Dispersing Carbon Nanotubes: Towards Molecular Understanding

Ricardo M. Ferreira Fernandes

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KTH Royal Institute of Technology
School of Chemical Science and Engineering
Department of Chemistry
Applied Physical Chemistry
SE-100 44 Stockholm, Sweden

University of Porto
Faculty of Sciences
Department of Chemistry and Biochemistry
Rua do Campo Alegre
4169-007 Porto, Portugal
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To my family

nanos gigantum humeris insidentes
Bernard of Chartres
Abstract

Carbon nanotubes (CNTs) exhibit unique and fascinating intrinsic electrical, optical, thermal or mechanical properties that lead to a plethora of potential applications in composite materials, electronics, energy storage, medicine, among others. However, the manipulation of nanotubes is not trivial and there are significant difficulties to overcome before achieving their full potential in applications. Because of their high aspect ratio and strong tube-to-tube van der Waals interactions, nanotubes form bundles and ropes that are difficult to disperse in liquids. In this thesis, the topic of dispersing carbon nanotubes in water was addressed by several experimental methods such as nuclear magnetic resonance (NMR) diffusometry and light/electron microscopy. The main goal was to obtain molecular information on how the dispersants interact with carbon nanotubes.

In dispersions of single-walled carbon nanotubes (SWNTs) in water, only a small fraction of the polymeric dispersant (Pluronic F127) was shown to be adsorbed at the CNT surface. Regarding dynamic features, the residence time of F127 on the SWNT surface was measured to be in the order of hundred milliseconds, and the lateral diffusion coefficient of the polymer along the nanotube surface proved to be an order of magnitude slower than that in the solution. The surface coverage of SWNTs by F127 was also investigated and the competitive adsorption of F127 and the protein bovine serum albumin, BSA, was assessed. F127 was found to bind stronger to the CNT surface than BSA does.

Low molecular weight dispersants, viz. surfactants, were also investigated. Using carefully controlled conditions for the sonication and centrifugation steps, reproducible sigmoidal dispersibility curves were obtained, that exhibited an interesting variation with molecular properties of the surfactants. Various metrics that quantify the ability of different surfactants to disperse CNTs were obtained. In particular, the concentration of surfactant required to attain maximal dispersibility depends linearly on alkyl chain length, which indicates that the CNT-surfactant association, although hydrophobic in nature, is different from a micellization process. No correlation between dispersibility and the critical micellization concentration, \( c_{\text{mc}} \), of the surfactants was found. For gemini surfactants of the \( n\)-\( s\)-\( n\) type with spacer length \( s \) and hydrophobic tail length \( n \), the dispersibility of multiwalled carbon nanotubes (MWNTs) also followed sigmoidal curves that were compared to those obtained with single-tailed homologues. The increase in spacer length caused an increase in the dispersion efficiency. The observations indicate a loose type of monolayer adsorption rather than the formation of micelle-like aggregates on the nanotube surface. With the future goal of embedding nanotubes in liquid crystal (LC) phases and thereby creating nanocomposites, the effect of the spacer length on the thermotropic behavior of the gemini 12-\( s\)-12 surfactant was investigated. Different mesophases were observed and a non-monotonic effect of the
spacer length was found and rationalized within a model of the surfactant packing in the solid state.

The relative binding strength of simple surfactants to CNTs was assessed by the amount of F127 they displace from the CNT surface upon addition. Anionic surfactants were found to replace more F127, which was interpreted as a sign of stronger binding to CNT. The data collected for all surfactants showed a good correlation with their critical dispersibility concentration that suggests the existence of a surface coverage threshold for dispersing nanotubes.

On the macroscopic scale, the formation of weakly bound CNT aggregates in homogeneous dispersions was found to be induced by vortex-shaking. These aggregates could quickly and easily be re-dispersed by mild sonication. This counterintuitive behavior was related to the type of dispersant used and of the duration of mechanical agitation and was explained as a result of loose coverage by the dispersant.

**Keywords:** carbon nanotubes, dispersion, surfactants, polymers, adsorption, liquid crystals, nuclear magnetic resonance, self-diffusion.
Sammanfattning

Kolnanorör (CNTs) uppvisar unika och fascinerande elektriska, optiska, termiska samt mekaniska egenskaper som kan leda till en uppsjö av potentiella tillämpningar inom kompositmaterial, elektronik, energilagring, medicin, etc. Det är emellertid inte trivialt hur dessa kolnanorör bör behandlas, det finns betydande hinder att övervinna innan man kan uppnå dess fulla potential inom de olika tillämpningsområdena. På grund av deras starka van der Waals-interaktioner bildar nanorör hårt bundna aggregat som är svåra att dispergera i vätskor. I denna avhandling berörs detta område, dispergering av kolnanorör i vatten, med flera experimentella metoder, bl.a. kärnmagnetisk resonans (NMR) diffusometri och ljus- och elektromikroskopi. Huvudsyftet har varit att få molekylär information rörande hur olika dispergeringsmedel interagerar med kolnanorör.

I dispersioner av enkel-väggs kolnanorör (SWNT) i vatten, kunde det påvisas att endast en liten del av det polymera dispergeringsmedlet (Pluronic F127) adsorberar på kolnanorörens yta. Beträffande dynamiska egenskaper så uppmättes uppehållstiden för F127 på SWNT till att vara i storleksordningen hundra millisekunder samt den laterala diffusionskoefficienten av F127 långs ytan en storleksordning långsammare än den i vattenlösning. Hur stor del av SWNTs yta som var täckt av F127 undersöktes också. Genom att studera den konkurrande adsorptionen mellan F127 och proteinet bovint serumalbumin (BSA), bedömdes det att F127 binder starkare än BSA till ytan.

Lågmolekylära dispergeringsmedel, s.k. surfaktanter, undersöktes med noga kontrollerade ultraljuds- och centrifugeringssteg. Utifrån dessa kunde reproducerbara sigmoidala dispergeringsskurvor erhållas, vilka upvisade ett intressant beroende av tensidernas molekylära egenskaper. Olika mått på de olika ytaktiva ämnenas förmåga att dispergera CNT kunde därmed erhållas. I synnerhet visade det sig att koncentrationen som krävs för att uppnå maximal mängd dispergerade nanorör berodde linjärt på alkylkedjelängd hos surfaktanterna. Detta tyder på att interaktionen mellan CNT och surfaktanten, även om den är av hydrofob karakter, är annorlunda än den som återfinns vid en micellisering. Inget samband mellan mängden dispergerade nanorör och den kritiska micellarisationskoncentrationen (cmc) av de surfaktanterna kunde påträffas. För tvillingsurfaktanter av n-s-n typ, där s är längden mellan svansarna och n är längden på de hydrofoba svansarna, var dispergeringsskurvorna för flerväggiga kolnanorör (MWNTs) också sigmoidala och kunde därmed jämföras med de som erhölls med enkelsvansade homologer. Det kunde observeras att en ökande s orsakade en ökning av dispergeringsmedlets effektivitet, vilket indikerar en svag monoskiptadsorption snarare än micelliskt aggregering på kolnanorör ytan. Med det framtida målet att dispergera nanorör i flytande kristaller (LC), undersöktes effekten av längden s på det termotropa beteendet hos tvillingsurfaktanter av typen 12-s-12. Det kunde
iaktas olika mesofaser och en icke-monoton effekt av s hittades, vilket förklaras av en modell som beskriver den fasta fasens ytaktiva packning.

