are rare due to the size and complexity of nanoparticles, and the lack of experimental methods that are able to probe the dilute concentration of these interactions. However, recent advances in neutron scattering methods advances experiments combined with molecular modelling have now paved the way for structural investigations of these solutions. Here, local ordering in a concentrated solution of carbon nanotubes is probed using neutron diffraction augmented with isotopic substitution. The investigation forms the first atomistically-resolved neutron scattering measurement of a solution of nanomaterials. Analysis was performed using molecular modelling via the EPSR method explained in Chapter 3.
6.2 Experimental and Data Collection

6.2.1 Sample Preparation

Super Purified HiPco™ single-walled carbon nanotubes were purchased from Nanointegris. HiPco SWCNTs are synthesised using high-pressure carbon monoxide process and contain < 5wt% residual iron catalyst. Sodium metal of 99.95% purity was obtained from Sigma Aldrich. HiPco powder was placed with sodium metal in a reaction tube. Solvation was achieved via reduction in metal-ammonia, by the valence electrons of sodium metal, as described in Section 2.4.6, yielding a charged carbon nanotube salt, or nanotubide, of composition Na(NH$_3$)$_{1.2}$C$_{10}$. Elemental concentrations of the salt were determined by CHN analysis using an Exeter Analytical CE440 Elemental Analyser. Combustion of the sample, separation of the combustion gases and measurement by thermal conductivity were all carried out in the dynamic mode. Duplicate measurement runs agreed to within 0.5%. Subsequent dissolution was then carried out in DMF solvent, as detailed in Section 2.4.6.

Various concentrations of the nanotubide salt in DMF solvent were prepared, encompassing the liquid crystalline[95, 233, 234] gel phase, mixed phase and the dilute regime wherein individualised nanotubes are expected. Photographs of typical solutions are shown in Figure 6.1, contained in vials in which they are prepared. The data and results presented in this chapter are of the 25 mg/mL samples i.e. the high concentration regime, at which solvent-SWCNT correlations are weighted at about 10% (pre-determined via level of scattering calculations).

![Figure 6.1](image)

**Figure 6.1:** Photographs of vials containing typical nanotubide solutions of varying concentrations in DMF.
6.2.2 Data Collection and Correction

Neutron diffraction data was collected on the Near and InterMediate Range Order Diffractometer (NIMROD) instrument at the ISIS spallation neutron source (Rutherford Appleton Laboratory, UK). For second order H/D difference experiments, measurements were taken of solutions containing the salt dissolved in three isotopomeric DMF samples:

1. hydrogenated DMF;
2. deuterated DMF; and
3. a 1:1 mixture of (1) and (2).

Samples were contained in flat-plate null scattering Ti\textsubscript{0.68}Zr\textsubscript{0.32} alloy cells of internal dimensions 35 mm x 35 mm x 1 mm. Once loaded onto the sample changer, the temperature was maintained at 21°C using appropriate sample environment equipment, in this case a built-in Closed Cycle Refrigerator.

Scattering data from the empty sample cells, empty instrument, and a Vanadium standard were collected beforehand so appropriate corrections could be made to the measured diffraction data, as outlined in Section 3.4.4.

6.3 EPSR Simulation

6.3.1 Building the Carbon Nanotube

An atomic coordinates file (.xyz) for a (7,6) chiral single-walled carbon nanotube with uncapped ends was created. The (7,6) chirality was chosen to be consistent with the most abundant chirality of nanotubes in the HiPco sample used. A applet developed by Roberto Veiga, and based upon the work of White et al.[235] was used to generate the coordinates file. The applet has been reliably implemented into the VEGA molecular modelling suite and is widely used for reliable xyz generation. At the time of writing, the applet could be accessed here [236].

A periodic image of the nanotube was then generated using the Visual Molecular Dynamics (VMD) software[237] and processing of the file was made in order manually create bonds between appropriate carbon atoms.
either end of the tube. This is in order to ensure the nanotube runs through the periodic boundary of the box. All carbon atoms had three bonds.

6.3.2 Building the Box

The .xyz file was then imported into Aten molecular modelling package[180] and the SWCNT was placed in the centre of a non-cubic parallelepiped cell with its longitudinal axis aligned in the $z$-direction. The volume of the box necessary to contain all species of the 25 mg/mL solution concentration was pre-determined. The $z$-dimension was kept at the distance of the carbon nanotube and the $x$ and $y$ dimensions were calculated in order to ensure the appropriate volume. Final box dimensions were 92.17, 92.17 and 47.68 Å, with the shorter distance being equivalent to the length of the nanotube. Periodic boundary conditions applied in all three principal directions. In this way, the SWCNT can be considered as “infinitely long” and the end-effects associated with its hemispherical caps can be neglected.

