Preface

Ever since the discovery of graphene in 2004, there has been considerable interest in two dimensional (2D) nanomaterials due to their distinctive properties and the prospect of potential applications. A 2D-nanomaterial may be obtained from the bulk layered material by procedures that can overcome the van der Waals attractive force that hold adjacent layers together. Historically this was first achieved by micro-mechanical cleavage by the deceptively simple procedure of peeling atomically thin single layers from the bulk material using scotch tape. The procedure, unfortunately, is not scalable and consequently alternate procedures, both top-down as well as bottom-up, have been extensively explored. One of the simplest methods to obtain defect-free 2D nanosheets is the sonication assisted liquid phase exfoliation of the bulk layered material in a suitable solvent.

The role of the solvent is crucial to the liquid phase exfoliation process, as the formation of stable dispersions require that the exfoliated sheets, produced on sonication, be prevented from re-aggregating. A wide range of solvents, solvent mixtures and surfactant solutions have been investigated and solvent systems that favour formation of stable dispersions identified. Much of the current understanding of the role of the solvent is based on phenomenological models, matching surface energies of the solvent and the layered material so as to minimize the surface tension between the two. What has remained elusive, however, is a molecular perspective of the nature of interactions between the solvent and the exfoliated nanosheet. This the focus of the present study. This thesis reports results of investigations on dispersions of graphene in aqueous and non-aqueous media as well as dispersions of boron nitride in water using solution and solid-state Nuclear Magnetic Resonance (NMR) spectroscopy aided by Molecular Dynamics (MD) simulations for interpreting the experimental observations.

The thesis is organized as five chapters with **Chapter 1** providing a brief overview of 2D nanomaterials with focus on graphene and boron nitride (BN); their properties and applications. The chapter discusses the methods for obtaining graphene and BN nanosheets with emphasis on the sonication assisted liquid phase exfoliation approach. The chapter also provides a brief review of the phenomenological models that have been advanced to understand the stability of dispersions of 2D nanomaterials in different solvents. The stability of the nanosheet dispersions require that solvent or ligand molecules be in close association with the nanosheets with properties and mobilities quite different from those of the bulk solvent molecules. The challenge for in-situ measurements is to be able to probe the bound or associated solvent/ ligand molecules in the presence of a large excess of the bulk. NMR methods from the solution chemists toolbox are known to provide methodologies that can distinguish bound ligand molecules from those in the bulk and are, therefore, ideal techniques for investigating nanosheet dispersions. In particular transfer Nuclear Overhauser Effect Spectroscopy (tr-NOESY) as well as Rotating-frame Overhauser Effect Spectroscopy (ROESY) are well suited for systems where bound and free solvent/ ligand molecules are in continuous exchange. This chapter also provides a brief overview of the NMR experiments used in studying nanosystem-ligand interactions. The results from NMR measurements provide a spectroscopic signature of solvent nanosheet interactions in the dispersions and in conjunction with Molecular Dynamics

(MD) simulations provide a molecular level understanding of the stability of the dispersions and the role of the solvent. The MD simulation methodology used in this study are discussed in **Chapter 2** along with the computational tools employed in the thesis. Graphene is perhaps the most studied 2D nanomaterial and its distinctive properties has paved the way for the commercial use of graphene-based materials in a variety of applications. Sonication of bulk graphite in an organic solvent or aqueous surfactant solutions has been considered a simple and scalable route for the production of defect free graphene nanosheets. In aqueous solutions the interaction of surfactant chains with the graphene sheets is crucial to the stability of the dispersion. In **Chapter 3**, 1H two-dimensional Nuclear Overhauser Effect spectroscopy (NOESY) and classical MD simulations have been used to probe these interactions in graphene dispersions stabilized by the cationic surfactant cetyltrimethylammonium bromide (CTAB). It is shown from the presence of intense negative transfer-NOESY cross peaks that the surfactant chains are quasi-bound to the graphene sheets and undergo rapid exchange with free surfactant ligands present in the dispersion. A surprising feature of the NOESY is the presence of cross-peaks between groups that are separated by more than 5_A along the chain even between protons of the `head' group of the CTA surfactant chain and protons of the `tail' methyl group. This observation of apparent very short separation of protons of distal groups of the surfactant chain corroborated reects the arrangement adopted by the surfactant chains in the quasi-bound state in the dispersion. Classical MD simulations of the dispersion provides a simple interpretation of these observations. The simulations show that surfactant CTA chains lie at on the graphene sheets adopting a random arrangement with the head of one chain in close proximity to the tail of another chain. This arrangement can give rise to cross peaks in the NOESY between groups that are apparently far separated along the chain. One of the most efficient organic solvents for the sonication assisted liquid phase exfoliation of graphite is N-methyl-2-pyrrolidone (NMP). Much of the success of phenomenological models based on surface energies has been correctly predicting that NMP would be good solvent because its surface energy and that of graphite are comparable. A molecular level understanding of the interaction of NMP and graphene sheets in the dispersion is, however, not available. In **Chapter 4**, it is shown that NMR methods can provide a spectroscopic signature for these interactions. The 2D ROESY NMR shows significant differences in the spectra of graphene dispersions in NMP and the pure solvent. MD simulations of a graphene sheet immersed in NMP solvent molecules show that these differences arise because of induced layering of solvent molecules in the vicinity of the sheet. The arrangement facilitates lowering of the rotational correlation time of the NMP molecules near the surface of the graphene sheet that are easily captured in the experimental two-dimensional ROESY NMR and which manifests as enhanced cross-peak intensities as compared to the bulk solvent.
Among the graphene analogues boron nitride nanosheets has been considered the closest because of the similarities in structures of hexagonal BN and graphite as well as the positions of the respective elements in the periodic table. Their aqueous dispersibilities are, however, very different. While graphene does not exfoliate or form stable dispersions in water the hydrophobic BN forms stable dispersions on sonication in water, without the need for surfactants or stabilizers. In **Chapter 5,** it is shown from zeta potential

measurements that the sheets are positively charged and the stability of the dispersions are electrostatic in origin. The observations indicate that BN reacts with water on sonication. Ab initio (Car-Parinello) MD simulations and reactive force-field (ReaxFF) MD simulations were performed to understand the reactivity, and the origin of the stability of the aqueous dispersions of BN. The simulations showed that water molecules dissociate at the edges of the BN sheets leading to the to the formation of NH bonds with the release of OH into the bulk. The simulations explain why the dispersions are basic and the exfoliated BN nanosheets in the dispersion positively charged. ^{1}H and ^{11}B solid-state NMR spectroscopy were used to identify the chemical species as predicted by the MD simulations. The combination of MD simulations and NMR measurements are able to provide a comprehensive understanding of the origin of the aqueous dispersibility of the hydrophobic BN nanosheets. The results are summarized in Chapter 6.