Den relativa bindningsstyrkan mellan de enkla surfaktanter och CNTs uppskattades genom den mängd av F127 som de avlägsnar från CNTs yta när de tillsätts dispersionen. Anjontensider visade sig avlägsna störst mängd F127, vilket tolkades som ett tecken på dess starkare bindning till CNT. Sammanfattningsvis kunde ses en god korrelation mellan den relativa bindningsstyrkan och tensidernas s. k. kritiska dispergeringskoncentration, vilket tyder på förekomsten av en sorts täckningströskel för surfaktanters förmåga att dispergera kolnanorören.

På makroskopisk skala, kunde bildandet av svaga kolnanorörsaggregat i homogena dispersioner visa sig induceras av virvelsblandning. Dessa aggregat kunde dock snabbt och enkelt återdispergeras genom en mild ultraljudsbehandling. Detta omvänt beteende kunde relateras till den typ av dispergeringsmedel som användes samt till hur länge den mekaniska omrörningen pågick och förklaras som ett resultat av en relativt svag interaktion mellan dispergeringsmedlet och kolnanorören.

**Nyckelord:** kolnanorör, dispersion, ytaktiva ämnen, polymerer, adsorption, vätskekristaller, kärnmagnetisk resonans, själldiffusion.
Resumo

Os nanotubos de carbono (CNTs) combinam num só material propriedades elétricas, óticas, térmicas e mecânicas únicas, que potenciam uma enorme diversidade de aplicações, desde materiais compósitos, à eletrónica molecular, ao armazenamento de energia até à nanomedicina. No entanto, devido às fortes interações de van der Waals que estabelecem entre si, os CNTs agregam-se em pequenos aglomerados, o que dificulta a sua dispersão em líquidos e posterior manipulação. Neste trabalho, com o objetivo principal de compreender a nível molecular as interações não-covalentes estabelecidas entre os CNTs e os respetivos dispersantes, estudou-se a dispersão de CNTs em água utilizando diferentes dispersantes (baixa e alta massa molecular) através de várias técnicas experimentais, tais como a ressonância magnética nuclear (RMN) de auto-difusão e microscopia de luz/eletrónica.

Para dispersões aquosas de nanotubos de carbono de parede única (SWNT), foi demonstrado que apenas uma pequena fração do dispersante polimérico (Pluronic F127) está adsorvido à superfície do CNT. Relativamente à dinâmica do polímero adsorvido no nanotubo, verificou-se que o tempo de residência do F127 na superfície do SWNT é da ordem de centenas de milissegundos, e o coeficiente de difusão lateral do polímero ao longo da superfície do nanotubo é uma ordem de grandeza mais lenta do que em solução. A cobertura da superfície de CNTs pelo F127 foi investigada e a adsorção competitiva entre o F127 e a proteína de albumina de soro bovino (BSA) foi também avaliada. Verificou-se que o polímero F127 se liga mais fortemente à superfície do SWNT do que a BSA.

A capacidade de dispersantes de baixa massa molar, i.e. tensioativos, para dispersar CNTs em água foi também estudada. Utilizando condições rigorosamente controladas nos passos de ultrasonicação e centrífugação, obtiveram-se curvas de dispersibilidade de CNTs em função da concentração de dispersante que apresentam um perfil sigmoïdal, o que permitiu extractar novos parâmetros que caracterizam a capacidade de dispersão dos diferentes tensioativos. Determinou-se assim a concentração mínima de tensioativo necessária para que ocorra dispersão de CNTs, designada concentração de dispersibilidade crítica (cdc). Adicionalmente, verificou-se que a dispersibilidade máxima de CNT varia linearmente com o comprimento da cadeia alquilica do tensioativo, o que indica que a associação CNT-tensioativo, embora de natureza hidrofóbica, é diferente do processo de micelização. Não se observou correlação entre a dispersibilidade e a concentração micelar crítica (cmc) dos tensioativos.

Para tensioativos gemini do tipo n-s-n, com espaçador s e comprimento da cadeia alquilica n, a dispersibilidade de nanotubos de carbono de parede múltipla (MWNT) em água, segue também uma curva sigmoïdal; os resultados foram criticamente comparados com a dispersibilidade de MWNTs promovida pelos respetivos tensioativos homólogos de cadeia simples. Verifica-se que o aumento do
comprimento do espaçador s conduz a um aumento na eficiência de dispersão, o que indica que a adsorção do tensioativo ocorre na forma de uma monocamada desorganizada não-compacta, em vez da formação de agregados micelares na superfície do nanotubo. Adicionalmente, com o objetivo futuro da incorporação de CNTs em cristais líquidos, criando-se assim um nanocompósito, o efeito do comprimento do espaçador s no comportamento termotrópico da família de tensioativos gemini 12-s-12 foi investigado. Diferentes mesofases foram observadas e verificou-se um efeito não monótono do comprimento do espaçador, que foi interpretado de acordo com um modelo de empacotamento do tensioativo no estado sólido.

A afinidade de diferentes tensioativos para a superfície dos nanotubos de carbono foi avaliada através da monitorização da fração de F127 deslocada da superfície do CNT após adição do respetivo tensioativo. Verifica-se que os tensioativos aniónicos substituem mais F127, o que foi interpretado como evidência de uma maior afinidade para com a superfície do CNT. Os dados recolhidos de todos os tensioativos mostraram uma boa correlação com a sua concentração de dispersibilidade crítica (cdc), o que sugere a existência de um limiar de cobertura da superfície para que ocorra dispersão de nanotubos.

À escala macroscópica, verifica-se que a agregação de CNTs dispersos em água é induzida pela aplicação de agitação do tipo vórtex. Estes agregados são rapidamente re-dispersos pela aplicação de ultrasonicação suave. Diferentes dispersantes foram avaliados e os resultados foram interpretados como consequência de uma menor ou maior extensão da cobertura da superfície do CNT.

**Palavras-chave:** nanotubos de carbono, dispersão, tensioativos, polímeros, adsorção, cristais líquidos, ressonância magnética nuclear, auto-difusão.
List of papers

I. Lateral diffusion of dispersing molecules on nanotubes as probed by NMR
Ricardo M.F. Fernandes, Matat Buzaglo, Michael Shtein, Ilan Pri Bar, Oren Regev, Eduardo F. Marques and István Furó

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*J Phys Chem C, 2015, 119, 22190–22197*

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Ricardo M.F. Fernandes, Bárbara Abreu, Bárbara Claro, Matat Buzaglo, Oren Regev, István Furó and Eduardo F. Marques
*Langmuir, 2015, 31, 10955-10965*

IV. Assessing surfactant binding to carbon nanotubes via competitive adsorption: binding strength and critical coverage
Ricardo M.F. Fernandes, Jing Dai, Oren Regev, Eduardo F. Marques and István Furó
*Manuscript*

V. Mechanical agitation induces aggregation of pre-dispersed carbon nanotubes
Ricardo M.F. Fernandes, Matat Buzaglo, Oren Regev, István Furó and Eduardo F. Marques
*Manuscript*

VI. Gemini surfactants as dispersants of multiwalled carbon nanotubes: a systematic study on the role of molecular structure
Jessica Rocha, Ricardo M.F. Fernandes, Oren Regev, István Furó and Eduardo F. Marques
*Submitted for publication*

VII. Strong spacer length effects on the thermal behavior and mesophase formation by gemini surfactants
Ricardo M.F. Fernandes, Yujie Wang, Pedro B. Tavares, Sandra C.C. Nunes, Alberto A.C.C. Pais and Eduardo F. Marques
*Manuscript*
The author contribution to the appended papers

I. Prepared all the samples, performed all the NMR experiments and data analysis. Participated in the writing of the manuscript.