The coordinate file was then read into into EPSR. The carbon atoms in the nanotube were tethered in place to restrict movement and ensure no overlaps between molecular species. A few iterations were carried out until the intramolecular energy was stable. After that, the other species were added, comprising 51 sodium atoms, 61 ammonia molecules, and 3070 DMF molecules, to achieve the stoichiometric composition $\text{Na(NH}_3\text{)}_{1.2}\text{C}_{10}$. Figure 6.2 shows different stages of the building. After each addition, EPSR builds the atomic and/or molecular coordinates according to the set of bonds defined. After all additions, molecular refinement was run until the intramolecular energy has equilibrated. Any time an atomic or molecular parameter is changed, molecular refinement was run a large number of times in order to get the atoms to actually move to their new bond lengths. It is also worth noting that some loss of information occurred, particularly dihedral angles. These needed to be re-inputted.
Figure 6.2: Snapshots of different stages in building the EPSR ensemble. [Key: Carbon (black); Oxygen (red); Nitrogen (blue); Hydrogen (grey); Sodium (yellow)]
6.3.3 Interatomic Potentials

To describe the interactions between atoms/molecules in the system, effective pair potentials were used in the form of Lennard-Jones potentials, in the form of:

\[
U_{\text{inter}}(r_{ij}) = U_{\text{LJ}} + U_{\text{Coloumb}},
\]

\[
= 4\varepsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{6}\right] + \frac{q_{\alpha}q_{\beta}}{4\pi\varepsilon_0 r_{ij}},
\]

as previously described in Section 3.5.3.

Table 6.1 shows the seed parameters used for the EPSR simulations, together with the atom nomenclature and schematics of each of the species. These parameters were used as a starting point, and differences in structural behaviour induced in the simulation were then be compensated for by the potential refinement method, as explained in Section 3.5.4. Table 6.2 shows the final parameters extracted after the simulation, showing minimal changes to the parameters which were initially used to seed the EPSR model.

Parameters for the DMF species were as those used to simulate the pure solvent model in Chapter 5, which were taken from the OPLS all-atom force field[160]. Sodium was ascribed a charge, $1e^+$. In order to keep net charge of the system neutral, the corresponding negative charge of $1e^-$ was distributed equally over the 508 carbon atoms of the nanotube, simulating charge delocalisation for a highly reduced sp$^2$ system. The seed parameters used for ammonia were obtained from those used in previously simulations here[26].
<table>
<thead>
<tr>
<th>Species</th>
<th>Schematic</th>
<th>Atom</th>
<th>$\varepsilon$ (kJ/mol)</th>
<th>$\sigma$ (Å)</th>
<th>$q$ (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNT</td>
<td>C</td>
<td>0.293</td>
<td>3.55</td>
<td>-0.10</td>
<td></td>
</tr>
<tr>
<td>DMF</td>
<td>C1</td>
<td>0.276</td>
<td>3.50</td>
<td>-0.11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td>0.439</td>
<td>3.75</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HMe</td>
<td>0.125</td>
<td>2.50</td>
<td>-0.06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H2</td>
<td>0.063</td>
<td>2.42</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>0.711</td>
<td>3.25</td>
<td>-0.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>0.878</td>
<td>2.96</td>
<td>-0.50</td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>Na</td>
<td>0.189</td>
<td>6.72</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>N2</td>
<td>0.879</td>
<td>3.36</td>
<td>-1.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H3</td>
<td>0.042</td>
<td>1.56</td>
<td>0.34</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1: Reference Lennard-Jones parameters (well-depth parameter and atomic mass) and charge, used as seed potentials in the EPSR simulation of $\text{Na(NH}_3\text{)}_{1.2}\text{C}_{10}$ in DMF.
### Table 6.2: Final Lennard-Jones parameters (well-depth parameter and atomic mass) and charge, extracted as is at the end of the EPSR simulation.

<table>
<thead>
<tr>
<th>Species</th>
<th>Atom</th>
<th>$\varepsilon$ (kJ/mol)</th>
<th>$\sigma$ (Å)</th>
<th>$q$ (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNT</td>
<td>C</td>
<td>0.292879999</td>
<td>3.54999995</td>
<td>– 0.098425000</td>
</tr>
<tr>
<td>DMF</td>
<td>C1</td>
<td>0.275900006</td>
<td>3.50000000</td>
<td>– 0.109999999</td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td>0.438899994</td>
<td>3.75000000</td>
<td>0.500000000</td>
</tr>
<tr>
<td></td>
<td>HMe</td>
<td>0.125400007</td>
<td>2.50000000</td>
<td>– 0.0599999987</td>
</tr>
<tr>
<td></td>
<td>H2</td>
<td>0.0627000034</td>
<td>2.42000008</td>
<td>0.000000000</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>0.699999988</td>
<td>3.25000000</td>
<td>– 0.140000001</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>0.800000012</td>
<td>2.96000004</td>
<td>– 0.500000000</td>
</tr>
<tr>
<td>Sodium</td>
<td>Na</td>
<td>0.189740002</td>
<td>6.72419977</td>
<td>1.000000000</td>
</tr>
<tr>
<td>Ammonia</td>
<td>N2</td>
<td>0.879000008</td>
<td>3.359999990</td>
<td>– 1.02600002</td>
</tr>
<tr>
<td></td>
<td>H3</td>
<td>0.0418399982</td>
<td>1.55910003</td>
<td>0.342000008</td>
</tr>
</tbody>
</table>

6.3.4 Running EPSR

Preliminary simulation runs showed that some atoms and DMF solvent molecules were drifting inside the carbon nanotube and getting
stuck. Re-processing the coordinate file was therefore necessary. Two pseudo-atoms with charge zero were added, one at each openings either end of the tube, and given LJ parameters so that that the interaction would be repulsive and short-ranged. However, this was found to be ineffective in stopping the different species penetrating the nanotube. Thus, minimum distance constraints were defined for $C_{\text{nanotube}}$-X pairs, where X included the sodium atom, the ammonia nitrogen and DMF’s nitrogen atom, while keeping the nanotube tethered in place. This constraint solved the problem. A size shrink factor and a very slow gradual rate of increasing the shrinking factor was also necessary in order to avoid different species (atoms and molecules) becoming intertwined, interlocking, and/or forming unphysical bonds. Some instances of these can be seen in Figure 6.2. The simulation was then run until the energy stabilised, after which the distance constraints were removed and the nanotube was untethered. A snapshot of the final equilibrated box is shown in Figure 6.3.