II. Participated in the planning, performed all the experimental work, data analysis and participated in the writing of the manuscript.

III. Participated in the planning, instructing and performed part of the experimental work. Contributed in the data analysis and writing of the manuscript.

IV. Planning, performed the majority of the experimental work and data analysis. Participated in the writing of the manuscript.

V. Planning, performed the majority of the experimental work and participated in the writing of the manuscript.

VI. Planning and part of the experimental work; contributed to the writing of the manuscript.

VII. Performed part of the experimental work and contributed to the writing of the manuscript.

Other papers of the author not included in this thesis:

Enhanced interfacial properties of novel amino acid-derived surfactants: Effects of headgroup chemistry and of alkyl chain length and unsaturation
Rodrigo O. Brito, Sandra G. Silva, Ricardo M.F. Fernandes, Eduardo F. Marques, José Enrique-Borges and M. Luísa C. do Vale

Serine-Based Bis-quat Gemini Surfactants: Synthesis and Micellization Properties
Sandra G. Silva, Ricardo M.F. Fernandes, Eduardo F. Marques and M. Luísa C. do Vale
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1. Introduction

1.1. Carbon nanotubes

The discovery of carbon nanostructures such as the fullerenes (in comparison, point-like and thereby zero dimensional 0D), carbon nanotubes (1D) and graphene (2D), strongly contributed to the development of nanoscience and nanotechnology. Within these nanostructures, carbon nanotubes appeared as candidates for a plethora of applications. In the next subsections the structure and properties of carbon nanotubes will be described, followed by a brief overview of the nanotubes synthesis. In the last part of this section the different approaches to disperse nanotubes will be discussed with particular emphasis on the dispersion in water using surfactants and polymers.

1.1.1. Structure and properties

Structure

Carbon nanotubes (CNTs) constitute a rather new allotrope of carbon, having been given renewed attention in 1991 by Iijima. In the nanotube lattice, each carbon atom is bound to three other atoms, forming a sp\(^2\) hybridized hexagon network. The carbon atoms are connected by three \(\sigma\) bonds. In addition, a \(\pi\) system is formed by electrons accommodated in the non-hybridized \(p\) orbitals of adjacent carbon atoms in the lattice. Moreover, the electrons that are participating in the aromatic \(\pi\) system can act as charge carriers, and hence make nanotubes electrically conductive.

![Theoretical construction of a CNT](image)

**Figure 1.** Theoretical roll-up of a carbon nanotube from a graphene sheet. Reprinted with permission from Springer-Verlag.

CNTs can be easily visualized by the roll up of a graphene sheet (the single atomic layer that constitutes graphite) into a hollow cylinder with the hexagonal rings seamlessly fused (Figure 1). The number of graphene sheets that compose the nanotube wall is used to classify the type of CNTs. Therefore, CNTs fall in two major categories, designated as 1) single-walled carbon nanotubes (SWNTs)—formed by one rolled-up layer of graphene; and 2) multiwalled carbon nanotubes (MWNTs)—composed by several (two or more) layers.

The dimensions of SWNTs and MWNTs are similar in terms of length, \(L\) (in favorable cases, up to hundreds of \(\mu\)m). However, as expected, the two types differ
considerably in their diameter, $d$. Typically, for SWNTs $d$ is in the range of 0.7–2 nm. MWNTs present higher $d$ values, which is dependent on the number of graphene layers that comprises the nanotube. The separation between the layers in the MWNT is typically 0.34 nm (same range as that for graphite). Thus, considering a MWNT with an inner diameter $d=2$ nm and outer diameter $d=20$ nm, it will be formed by 53 coaxial tubes. Moreover, MWNT samples are typically composed by nanotubes with different number of concentric layers; thereby $d$ is rather polydisperse.\textsuperscript{6,8}

![Three SWNT with different structures. Armchair (left), zigzag (center) and chiral (right). Reprinted with permission from the authors.\textsuperscript{9}](image)

Considering a SWNT, rolling up of the graphene sheet into a cylinder may produce nanotube structures with different diameters and topologies. Figure 2 summarizes the three general structures formed: armchair, zigzag and chiral. These structures differ from each other as concerning the direction (with respect to the bond angles within the sheet) of the axis of the hypothetical cylinder around which the sheet is rolled up.

![Graphene honeycomb lattice with the lattice real space unit vectors vector ($\vec{a}_1^*$, $\vec{a}_2^*$) which defines the chiral vector $\vec{C}=4\vec{a}_1^*+2\vec{a}_2^*$ of the (4,2) tube, and characterizes the circumference $C$ of the tube. The red rectangle represents the unit cell of the (4,2) SWNT, defined by the translational vector T. The chiral angle $\theta$ is defined between $a_1$ and $C$. The zigzag and the armchair patterns are highlighted.](image)
The simplest way to quantify the structure of an individual SWNT is using a vector model (Hamada indices).\(^6\)\(^-\)\(^8\) As shown in Figure 3, using the graphene lattice real space unit vectors \((\vec{a}_1, \vec{a}_2)\) and a pair \((n, m)\) of integers one can characterize the nanotube structure by the chiral vector \(\vec{C}\):

\[
\vec{C} = n\vec{a}_1 + m\vec{a}_2
\] (1.1)

In the carbon nanotubes, the graphene sheet is rolled-up in such a way that the \(\vec{C}\) chiral vector becomes the circumference \(|\vec{C}|\) of the nanotube. Therefore, the diameter of the nanotube can be easily calculated by:

\[
d = \frac{\vec{C}}{\pi} = \frac{a\sqrt{n^2 + nm + m^2}}{\pi}
\] (1.2)

where \(a = |\vec{a}_1| = |\vec{a}_2| \approx 0.249\) nm. The orientation of the hexagonal rings in the honeycomb lattice relative to the nanotube axis is defined by the chiral angle \(\theta\), which is defined as the angle between \(\hat{a}_1\) and \(\vec{C}\), calculated according to:\(^9\)

\[
\theta = \arctan(\sqrt{3m/(2n + m)})
\] (1.3)

Due to hexagonal symmetry of the graphene sheet, the chiral angle varies between 0° to 30°. Figure 3 shows that the chiral angle is 0° to zigzag nanotubes and 30° to armchair nanotubes. Armchair and zigzag nanotubes are characterized by a high symmetry and they do not have any enantiomeric pair, i.e. the mirror image is superimposable with the original structure. For chiral nanotubes, a specific \((n,m)\) SWNT has two enantiomers.\(^6\)\(^,\)\(^7\)

In summary, nanotubes are described by the pair of indices \((n,m)\). These two numbers allow the calculation of the nanotube diameter and the chiral angle \(\theta\). It is expected that nanotubes with different chirality \((n,m)\) display different properties as is described in the next section.

**Properties**

Nanotubes are characterized by the high \(L/d\) aspect ratio, achieving in most cases lengths \(10^3\) times (or more) larger than the diameter.\(^{11}\) Because of the high aspect ratio \(L/d\), CNTs are commonly designated as quasi-one-dimensional materials. Therefore, it is not surprising that their properties are strongly direction-dependent, i.e. anisotropic. The \(\sigma\) and \(\pi\) bonds established between the carbon atoms in the hexagonal lattice, combined with the high aspect ratio and the nanometer-size of the nanotubes confers to this carbon allotrope unique electric, optical, mechanical and thermal properties.
The electronic properties of CNTs arise due to the confinement of electrons in the nanotube. Moreover, depending on the structure, CNTs can be metallic, like copper, or semiconducting, like silicon. Band gap calculations predict that metallic nanotubes fulfil the condition:

\[(n - m) = 3q\]  

where \(q\) is an integer. Therefore, all armchair nanotubes are metallic (e.g. \(4-4=3q, q=0\)). Moreover, this equation implies that for each of the two other general nanotube classes (zig-zag and chiral), \(1/3\) are metallic and \(2/3\) are semiconducting. Additionally, the curvature of the graphene sheet into nanotube introduces some strain in the bond angles (i.e. carbon atoms are pyramidalized in the nanotube structure) and the \(\pi\) orbitals are slightly misaligned. Consequently, the curvature effect shifts metallic non-armchair tubes towards semiconducting, but since the size of the gap is rather small at room temperature, these tubes in practice display metallic behavior.

Carbon nanotubes absorb light in a broad wavelength range, from UV to near-infrared, with absorbance strongly dependent on wavelength. Absorption by individual SWNT at discrete wavelengths is determined by the van Hove singularities, corresponding to electronic transitions between different states. Because of the 1D geometry of CNTs, electrons are located in discrete energy bands, and only certain transitions are permitted leading to discrete peaks in the spectra.

The band gap energies in the nanotubes are related to the peaks in the optical absorption spectra, because both are connected to the density of the electronic states. Since the structure of the nanotube dictates the density of electronic states, the absorption peaks (van Hove singularities) can be used to determine the nanotube structure. Transitions indexed as by \(E_{11}^S, E_{22}^S, E_{11}^M\), etc where the subscripts refer to the electronic energy bands and superscripts represent metallic (M) or semiconducting (S) tubes. The metallic \(E_{11}^M\), transitions arise in the UV-vis region from 350-620 nm, overlapping at some extent with the \(E_{11}^S\). Despite the theoretical possibility to determine the different types of nanotubes in a sample by optical absorption, in practice the overlap between the absorption bands frequently hampers this. Moreover, the bundling of nanotubes, generally, broadens and slightly red-shifts the peaks, making identification even more difficult.

It is well established that CNTs are the stiffest and strongest material produced so far. The strong sp\(^2\) C\(=\)C bonds in the CNT lattice confer to it high mechanical resistance. Axial tensile tests reported values around 1000 GPa for the tensile modulus, roughly 5 times higher than that for steel. In terms of tensile strength, nanotubes can achieve 63 GPa, a value approximately 50 times higher than that for steel. However, under compression nanotubes can buckle relatively easily. Measurements of the radial elasticity suggest that van der Waals forces can deform
two adjacent nanotubes and that the radial tensile modulus is in the order of 30 GPa.\textsuperscript{15-17}

Crystalline carbon presents the highest thermal conductivities, $k$, of all known materials.\textsuperscript{12} Calculations of an isolated (10,10) nanotube predicted a value of $k=6600$ W·m\textsuperscript{-1}·K\textsuperscript{-1} at room temperature (for sake of comparison, for copper $k=400$ W·m\textsuperscript{-1}·K\textsuperscript{-1}).\textsuperscript{18} Experimental studies on SWNT have given values varying from 2000-10,000 W·m\textsuperscript{-1}·K\textsuperscript{-1} at room temperature. Thermal conductivity of CNTs, like to the other properties, is anisotropic. It is extremely high along the nanotube axis, however, the radial thermal conductivity is order of magnitudes lower.\textsuperscript{19}

Thus far, it was elucidated that nanotubes with different structures display different properties. However, to explore the full potential of nanotubes properties, it is important to have them in their individual state, and not in mats, bundles and ropes (see Figure 4). Additionally, it is also necessary to develop synthetic processes to produce them in bigger scales. In the next section, the methodologies to synthesize nanotubes will be briefly described.

### 1.1.2. Synthesis

Carbon nanotubes can be visualized by rolling up graphene sheets into a hollow cylinder. However, CNTs are in reality grown using other approaches. Thus far, there are three main ways to produce CNTs: \textit{arc discharge}, \textit{visible light vaporization} and \textit{chemical vapor deposition} (CVD) which are briefly outlined below; for additional details the reader is referred to a number of textbooks.\textsuperscript{1, 6, 8, 10, 12}

In the \textit{arc discharge} method, the ends of two graphite rods are placed close to one another under reduced pressure. The chamber is usually filled with an inert gas like helium (or argon) at a pressure around 0.7 atm. An electric arc is established between the graphite rods which increases the temperature in the surface enough to sublimate carbon. A deposit (soot) formed on the cathode contains then CNTs. With no metal catalyst, the nanotubes generated are MWNTs; introducing catalyst SWNTs are formed. This method is easy to set up and operate and quite inexpensive. However, the CNT yield is low and an extra purification step is necessary.\textsuperscript{6}

In the \textit{visible light vaporization} method (using a laser or a solar furnace as source) light is focused at high intensity on a graphite block placed in a chamber filled with He or Ar at a reduced pressure. The solid graphite is then converted into small vaporized particles. By providing a suitable temperature gradient in the system by an inert gas flow, those particles are collected and upon collision recombine into nanotubes. A catalyst can be introduced to tune the type of CNT that is formed. This process is not easy to scale up, the cost is quite high and is difficult to operate. On the other hand, the yield of nanotubes formed is around 50\% and the nanotubes produced have low defect density.\textsuperscript{6}

In the \textit{CVD} method, multiple carbon based materials (e.g. C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}, CO) can be used as the source of carbon during the growth of CNTs. Basically, the CVD is a
thermal reaction where a catalyst (e.g. nickel, cobalt, iron) is used to break down the source molecules and feed the growth of the nanotube. In contrast to the previous methods, in CVD the presence of catalyst is mandatory. Typically, the temperature involved is rather low.\textsuperscript{6}

The CVD method produces SWNTs with a relatively high yield, which makes this method a good candidate to manufacture nanotubes in industrial quantities. Therefore, this method is one of the most studied (e.g. combination of different catalysts with different hydrocarbons at different pressures). Among the variants of CVD method, the two most important processes to produce high purity SWNTs are HiPCO\textsuperscript{®} and CoMoCAT\textsuperscript{®}. In HiPCO (High-Pressure Carbon Monoxide Process), SWNT are grown by the thermal decomposition of iron pentacarbonyl, Fe(CO)\textsubscript{5}, in a flow of CO at high pressures and temperatures.\textsuperscript{20} In CoMoCAT (Cobalt-Molybdenum Catalysis), CNTs are grown on a silica support with Co:Mo immobilized, by CO disproportionation (decomposition into C and CO\textsubscript{2}).\textsuperscript{21}

The development of the methods for CNT synthesis is still a hot topic where tailoring the processes in order to obtain a particular type of CNT is much sought after. Typically, different approaches produce a mixture of nanotubes with different chiralities rather than a unique chirality. Thus, processes to separate the different types of nanotubes are still needed.