![Figure 6.3: Snapshots of the various stages in building the EPSR ensemble leading to the final equilibrated box [bottom]. [Key: Carbon (black); Oxygen (red); Nitrogen (blue); Hydrogen (grey); Sodium (yellow).]](image)
6.4 Results and Analysis

6.4.1 Data Fitting

Once an ensemble of molecules was constructed with an internal structure which reproduces (or is close to) that obtained from the diffraction experiment, an empirical potential was added in the form of a series of power exponential functions, as explained in Section 3.5.5, until a satisfactory agreement is reached. Ensemble average structural information was then accumulated. The total structure factors for each isotopically distinct sample were obtained. These functions are plotted in Figure 6.4, showing good agreement between the experimental and simulation structure factors at both small- and large-$Q$ distance ranges.

![Figure 6.4: Total structure factors obtained from neutron diffraction measurements of SWCNT solutions (black triangles), and fit to EPSR refined simulation (red lines).]
Direct Fourier transformation of the structure factors in Figure 6.4 yields the total radial distribution functions, \( f(r) \). These are plotted in Figure 6.5, and show also a good agreement and indicate a rich variety of molecular correlations located below 4 Å.

![Radial distribution functions](image)

**Figure 6.5:** Radial distribution functions, \( f(r) \)s, for the three nanotubide solution samples – obtained by Fourier inversion of the structure factors shown in Figure 6.2) – showing a range of correlations occur below 4 Å.

As a first case for comparison, Figure 6.6 plots the obtained diffraction data for the solution against those for the pure DMF samples from Chapter 5. As apparent from the figure, the two show similar scattering patterns, despite the high concentration of the nanotubes in the system. This result highlights the importance and need for computer simulation techniques such as molecular modelling to access detailed molecular level structural information and further interrogate these data, in order to further uncover information lying beneath these very small differences.
Figure 6.6: The experimentally derived total structure factors, $F(Q)$, for neutron diffraction data collected for pure DMF and for samples of SWCNTs in DMF, showing almost identical distributions.
6.4.2 Solvent–Solvent Structure

The solvent-solvent structure is first explored by calculating the DMF centre-of-mass–centre-of-mass radial distribution function (RDF), that is the \( g_{\text{DMF-DMF}}(r) \), for molecules in the solution box and comparing it to that obtained for the pure solvent. The two functions are shown in Figure 6.7. Clearly, the RDFs show almost identical features, indicating that despite the presence and dissolution of the SWCNTs at a high concentration, the intrinsic inter-solvent structure is not disrupted.

![Figure 6.7: The centre-of-mass–centre-of-mass DMF-DMF radial distribution functions, \( g_{\text{DMF-DMF}}(r) \), in the pure solvent compared to those in the solution.](image)

6.4.3 SWCNT–Solvent Structure

We then turn to investigate the SWCNT-solvent structure. Due to the non-cubic nature of the simulation box and the 1D nature of the SWCNT, the RDF of DMF molecules is calculated cylindrically outwards from the centre of the nanotube, rather than spherically. This was done by defining a reference vector which lied longitudinally along the centre of geometry of the nanotube. This cylindrical RDF is plotted in Figure 6.8. and reveals three distinct and well-defined shells with peak distances at approximately 8.5, 12.8 and 17.7 Å from the centre of the nanotube. These distances correspond to distances of 4.5, 8.8, and 13.7 Å from the nanotube’s surface.
Average coordination numbers within each of these solvation shells were calculated by integration under each peak, with the trough end of each peak used as an upper limit on the integration. The distances corresponding to each solvation shell and associated coordination numbers distances are summarised in Table 6.3. The first three solvation shells are characterised by 73, 157 and 241 DMF molecules, respectively.

<table>
<thead>
<tr>
<th>DMF Solvation Shell</th>
<th>$r_{\text{min}}$ (Å)</th>
<th>$r_{\text{max}}$ (Å)</th>
<th>Peak (Å)</th>
<th>CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.4</td>
<td>10.0</td>
<td>8.5</td>
<td>73</td>
</tr>
<tr>
<td>2</td>
<td>10.0</td>
<td>15.5</td>
<td>12.8</td>
<td>157</td>
</tr>
<tr>
<td>3</td>
<td>15.5</td>
<td>20.1</td>
<td>17.7</td>
<td>241</td>
</tr>
</tbody>
</table>

Table 6.3: Distance ranges and coordination numbers (CN) of the first three solvation shells of DMF in the solution box, consistent with the cylindrical RDF shown in Figure 6.9.