1.1.3. Functionalization and dispersion of nanotubes – overview

As it was mentioned, the properties of the nanotubes are dictated by the structure of the material. However, current synthetic methodologies cannot produce a particular type of CNT with a specific chirality. Instead, clusters of nanotubes with different chiralities and diameters are produced all together. Furthermore, all production methods yield CNTs in the form of bundles (Figure 4) due to the strong tube-to-tube van der Waals interaction, which makes the hydrophobic nanotubes virtually insoluble in common liquids. Therefore, in order to get the full potential of the nanotube applications, two major drawbacks need to be overcome: 1) dispersion in a solvent and 2) efficient separation according to the chirality.\textsuperscript{3, 5, 22, 23}

Figure 4. a) TEM image of a SWNT bundle (reproduced with permission from the American Association for the Advancement of Science\textsuperscript{24}); b) SEM Image of entangled MWNT agglomerates (reproduced with permission from Elsevier \textsuperscript{25}).
Because the terminologies “solubilization” and “dispersion” of nanotubes are used ambiguously in the literature, the term “dispersion” must be clarified. For nanotubes distributed homogeneously in a solvent the term dispersion is more accurate because carbon nanotubes do not form true thermodynamically stable “solutions” but more likely are metastable. Henceforth, within this thesis the terms dispersion and dispersibility are used.  

Up to now, three main pathways have been explored to disperse nanotubes in liquid medium: 1) in organic solvents; 2) by covalently functionalize and 3) by noncovalently functionalize the CNT. The three methods to disperse CNTs are briefly discussed below. The noncovalent functionalization of CNTs in water is discussed in more detail in section 1.1.4.

**Organic solvents**

The use of organic solvents is one of the possible approaches to separate and disperse nanotubes in liquid medium. Carbon nanotubes are hydrophobic, thus it is expected that organic solvents wet CNTs. However, CNTs are only dispersed in a rather limited number of solvents, such as *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylformamide (DMF), o-dichlorobenzene and chloroform.  

Coleman and coworkers, based on thermodynamic considerations, proposed that organic solvents would spontaneously disperse nanotubes if the Gibbs energy of mixing, $\Delta G_{\text{mix}}$, is negative. Typically, dissolution is driven by the entropy of mixing $\Delta S_{\text{mix}}$. However, the CNTs are extremely large and thereby the entropy of mixing, $\Delta S_{\text{mix}}$, is small and is generally not sufficient to overcome the positive enthalpy of mixing, $\Delta H_{\text{mix}}$ (due to strong attraction between nanotubes). Therefore, nanotubes will be dispersed when $\Delta H_{\text{mix}}$ is negative. It is known that $\Delta H_{\text{mix}}$ can be approximated by the Hildebrand–Scatchard equation. Hence, dispersion of CNTs will be facilitated when the Hildebrand solubility parameter of the solvent matches that of CNT (the solute).

Bergin *et al* investigated the dispersibility of nanotubes in several solvents. The solubility of nanotubes was analyzed both under the Hildebrand and Hansen parameters. The authors showed that solvents with surface energies very close to the surface energy of graphite (40 mJ·m$^{-2}$) tend to successfully disperse CNTs. However, this does not mean that all solvents with surface tension equal to 40 mJ·m$^{-2}$ will successfully disperse nanotubes. Thus, surface energy solubility parameters connected with Hansen parameters were developed. However, despite advances in modeling, a deeper understanding of nanotube behavior in organic solvents is still needed.
**Covalent functionalization**

Dispersibility can be affected by covalently attaching hydrophilic groups to the nanotube surface. Those groups are going to 1) interact with the solvent enhancing the dispersibility of nanotube and 2) enhance the repulsion between the nanotubes hence diminishing the cohesion between them. The main drawback of this approach is that chemical bonding with the CNT wall changes the carbon sp² hybridization state to sp³. Moreover, during this process often harsh chemical conditions are used (e.g. high acidity) that can introduce structural defects in the nanotube wall. Consequently, this approach is less attractive due to the loss of CNTs properties that are extremely dependent on the sp² hybridization (particularly, the electrical and optical properties).5, 34

**Noncovalent functionalization**

Among the several methods to disperse carbon nanotubes, noncovalent functionalization is widespread. They are based on having some molecules (like surfactants and polymers) physically adsorbed to the CNT surface. In contrast to covalent functionalization, no chemical reactions take place in the nanotube walls. Hence, the sp² hybridization of carbon atoms is kept intact and the π system is not disrupted. Moreover, different molecules may adsorb differently to CNTs with different chirality. Thus, noncovalent methods open the possibility to sort CNTs using techniques such as electrophoresis,35 36 density gradient ultracentrifugation,37 or gel chromatography.38 In section 1.1.4. noncovalent functionalization of CNTs in water will be discussed further.

**1.1.4. Dispersibility and colloidal stabilization of CNTs in water**

Since water is non-toxic, and performs as solvent in many industrial processes, it is important to study the dispersibility and stabilization of non-covalently functionalized CNTs in water (see above). In this methodology, ultrasonication is used to create temporarily a gap in the nanotubes bundle (overcoming the tube-to-tube attractive interactions). The dispersant molecules with affinity to the nanotube adsorb at the pristine surfaces provided by sonication and ultimately, prevent reaggregation of the nanotube. This process of exfoliation is known as the unzipping mechanism (Figure 5),39 where the high local shear forces produced by ultrasonication open gaps at the ends of nanotubes bundles (Figure 5 b). These gaps become new available sites where surfactant may adsorb, preventing nanotube reaggregation (Figure 5 c). Due to the turbulent regime of the system during sonication, the opening-up of the gap proceeds randomly yet continuously. The surfactant coverage is built up along the opened sections of the gap either by surface diffusion or bulk diffusion within the solvent phase until a nanotube can be completely separated from the bundle (Figure 5 d). This mechanism describes the exfoliation process in general. However, the microscopic picture of the CNT
exfoliation is more complex. In general, efficient dispersion of nanotubes requires that the dispersants have 1) an anchoring part that attaches to the CNT surface, and 2) a stabilizing part that interacts favorably with water.

Figure 5. The unzipping mechanism of exfoliation: (a) a bundle of CNTs; (b) high local shear forces open a gap at the bundle end; (c) surfactant molecules adsorb in the new area created, and prevent nanotube reaggregation. The opening progresses along the nanotube length, akin to unzipping; (d) a nanotube coated by surfactant is released and remains dispersed in solution.

Pristine carbon nanotubes lack charge or permanent dipole moment. Therefore, no strong molecular interactions are expected to occur with water dipoles, which makes nanotubes virtually insoluble in water. Moreover, the lack of interaction with water results in a hydrophobic surface, characterized by a possible entropically unfavorable orientation of water molecules adjacent to the surface. This phenomenon is general for all hydrophobic molecules and moieties. Therefore, when a hydrophobic surface and a hydrophobic moiety are coming together, the entropically unfavorable organized water is released to the bulk, thereby reducing the total Gibbs energy of the system.\(^4^6\) The hydrophobic interaction is the driving force to adsorption on the nanotube surface. Indeed molecules with hydrophobic moieties, such as surfactants, block co-polymers and proteins have been exploited to disperse nanotubes.\(^5^, 4^1^\textendash 4^5\)

In addition to hydrophobic interaction, another important molecular interaction exists between aromatic molecules, i.e. the so-called $\pi-\pi$ interaction.\(^4^6\) Since nanotubes are aromatic these interactions can also lead to adsorption on the nanotube surfaces.\(^5^, 3^4\textendash 4^7\)

Adsorption of molecules to CNTs is a prerequisite to disperse them, yet not enough per se. In order to keep nanotubes apart after sonication, it is also important to create a repulsive barrier that prevents their re-aggregation.

Noncharged molecules, such as block copolymers and nonionic surfactants, are also known to effectively disperse carbon nanotubes. In this case the repulsive barrier for the nanotube dispersibility arises from steric stabilization.\(^4^8\) In this process the hydrophobic part of the polymer (or surfactant) adsorbs on the nanotube
while the hydrophilic part produces a layer that will be strongly hydrated and expands out and away the nanotube surface towards the solvent to gain configurational entropy. When nanotubes coated with the dispersant approach each other the adsorbed layers produce a strong repulsion due two main effects: 1) reduction of the configurational entropy of the hydrated moieties leading to an increase in the Gibbs energy of the system and 2) unfavorable mixing of the adsorbed layers due to osmotic repulsion.\textsuperscript{49, 50}

For charged species, this may be the electrostatic repulsion. Ionic surfactants adsorbed on carbon nanotubes confer in effect charge to the nanotube and, with a diffuse layer of counterions, dress the nanotubes in an electrical double layer. The diffusive nature of the counterions creates a measurable surface charge, quantified as zeta potential, $\zeta$.\textsuperscript{23, 49} The repulsive interactions between the electrical double layers stabilize the nanotube dispersion. The effect of the mutually opposing electrostatic and van der Waals potential energy barriers is summarized in the DLVO theory, which predicts the colloidal stability of the dispersions.\textsuperscript{49,53} Conversely, the $\zeta$ potential gives information about the binding of surfactant to the CNT surface.\textsuperscript{52}

The DLVO theory only takes into account the attractive van der Waals and repulsive double layer interactions. However, steric forces, hydrodynamic forces, and hydration forces \textit{inter alia} are not considered by the theory.\textsuperscript{40}

Thus far, the type of interactions established between dispersants and CNTs and the stabilization mechanism (electrostatic and steric) was presented. The combinations of these factors for each dispersant molecule are the key features to control the nanotube dispersion in water. In the following two subsections, I will discuss the ability of different dispersants (both surfactants and polymers) to disperse CNTs, and detail the different mechanisms of interaction and the possible configuration/model of the dispersant around the CNT.

**CNTs dispersibility by surfactants**

Due to their amphiphilic structure, surfactants adsorb at interfaces, modifying properties such as surface tension, wettability and surface charge of the interface.\textsuperscript{53} These properties play an important role in the dispersibility and stabilization of nanotubes in water. In addition, at a critical concentration, surfactants self-assemble in mesoscopic structures, e.g. micelles. The properties and the bulk phase behavior of surfactants in water will be described in more detail in the section 1.2.1.

Surfactants with different chemical structure are expected to adsorb and disperse nanotubes to a different extent. A large number of works in the literature address this question.\textsuperscript{5,22,23,34,41,42,54-64} However, due to the widely different conditions of sample preparation and the variation of the properties of pristine nanotubes used, the results from different works can typically not be compared.\textsuperscript{63} This makes it difficult to safely discern trends.
In an early report Bandyopadhyaya et al. tested several surfactants to disperse SWNTs.\textsuperscript{64} Later, Smalley and coworkers also reported the use of surfactants to disperse as-produced HiPCO SWNTs.\textsuperscript{42} Among the ionic surfactants, it was reported that the surfactant sodium dodecyl benzene sulfonate (SDBS) gives the most well resolved (absorption and fluorescence) spectra and, thereby, most individual SWNTs. Islam and coworkers carried out a systematic study of sodium dodecyl sulfate (SDS), SDBS and TritonX-100, showing that SDBS and Tx-100 are more effective in dispersing SWNTs. The authors suggested that surfactants with benzene rings will enhance the dispersibility of the SWNT due to $\pi-\pi$ stacking interactions.\textsuperscript{41} Other studies have also indicated that surfactants with aromatic moieties present higher capability to disperse CNTs.\textsuperscript{47, 57, 65} Additionally, bile salts are also reported as good nanotube dispersants.\textsuperscript{54, 62, 66}

Surfactants are expected to adsorb in some morphology onto the CNT surface. It remains difficult to assess this morphology, since the available methods are model-dependent and/or somewhat invasive. Yet, cryo-transmission electron microscopy (cryo-TEM), small-angle neutron scattering (SANS) and molecular dynamics simulations seem to provide some insight (Figure 6). SANS studies suggested a random adsorption of surfactant monolayer onto the CNT.\textsuperscript{61} On the other hand, cryo-TEM observations shown both CTAB spherical micelles adsorbed on SWNTs (Figure 6 d)\textsuperscript{67} and ordered arrays of CTAB cylindrical micelles embedding CTAB-coated SWNTs (Figure 6 e).\textsuperscript{68} Molecular dynamics simulations pointed that weakly amphiphilic molecules may form a random monolayer (Figure 6a), whereas more hydrophobic surfactants form aggregates at the CNT surface (Figure 6 b-c).
addition, simulations have shown that, in equilibrium, a dynamic balance between the surfactant in the free and adsorbed state is established.\textsuperscript{56, 69} Not only the chemical structure of the dispersants is important, but also the concentration of the dispersant is a key parameter in the CNT dispersibility in water. For instance, during exfoliation, the kinetics of the surfactant adsorption at the pristine surface in the gap opened up by sonication is dependent on the surfactant flux, which must depend on the surfactant concentration. In addition, the adsorption of surfactants onto a surface is also concentration-dependent.\textsuperscript{53} Studies as a function of surfactant concentration, $c_s$, showed that the concentration of dispersed CNT, $c_{CNT}$, increases with $c_s$ until a plateau is obtained.\textsuperscript{50, 70} However, at even higher surfactant concentration, $c_{CNT}$ decreases, due to the depletion effect caused by increasing concentration of free surfactant micelles in the dispersion.\textsuperscript{63, 71-73} Moreover, it has been reported that micellization is not a prerequisite to disperse nanotubes.\textsuperscript{74} Nevertheless, there is a lack of fundamental understanding of the adsorption isotherms that describe the adsorption of surfactants onto carbon nanotubes.\textsuperscript{73}

Besides the surfactant concentration, the strength of the intermolecular interactions and the partition equilibrium established between the free surfactant in bulk and the adsorbed onto CNT are all important factors in the CNT dispersibility. However, comprehensive studies are scarce. A NMR diffusometry study shown that the residence time of ionic surfactants adsorbed onto the CNT surface, are below the NMR-accessible time scale (i.e. below the millisecond) which makes the calculation of the surfactant fraction adsorbed at nanotube difficult and prone to high uncertainties.\textsuperscript{75} In this thesis, we investigate the effect of the chemical structure and the concentration of the surfactants on the dispersibility of CNTs in water and the surfactant binding strength to CNT surface.