The coordination number analysis reveals that over 15% of all DMF molecules (471 of 3070) are within the first three solvation shells. Using these numbers, the packing density of DMF in the first solvation shell was calculated by working out the number of DMF molecules per cylindrical solvation shell. This was found to be 0.0128 DMF molecules per cubic angstrom (molecules/Å³) for the first solvation shell. The literature quoted
density of the solvent is 0.944 g/mL, equivalent to 0.0077 molecules/Å³, and matching the packing density of DMF molecules in the first solvation shell as calculated from the pure DMF model in Chapter 5, found to be 0.0072 DMF molecules/Å³. Strikingly, this difference represents a packing density that is 65% larger in the first solvation shell. This enhanced short-range order of solvent molecules at the nanotube surface is similar to that measured for solvating ammonia molecules around fullerides[7] where the solvent shells were found to be up to four times the density of the bulk solvent, and implicates some correlation or enhanced packing around the carbon nanotube. It is also worth noting the existence of an excluded region where the $g(r)$ drops to almost zero after the first solvation shell, between 9.8 and 10.4 Å in Figure 6.8, suggestive of solvent templating induced by the SWCNT.

To find out how the solvent molecules are ordered within these solvation shells, RDFs of DMF’s atomic species from the nanotube are shown in Figure 6.8. The correlations show very well-defined peaks in the first solvation shell, indicative of a very highly ordered shell. The preferred mode of orientation of DMF molecules in the first solvation shell was determined. This is shown in Figure 6.8, inset, with the carbonyl hydrogen atom and one of the methyl hydrogen atoms pointing towards the carbon nanotube.

![Radial distribution functions of atomic components of DMF from the centre of the carbon nanotube.](image)

**Figure 6.9:** Radial distribution functions of atomic components of DMF from the centre of the carbon nanotube.
6.4.4 Orientational Ordering of DMF

The preference found in Figure 6.9 for DMF molecules to orient themselves in a way that the two hydrogen atoms are closer to the nanotube axis is confirmed via the snapshot in Figure 6.10, which reveals a high concentration of hydrogen atoms (shown in grey) near the nanotube, more so any other atomic species.

![Figure 6.10: Zoomed in snapshot of the positions of DMF molecules around the central nanotube in the final equilibrated ensemble, showing distances up to 15 Å away from the centre of the nanotube. [Key: Carbon (black); Oxygen (red); Nitrogen (blue); Hydrogen (grey)]](image)

To explore the extent to which this configuration might be dominant, orientational distribution functions for DMF molecules were calculated cylindrically outwards from the nanotube. A vector describing the direction along which the nanotube lays was used, along with a point (on which this vector lays) to define the centre of the nanotube. While setting up the simulation, the geometric centre of nanotube was chosen to lie on the origin, therefore the point was chosen to be $(0, 0, 0)$. The vector was defined as $(0, 0, 5)$ depicting the vertical direction of the nanotube. Any $(0, 0, n)$ vector will have sufficed. The DMF molecule was defined through three axes as shown in Figure 6.10, such that the $x$-axis lies in the Nitrogen $\rightarrow$ Oxygen direction, and the $y$-axis as one of the methyl carbon atoms. The direction of the dipole moment is in the Oxygen $\rightarrow$ Nitrogen direction.
6.4. Results and Analysis

(Figure 5.10, vide supra). The z-axis, that is the cross product of the x- and y- axes, thus lies out of the plane of the molecule. For each molecule, the minimum distance (that is the perpendicular distance) between the centre-of-mass and the defining vector was then calculated, and the dot product between the perpendicular vector and each axis of the molecule was summed into distance bins of 1 Å and angle bins of 5°.

![Principal axes definition for DMF molecule](image)

**Figure 6.11:** Principal axes definitions for DMF molecule. The DM axis represents the direction of the dipole moment in DMF[230].

In this away, angle vs. distance maps were produced. The distribution of the angle $\theta$ between the x-axis of the DMF molecule and the normal to a vector defined along the length of the carbon nanotube is calculated. This is shown in Figure 6.1 for the distance range corresponding the first three DMF solvation shells, as well as distances further out from the nanotube, up to 50 Å. As defined, angles of $\theta = 90^\circ$ would indicate that the dipole moment of DMF molecules is oriented perpendicular to the vector that is normal to the nanotube’s longitudinal axis, i.e. that the dipole lies parallel to the nanotube. On the other hand, $\theta = 180^\circ$ would indicate that the dipole moment of DMF molecules aligns parallel to the nanotube’s axis, i.e. lies perpendicular to the nanotube’s axis. In all three DMF solvation shells, the distribution of the molecules is skewed towards $180^\circ$, indicative of a preference for the dipole to lie tangentially to the nanotube surface. Remarkably, the distribution continues to be largely skewed in the second and even third solvation shell, indicating a preference for the carbonyl side of the molecule to be near the nanotube, even up 20 Å. The phenomenon only appears to be completely lost at distances above 35 Å, where the bulk of the solvent becomes completely randomly oriented.
6.4. Results and Analysis

Figure 6.12: Orientational distribution of the vector lying along the dipole moment of DMF, calculated at increasing distances from the centre of the nanotube, showing the first three solvation shells (SS) of DMF. $\theta$ is the angle between the axis lying along the dipole moment of DMF and the vector that is normal to the nanotube.

The trend is strongest at distances closer to the nanotube, so this preferential orientation was probed further by calculating angle distributions for discrete distance ranges starting from 7-8 Å where the first solvation shell onsets. These distributions are plotted in Figure 6.13, up to 13 Å.
The orientational ordering is indeed strongest nearest to the carbon nanotube, as is evident by the function at the shortest distances range, 7-8 Å, where the distribution peaks around 107°. Schematics of this orientational configuration are drawn at the bottom of Figure 6.13, and inset. Indeed, the number of DMF molecules within this distance will form only a minor proportion but these distance-segmented functions confirm the preference for the dipole to line up tangentially (close to 90°) the NT surface.

**Figure 6.13:** Orientational distribution of the vector lying along the dipole moment of DMF, calculated at increasing distances from the centre of the nanotube. θ is the angle between the axis lying along the dipole moment of DMF and the vector pointing towards the nanotube. Therefore, there is a slight preference for the nitrogen to point towards the NT and the oxygen to point away from it.
6.4.5 SWNCT–Cation Correlation

The next point of investigation concerns the positions, ordering, and influence (or lack thereof) of the sodium cations in the solution. First, the RDF of sodium atoms from the centre of the nanotube is calculated. This RDF is shown in Figure 6.14, first alone and then alongside the distribution of DMF molecules from the nanotube.

![Figure 6.14](image)

**Figure 6.14:** The radial distribution functions for sodium atoms from the centre of the nanotube plotted alone for clarity, and again alongside DMF’s cylindrical RDF from the nanotube.

A sharp peak at 8.1 Å indicates a shell of sodium atoms sit between 3.6-4.5 Å from the SWCNT surface, or 7.6-8.5 Å from the SWCNT central axis. By integrating under the peak, this shell is found to contain 18 sodium atoms. The positional arrangement of sodium atoms in the box
are shown in Figure 6.15. These confirm that the sodium ions seem to coordinate close to the surface of carbon nanotube, while others appear to be randomly positioned further out. The remaining 33 sodium cations are dissociated and distributed within the solution as shown Figure 6.15. Their distribution in the solution resembles somewhat the formation of an electric double-layer which surrounds the nanotube surface, as predicted by models discussed in Section 2.5.2. Remarkably, beyond the first band of condensed cations, no other sodium cations be found within any of DMF’s three solvation shells, in what appears to be a cation-free region in the distance range between 8.9 and around 25 Å, which is seen to be featureless in Figure 6.14.

**Figure 6.15:** Snapshots of the positions of sodium cations around the central nanotube in the final equilibrated ensemble, showing sodium cations within 15 Å from the centre of the nanotube. [Key: Carbon (black); Sodium (yellow)]

**Figure 6.16:** The positions of all sodium cations around the SWCNT. Note the cation-free region in between the closely coordinated cations and the rest. [Key: Carbon (black); Sodium (yellow)]
Next, the solvation of the sodium cations is investigated via site–site intermolecular correlations between the sodium atom and selected constituent atoms in DMF. These Na–X correlations are shown in Figure 6.16. Strong associations exist between the sodium atom and the carbonyl group of the DMF molecule, with $g_{\text{Na–C}_2}(r)$ and $g_{\text{Na–O}}(r)$ correlations occurring at 5.1, 4.2 Å, respectively. The $g_{\text{Na–N}}(r)$ also shows clear structure at 5.8 Å. It seems therefore that the sodium atoms are strongly solvated by the DMF, with DMF coordinated along the dipole towards the sodium, with the oxygen as its nearest neighbour. By inspection of the cylindrical distribution functions of the sodium and the DMF in Figure 6.14(b), it can also be deduced that the sodium cations are embedded within the first DMF solvation shell, and they sit loosely at the inside of the second and third shells, nearest to the carbonyl side of the DMF molecule, and closest to the DMF’s oxygen atom, as might be expected of a solvated cation given the DMF dipole and the electron rich oxygen.

Figure 6.17: Site–site radial distribution functions showing correlations between the sodium atom and atomic species in DMF. Inset: Atom nomenclature for the DMF molecule.
6.4.6 Ammonia Association

The last remaining species in the solution is ammonia, the presence of which in the system is a consequence of the SWCNT reduction before the salt’s solvation. A qualitative view of the the positions of these ammonia molecules in the box and nearest to the carbon nanotube can be seen in the snapshots in Figure 6.18.

Figure 6.18: Snapshots of the positions of ammonia molecules around the central nanotube in the final equilibrated ensemble, showing (top) two different views of ammonia molecules within 20 Å from the centre of the nanotube, and (bottom) all ammonia molecules in the box. [Key: Carbon (black); Nitrogen (blue), Hydrogen (grey)]
The RDF for the NH\textsubscript{3} molecules from the centre of the nanotube is plotted in Figure 6.18(a), and again in Figure 6.18(b) alongside the DMF molecules’ RDF from the nanotube. The function reveals a sharp peak at 8.2 Å, representing some coordination of ammonia molecules to the nanotube. While this peak occurs at a distance closer than the SWCNT–DMF correlation, the coordination number reveals that only 2 ammonia molecules reside within that distance, representing a very small fraction of the ammonia – a mere 3.3% of all molecules in the box. A second broader peak can be seen at 11.1 Å, extending up to 14.1 Å, which contains only 5 molecules. The majority of the ammonia molecules reside in the bulk of the box (and thus the bulk of the solvent).

Figure 6.19: The cylindrical radial distribution function (RDF) for ammonia molecules from the centre of the nanotube plotted (a) alone for clarity, and (b) alongside DMF’s cylindrical RDF from the nanotube.
The ammonia molecules do not exhibit any preferential orientation with respect to the SWCNTs either, as revealed in Figure 6.19, barring the first few correlations that correspond to the 2 molecules nearest to the SWCNTs. This might suggest that the formation of strongly ordered DMF solvation shells is seemingly forcing the ammonia molecules outwards and away from the nanotube. This suggests that the DMF solvent molecules are more effective or more involved in solvating the SWCNTs.