**CNTs dispersibility by synthetic and natural polymers**

Up to now, both synthetic and natural polymers \textsuperscript{45, 64, 76-92} have been used to disperse carbon nanotubes in water. Similar to surfactants, it is expected that one segment (or block) of the polymer interacts with the nanotube surface, whereas the other segment interacts with the solvent. However, due to the high molecular weight, polymer–nanotube interactions are likely to be somewhat different than surfactant–nanotube interactions. Thus, to describe polymer–nanotube interactions two main models have been proposed: the “polymer-wrapping” model\textsuperscript{76} and the “loose adsorption” model.\textsuperscript{93} The two models differ in the strength of attachment of the polymer to the nanotube. The polymer-wrapping suggests strong and specific polymer-nanotube interactions. On the other hand, the loose adsorption model assumes nonspecific interactions between the polymer and the nanotube, restricted to the adsorbing block (or end group).\textsuperscript{94}
In the wrapping model, the polymer coats the nanotube by forming a helical structure in close contact with the nanotube surface. Molecular dynamics simulations indicated that polymers with flexible chains and bulky aromatic side groups (Polymethyl methacrylate and polystyrene) form a random interchain sheet (Figure 7 a). On the other hand, polymers with stiff backbones tend to settle in a wrap around the nanotube with a helical configuration (Figure 7 b). As concerning biopolymers, single-stranded (ss) DNA has been referred to helically wrap SWNTs through π–π interactions between the nucleobases and the nanotube aromatic surface. The resulting DNA-nanotube complex is stabilized in water due to interactions established with the hydrophilic (charged) groups of DNA. Additionally, ssDNA was reported to preferentially interact with SWNTs with a particular chirality. Hence, using specific DNA sequences and adjusting the pH, it has been possible to separate SWNTs with different chirality.

The loose adsorption model is based on a weaker interaction between the polymer and the nanotube surface. In this model, the native conformation of polymer is not substantially changed. Typically, block copolymers tend to adopt this configuration around nanotubes, where the hydrophobic block acts as an anchor in the nanotube surface and the hydrophilic block expands towards the solvent (Figure 7 c). Experimental and simulation studies have shown that block copolymers adsorb to the nanotube surface through a non-wrapping mechanism. Granite et al and others used SANS to get some molecular insight in order to support this model. Indeed, SANS data shown that polymer chains are loosely adsorbed onto the nanotube surface. In addition, the dynamics of block copolymer (Pluronics F127)-CNT systems was investigated by NMR diffusometry, confirming an exchange between the adsorbed and free polymer in the bulk within the NMR time scale, opening the door to additional NMR studies explored in this thesis.

Proteins are also known for their ability to disperse CNTs in water. Proteins are polymers of amino acids that can fold in so-called secondary structural motifs like α-helices, β-sheets and in less ordered loops, and then can have these motifs arranged in yet more complex (tertiary and quaternary) order. They present a large diversity of sizes and shapes. This feature is assumed to be related to the fact that...
protein folding creates both hydrophobic pockets and hydrophilic regions, that is, an amphiphilic character. Hence, the hydrophobic pockets interact with the nanotube surface and the hydrophilic ones stabilize the nanotube in water by preventing reaggregation. In addition, proteins composed by amino acid residues containing aromatic rings (e.g. tryptophan, tyrosine, phenylalanine and histidine), may also interact with nanotubes through π-π interactions. Due to the complex structure, the models presented above are not straightforward to apply.\textsuperscript{43, 88, 107} Calvaresi \textit{et al} reports the interactions that control the binding of proteins to CNTs to be divided in four types: 1) van der Waals interactions (polarizability of groups in amino acid residues and π-π stacking), 2) hydrophobic interactions (an amino acid with a hydrophobic side chain tends to bind to the hydrophobic CNT surface), 3) amphiphilicity (i.e. amphiphilic residues behave similarly to surfactants) and 4) electrostatic interactions. Yet, it was found that proteins with similar content of individual amino acids bind CNTs to a different extent, which indicates that the secondary and tertiary structure also play an important role.\textsuperscript{43}

One of the proteins widely used to disperse CNTs in water is the Bovine Serum Albumin (BSA). Thus, due to the complexity of protein-CNT interaction, BSA can be used as a model in order to understand and systematize the dispersibility of CNTs by proteins, which has relevant implications to biological and biomedical applications. Thus far, several works have been performed in order to understand the CNT exfoliation induced by BSA\textsuperscript{87} and the effect of pH\textsuperscript{83} on the dispersibility of CNTs. It has been reported that the electric charge and the conformation of protein affects the CNT dispersibility. In addition, NMR diffusion studies in the BSA-SWNT system have shown that only a small fraction of protein is bound to the nanotube and is in fast exchange (over the time scale of the diffusion NMR experiments) between the adsorbed and free state. In order to understand BSA-nanotube interactions better, adsorption studies have also been carried out.\textsuperscript{108} In this thesis NMR diffusometry experiments employing BSA and Pluronics F127 to disperse CNTs were carried out with the goal to evaluate the adsorption competition between BSA and F127 to the CNT surface.

1.2. Soft matter

Soft matter comprises a large diversity of materials, such as surfactants, polymers, liquid crystals, colloids (e.g. foams, emulsions and gels) and other types of systems organized at the mesoscopic level. The term soft matter originates from the macroscopic mechanical properties. Soft matter can be characterized as a class of materials that yield a large response to a small perturbation. That means that a material is considered soft if it deforms easily (and typically in a plastic way) under an external stimulus (e.g. mechanical deformation, electric or magnetic field, etc).\textsuperscript{109,110}
Soft materials consist of structural units that are much larger than atoms, and often have some degree of self-assembled ordering. Under certain conditions, many soft materials can be induced to flow. This is a consequence of the lack of the three-dimensional atomic organization that is found in a crystalline solid. In terms of structure, these materials present molecular arrangements somewhere between those of a crystalline solid and a conventional liquid. Typically, soft materials are held together by weak intermolecular interactions (repulsive and attractive). From the viewpoint of kinetic energy, they present a molecular kinetic energy close to $k_B T$ and thus, their structure can be easily altered at relatively low temperatures.

In our everyday lives, soft matter is present everywhere, for instance in materials such as shampoo, toothpaste, cosmetic creams and food emulsions, like butter, ice-cream and mayonnaise. Additionally, advanced soft materials are also present in modern technologies such as liquid-crystal displays, paints and biomaterials for medical applications.

The combination of soft materials with hard materials (such as CNTs), is an important and relevant topic from both the fundamental and applied point of view. It is important to investigate the properties of soft and hard materials, firstly, individually and second, in combined forms. From a more fundamental point of view, we must understand the role of the molecular interactions in the hard—soft interface, in order to learn how to tune the desired properties of the final composite. For example, recent work has been published where nanotubes were combined with an elastomer, originating a new material that can be stretched up to 1320% with minimum change of the electrical resistance (about 5 %). This superelastic conductor can be used, for instance, in artificial muscles or other superelastic electronic applications.

In the previous sections, the structure and properties of nanotubes were presented in detail. Before exploring any hard—soft combination, it is relevant to know the typical behavior of soft materials alone. Thus, in the following sections (1.2.1 up to 1.2.3), the soft materials that were explored in this thesis—surfactants, polymers and liquid crystals—will be described in more detail.

1.2.1. **Surfactants**

Surfactants are molecules composed of two parts with different affinities for a given solvent. The part with affinity to the solvent is designated as lyophilic, while the part insoluble in the solvent is called lyophobic. When the solvent is water, the parts are designated as hydrophilic and hydrophobic, respectively. The hydrophilic part is also called the polar headgroup and the hydrophobic part the tail (Figure 8a). Surfactants are classified as amphiphiles because they contain both water-loving and oil-loving parts. The charge of the polar headgroup is typically used to classify the surfactant. The most common surfactants are cationic, anionic, zwitterionic and nonionic.
Figure 8. Schematic representation of a surfactant molecule (a) and surfactant behavior in water (b).