![Figure 6.20: Radial distribution functions showing correlations between the carbon nanotube (C atom) and atomic species constituting the ammonia molecule (the N2 and three H2 atoms).](image)

The association of ammonia molecules with the cation is also explored. The two cylindrical RDFs are plotted alongside each other in Figure 6.21. The radial distance is plotted up to 30 Å for clarity. Clearly, no strong positional correlational is found between the sodium atoms and ammonia molecules, except nearest to the nanotube, corresponding to a mere 2 ammonia molecules (see snapshot in Figure 6.21, inset).
6.4.7 Charge Distribution

The solubility of nanoparticles, including nanotubides, is typically modelled through an adaption of DLVO colloid theory (as explained in Chapter 2). In this model, colloids avoid agglomeration due to van der Waals attractions through the formation of a classic Stern electrical double layer (EDL) against its inherently charged colloid surface, in this case the negatively charged carbon nanotube. The double layer consists of counter-ions in a surface-bound Helmholtz layer and a diffuse Gouy-Chapman layer, causing a charge field which dissipates at increasing distances from the colloid due to screening from the increasing volume of electrolyte. Given that the validity of DVLO theories to describe nanoparticle (as opposed to micron scale particle) dispersions has recently been called into question (as discussed in Section 2.5.1), and given the simplification offered by the absence of counter-ions (since DMF is aprotic there, is no dissociation of the solvent), the charge distribution as a function of distance from the surface of the nanotube was determined. This is in order to compare to the classical EDL potential, where the potential has the maximum value on the particle surface and drops with increasing distances from the surface (as shown in Figure 2.11).
Composite charge distributions as a function of distance were calculated for every molecular, and every atomic component in the system. The results for molecular species are shown in Figure 6.22. Three curves are shown, in order to distinguish the contribution of each species to the total distribution (black). The potentials converged to zero in all three cases, even though this is not evident in the graph which plots the x-axis values up to 45 Å only (half the EPSR box size). In all curves, there is an absence of charge up to 4.5 Å, after which a total of 51 charges contribute the large repulsive peak present at that distance. The cylindrical RDFs are plotted inset in order to display the positions of species. As expected, the overall curve is only dependent on the distribution of ions, however the solvent arrangement can give rise to local charge fluctuations averaged out over the length of the molecule. The curve for the SWCNT and sodium is characterised by a region of constant negative charge between 4.8 and 7.8 Å corresponding to the condensed layer of sodium cations in that region. The influence of the ammonia molecules are evident at the tail end of that region. The influence of DMF is visible too, via negative and positive contributions of the molecule’s atomic components to the potential, with the more positive end of the molecule sat nearer to the SWCNT surface, and the more negative residing on the other side, thereby representing polar ordering in that distance range, not due to the DMF molecule’s intrinsic dipole moment but interlinked electrostatics between the solvent molecules and the strong cation condensation.

The results are qualitatively similar to the charge distribution proposed for a double-layer model which is often used to explain colloidal stability, with the potential diminishing at increasing distances from the charged particle’s surface. However, remarkably, an excluded region exists where no cations is present. This oddity could associate with important phenomenological effects which might lead into a big insight, thus further examination is required.
Figure 6.22: Potential distribution from the carbon nanotube surface cylindrically outwards up to 45 Å (half the size of the EPSR simulation box). Inset, the previously calculated cylindrical radial distribution functions for each of the species from the central nanotube are re-plotted.
6.5 Discussion

In this chapter, the structure of a concentrated solution of carbon nanotubes in DMF solvent is investigated using advanced neutron scattering techniques, augmented with isotopic substitution of hydrogen and deuterium of DMF. The data analysis was performed using the EPSR method, to construct a simulation model which agreed with the diffraction data. Interrogation of the EPSR model allowed a full spatial and orientational study of the structure of the solution to be conducted, in what is the first atomistically-resolved neutron scattering measurement of local ordering in a nanomaterial solution.

First, solvent-solvent and SWCNT-solvent structure were explored. Equipped with insights from the structural model for the pure solvent, comparisons could be made between the pure DMF solvent system and that of the SWCNT solution. Though the centre-of-mass–centre-of-mass radial distribution functions of DMF molecules appeared very similar in both systems, a more in-depth exploration revealed a plethora of structural features. First and foremost, intense ordering of the solvent molecules around the SWCNT was shown, characterised by three very well-defined solvation shells, containing 73, 157 and 241 DMF molecules, respectively. The packing density of molecules was found to be 65% larger in the first solvation shell than in bulk, implicating enhanced short-range ordering of solvent molecules near the nanotube surface. The precise orientation of the DMF molecules in the first solvation shell was also revealed to find that the most probable configuration of DMF molecules is that where a carbonyl hydrogen atom, and one of the methyl hydrogen atoms, point towards the carbon nanotube. Further orientational correlational analysis then revealed a preference for DMF molecules to adopt a conformation where their dipole moments lie tangentially to the carbon nanotube’s longitudinal axis. This phenomena appeared most dominant in the first solvation shell but extended into the second and third shells, where it was still skewed towards 180°.

Upon examination of the positions of sodium cations, a third of those were found to condense on the surface of carbon nanotube. The rest were randomly positioned further out. Their distribution in the entire box resembles somewhat the formation of an electric double-layer
which surrounds the nanotube surface, as predicted by classical DLVO-OM models. However, it is worth noting that in spite of the qualitative similarities, quantitatively, Oosawa-Manning theory seems to fail in explaining the degree of cation condensation in this box. Condensation occurs when the distance between unshielded charges on the nanotube surface is smaller than the distance within the solvent at which the interaction of like charges is comparable to $k_B T$ – the so-called Bjerrum length, $l_B$, as explained in Section 2.4.3. Using Eq. (2.17), the bjerrum length for DMF, $l_{DMF}^{Bj}$, at room temperature, is 152 Å. In this EPSR model, 18 of the 51 sodium atoms can be seen to be condensed on the SWCNT surface, leaving 33 un-condensed charges. When normalised to the SWCNT surface area (1341.2 Å²), a SWCNT inter-charge spacing of 6.4 Å can be calculated; that is, over 25 times closer than the Bjerrum length, so a higher degree of condensation would be expected. As such, using polyelectrolyte theory to explain these charged nanotubes systems is unsuitable.

An association was also found to exist between the sodium atom and the DMF molecules, more specifically the electron-rich oxygen atom in DMF. The partial association of oppositely charged ions in electrolyte solutions is typically described by ion-pair behaviour and whether the result may be predictive of solvent-separated ion pairs in the solution, is work in progress. Indeed, a major reason why DLVO theory fails for biological and colloidal systems is due to specific ion effects[238]. Exploring this further might elucidate the cation-free region seen in the distribution of the sodium in the box, or at least or some offer some sort of indication of the extent to which it exists. In this context, it is also worth noting that this cation free region may be an artefact caused of the simulation.

In conclusion, the findings reveal a rich variety of structural features and interactions in nanoparticles solutions, including nanoparticle templating of coordinating solvent molecules, girth of sodium ions adhering to the charged nanotube and a potential void forming. Though provisional, the findings oppose the current understanding of these nanoparticle systems and contribute crucial insights that differ from traditional standpoints in understanding the dissolution of these systems.
Chapter 7

Conclusions

7.1 Project Aims

Alongside their widespread adoption in a range of industrial applications, the three solvents, NMP, DMF and DMA, are very effective in dispersing and dissolving nanomaterials. Yet, their liquid structures, which ultimately dictates their solvation properties, had not yet been established. The first aim of this project was therefore to probe the liquid structures of these solvents. This was performed using advanced neutron diffraction methods in conjunction with isotopic substitution. The analysis of the diffraction data was carried out via Monte Carlo molecular modelling using the Empirical Potential Structure Refinement (EPSR) method.

The second part of the project formed the first concerted effort to probe, experimentally, the structure of a nanomaterials solution, in order to explore ordering and intermolecular interactions in such a system. These fundamental interactions that permit the dispersion of a wide variety of nanomaterials, yet is not very well understood, and classical theories developed for micro-scale models are still being used despite significant deviations that have been predicted and demonstrated.

7.2 Summary of Findings

The first of the three solvents studied was NMP, which has long been recognised as a very important but unusual solvent, yet the origin of its atypical behaviour was unclear. Neutron scattering data and
molecular modelling analysis revealed a variety of structural features in the liquid. Firstly, a large population of parallel ring approaches was found, similar only to structurally simple benzene, despite NMP’s non-aromaticity. Moreover, despite having a (usually) structure-reducing methyl group, NMP exhibits dense intermolecular packing – greater than all related solvents, apart from benzene. This packing does not occur from hydrogen bonding or ring interactions, but from the dipole-dipole interactions between neighbouring atoms which mediate longer-range molecular organisation in the solvent – a phenomenon found to extend beyond its first solvation shell and into the nanometre range.

DMF and DMA also revealed a wealth of structural information pertaining to spatial and orientational correlations in each of these solvents. As expected of the smaller molecular, the solvation shells in DMF occurred at shorter distances. On average, the total number of molecules in the first solvation shell (coordination number) was calculated to be 12.8 for DMF and 13.0 for DMA. Spherical density functions for both solvents revealed a higher degree of ordering in DMF, with DMA’s isosurface appearing less structured on the whole. Analysis to the level of orientational correlation functions implicated a stronger effect of polar ordering in DMF than DMA too. Further analysis elucidated the important issue of hydrogen bonding that had been often discussed in the literature, that is the extent of C–H - - O hydrogen-bonding in these liquids (in particular in DMF). Analysis of relevant distances, directionality distributions and coordination numbers all pointed to weak hydrogen bonding in both solvents. On average, curiously, a stronger association between the hydrogen bonding donating and accepting groups was found in DMA for which all previous analysis had indicated less local order.

The last part of this work presented the first ever atomistically-resolved neutron scattering measurement of local ordering in a concentrated solution of reduced single-walled carbon nanotubes (SWCNTs) in DMF. Equipped with insights gained on the structure of the pure solvent, comparisons were made as to how the presence of a nanoparticle influenced both local and system solvent structures. Radial distribution functions calculated for solvent molecules from the carbon nanotube showed three distinct, ordered solvation shells, with increased packing density in the first shell,
i.e. nearest to the tube. Additionally, DMF molecules within the shells were preferentially oriented with dipole moments lying tangential to the nanotube axis. Though the phenomenon was found to be strongest nearest to the tube, orientational order was seen to extend well into the third solvation shell, where a preference was seen for the carbonyl side of the molecule to be near the nanotube with both hydrogen atoms pointing towards the nanotube.

A notable percentage of sodium cations were found to coordinate to the charged carbon nanotube surface, though the extent of condensation was not in perfect agreement with the Oosawa-Manning polyelectrolyte model. The non-condensed cations were randomly distributed in the bulk DMF, and there was a region between condensed cations and (approximately) the outer edge of the third solvation shell which remarkably showed no sodium cations – a curious finding which required further examination. A partial association was found between the sodium cation and the oxygen atom in DMF, and whether this might be ion-pair behaviour is currently work in progress.

As for the ammonia molecules, they appear to sit in the bulk of the box, and thus the bulk of the solvent; no orientational preference with respect to the SWCNTs or sodiums was seen and their involvement in solvation of the SWCNT appears negligible. The findings contribute crucial insights that differ from traditional standpoints in understanding nanoparticle dissolution, and emphasise the complexity of interactions involving a solute and a solvent, shedding light on the interrelated solvent effects that arise as a consequence of many-body interaction.
7.3 Future Work

While SWCNTs are the best known and perhaps the most studied low-dimensional material in the liquid phase, metal oxides and hydroxides, dichalcogenides, boron nitride (BN), clays (the most important class of natural 2D silicate minerals) and other materials that are one or several atoms thick have been receiving increasing attention. These functional materials offer high specific surface area, as well as electronic structure and properties that differ from their bulk counterparts due to the low dimensionality. It is expected that the work herein will open up the path for studies of these materials, especially in solution, and encourage researchers to explore the native properties and functions they possess, which in turn result in a better understanding of the world of nanoparticles systems, their properties, and underlying mechanisms, particularly in the liquid phase.

Important future work in the form of investigations that would enhance the scientific importance of the research detailed in this thesis and broaden the impact of this effort include:

**Comparison of Solvation Across Solvents:** There is at present a paucity of data that compare the solubility of some given species in the solvents studied. It would be interesting to examine comparisons in dissolution across the three solvents studied, as well as others, in a systematic study involving a charged or an uncharged species for example. This would elucidate differences across the solvents and enhance the impact of the findings.

**Linking Macroscopic Properties to Molecular Structure:** Thermodynamic properties have been used in the past to infer molecular scale structure, and so it would be interesting to attempt to draw direct links between solvents’ macroscopic properties and their molecular level structure, especially for the three solvents studied here whose structures have been uncovered in unprecedented detail. Examples might include boiling and freezing temperatures, excess molar volumes and excess entropies. A thorough investigation of these links could be an intriguing extension of the current work.
Thermodynamics and Temperature Regimes: While the thermodynamic driving force for the spontaneous dissolution of nanotubide has been proposed to be driven entropically through a balance of counter-ion solvation and OM condensation, it is more likely that both enthalpically and entropically driven dissolution may be possible in differing systems. In this regard, it would be compelling to use calorimetry in order to estimate the enthalpy of dissolution in these systems, at different temperature. This might allow the underlying theoretical basis to be quantified and elucidate anomalous properties from these solutions. For example, nanotubide salts were recently observed to crash out of solution upon heating, which might implicate the solution is enthalpically favourable, and entropically unfavourable.

Nematic Phases: An interesting approach to understanding the nanotubes in solutions could be to study the phase diagram at various concentrations. By preparing very high concentrations of these solutions, where novel gel and liquid crystalline phases are expected to form, a phase diagram can derived. The liquid crystal state is a distinct phase of matter observed between the crystalline and isotropic states and liquid crystal ordering is an opportunity to develop novel materials and applications. In this regard, the use single-chirality SWCNTs will help investigate of whether a nematic phase can form with this nanotubide system. Work is currently in progress to bulk synthesise single chirality SWCNTs, which will be of interest on a thermodynamical level too as their lattice enthalpies will different significantly to conventional mixed-chirality SWCNT samples.

Further Simulations: As mentioned in the discussion in Chapter 6, the positions of the sodium atoms near the carbon nanotube and their absence within the well-ordered solvation shells is an oddity with potentially important phenomenological effects. To determine whether this phenomenon is real, as opposed to an artefact of the EPSR simulation, investigative simulations can be constructed. One test which might be informative would include setting up three different simulations wherein the positions of all sodium atoms are initially placed near the tube, away from the tube, and in the distance region. The simulations can be re-run, with all other parameters being equal, to inspect whether they all equilibrate to
the same positions found here.

The effect of SWCNT concentration on the structure of the solution should be investigated also, as well as the effect of different stoichiometries of the sodium cation. This is crucial in order to develop the understanding of the stability of these solutions. Other simulations can be performed on salts of other carbon nanoparticles dissolved in DMF. In this way, the uniqueness of nanoparticle interactions can be explored. Furthermore, the intense ordering of the DMF molecules and orientational order might suggest restricted rotation of the molecules in solution. In this regard, complementary molecular dynamic simulations might allow the calculation of diffusion constants and thereby further elucidate the solvent’s interaction with the SWCNT.

Finally, a word on simulations. The close agreement between simulation and experiment in all the systems studied herein demonstrates the impressive ability for the molecular modelling methods used herein to describe the real solutions. But it is worth noting that, whilst the preparation of structural models of liquids may be appealingly powerful, there clearly is much scope still to improve the EPSR method. Improvements can be made through development of a realistic many-body potential which could enable testing of a range of possible structures against the data. I believe work on this is currently in progress. What’s more, in this way, different starting configurations can be tested to investigate the role of that the empirical potential plays in driving the simulation towards agreement with the data. Improvements are under way.
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