The amphiphilic character of the surfactant is the key role for the surfactant behavior in water. The solubility of surfactant in water is quite low, and surfactants are prone to self-assemble in water (or polar solvents) and adsorb at interfaces, lowering drastically the interfacial tension. Figure 8 b summarizes the surfactant behavior in water at low concentration.\(^{114}\)

One of the main features of surfactants is the self-assembly property. The molecular interactions between the hydrophobic tail and water dipoles are not favorable; therefore, when a surfactant is solubilized, the water molecules form a “cage” that is extremely organized around the hydrophobic tail in order to minimize water-hydrocarbon interaction. This organization has a high entropic cost and is the driving force behind the hydrophobic effect.\(^{40,115}\) When two hydrocarbon chains are in close contact, the water that was organized around the hydrocarbon is released into the bulk, which leads to a global increase in the entropy of the system. Hence, association of surfactant unimers is entropically favorable and results in a lower Gibbs energy of the system. Indeed, when the unimer achieves a critical concentration in water, the surfactant self-assembles in micelles. This concentration is defined as the critical micelle concentration (\(cmc\)).\(^{113-115}\)

Surfactants in water exhibit a rich phase behavior. Micellar solutions and liquid crystals (hexagonal, lamellar and cubic phases) are commonly found in the phase diagram as a function of surfactant concentration. Figure 9 displays the Fontell scheme, which represents a somewhat idealized sequence of self-organized structures as a function of surfactant concentration. A more quantitative description that rationalizes the packing of surfactants into different aggregates is given by the surfactant packing parameter \(P_s\) defined as the ratio

\[
P_s = \frac{V_{hc}}{a_{hg}l_{hc}}
\]  

(1.5)
of the volume of the hydrocarbon chain of the surfactant ($V_{hc}$) to the volume ($a_{hg} l_{hc}$) of a hypothetical cylinder defined by the effective area of the polar head group ($a_{hg}$) and the length of the fully extended hydrocarbon chain. Typically, $P_s$ increases to the right in the Fontell scheme. When $P_s$ is about 1/3 (corresponding to a surfactant with a geometric shape similar to a cone) the formation of micelles ($L1$) is favored; for $P_s=1$ lamellar phase ($L_{α}$) is preferred. In the case of $P_s>1$ the formation of reverse structures is preferred.

Figure 9. Fontel scheme showing the ideal dependence of mesophases with the concentration of the surfactant. Adapted with permission from Springer.\textsuperscript{14}

1.2.2. Polymers

A polymer is a macromolecule that is built up by covalently linking smaller chemical units, referred as monomers. Polymers are commonly divided into biological and non-biological macromolecules. Biopolymers consist of nucleic acids, proteins and polysaccharides, while non-biological (i.e. synthetic) comprises common plastics and adhesives.\textsuperscript{15} Polymer science is a vast area, comprising proteins, cellulose, silk, polystyrene, nylon, rubber, etc.\textsuperscript{16} Within this section, the discussion will focus only on polymers in aqueous solution.
Synthetic polymers are classified according to their structure and composition. As concerning the structure, a polymer can either be 1) linear, 2) branched or 3) cross linked (forming a network). Polymers are also classified according to composition. A polymer synthesized with more than one type of monomer is called a copolymer. Figure 10 shows how the monomers in the copolymer can be organized in different ways: 1) randomly, 2) distributed in blocks, or 3) one of the monomers can be grafted onto the backbone of the other polymer. In block copolymers, the polymer chain consists of blocks of one repeating unit followed by one or more blocks of other repeating units. If any of the monomers carries a charged group, one can refer to the polymer as a polyelectrolyte.

Block copolymers can be made of alternating hydrophilic and hydrophobic blocks, hence becoming amphiphilic. The most common block copolymers are of the poly(alkene oxide) type, where the hydrophilic segment is poly(ethylene oxide), PEO, and the hydrophobic segment is poly(propylene oxide), PPO. There are many possible combinations for PEO-PPO block copolymers. Among them, Pluronics, which have a general structure (PEO)_x-(PPO)_y-(PEO)_x, have gained high importance. Being amphiphilic, they can self-assemble in water at a critical micelle concentration; the size of the blocks, the proportion of PEO to PPO units and temperature are parameters that affect the cmc. Pluronics also display a rich phase behavior exhibiting a large number of liquid crystalline phases.

1.2.3. Thermotropic liquid crystals

Liquid crystalline (LC) phases combine order and mobility at molecular and supramolecular level. Due to this unique combination, such systems are sensitive to external (magnetic, electric, chemical or mechanical) stimuli by finding a new configuration of minimum energy. Hence, LC materials can be used, for instance, as
optoelectronic devices, temperature sensors, polarized light emitting materials and photoconductors.\textsuperscript{118, 119}

The liquid-crystalline state is an intermediate state between the crystalline solid phase and the liquid phase. The molecules that originate liquid crystals are called mesogens and the liquid-crystalline phases are also named mesophases.\textsuperscript{120} Typically liquid crystals fall into two main categories: 1) lyotropic liquid crystals, formed by the action of solvent due to unfavorable interaction with the solvophobic part of amphiphilic molecules; and 2) thermotropic liquid crystals, formed in the absence of solvent, only by the action of temperature.

In the case of thermotropic liquid crystals, upon heating the crystalline solid of the mesogenic compound, there is gradual introduction of some type of orientational and/or positional disorder of the molecules and hence formation of mesophases, before the totally disordered (isotropic) liquid state is reached.

The formation of thermotropic liquid crystal requires mesogens to be anisotropic in shape (i.e. molecular structure must be spatially different in one of the 3-D axis) or have an amphiphilic character. Typically, the shapes of molecules that accomplish these requirements are rod-like (also called calamitic molecules) or disk-like. Due to their amphiphilic character, surfactants also form thermotropic liquid crystals. Figure 11 presents some typical mesogens.

![Molecular structure of typical mesogens forming liquid-crystalline phases](image)

Figure 11. Molecular structure of typical mesogens forming liquid-crystalline phases: (a) calamitic molecule, (b) discotic molecule and (c) amphiphilic molecule (gemini surfactant).

The driving force of the formation of thermotropic liquid crystals is the anisotropic character of the molecules, viz. shape, charge, polarity and molecular geometry which results in the segregation in space into distinct microdomains producing long-range orientation and positional order.\textsuperscript{118, 119}
In a liquid crystal, the molecular orientational order can be quantified by the order parameter $S$, described by means of a second Legendre polynomial:\(^\text{121}\)

$$S = \frac{3}{2} \cos^2 \theta - \frac{1}{2}$$

(1.6)

where $\theta$ is the angle between the molecular axis of each mesogen and the unit vector $\hat{n}$ that points along the preferred average molecular orientation (Figure 12 a). The parameter $S$ is 1 for perfectly ordered crystalline solids and 0 for liquids and gases. The $S$ value ranges between 0.3 and 0.8 for typical liquid crystals. As expected, with increasing temperature, the order parameter $S$ of the thermotropic liquid crystal decreases until zero when the phase is completely melted.

Mesogens form very different types of liquid crystals according to their shape and/or amphiphilicity. Rod-like mesogens (or calamitic molecules) typically form nematic phases, where molecules only have an average orientation in space and there is no positional order, i.e. molecular positions are not correlated in space. The order is thus only orientational, with the molecules presenting an average orientation in space (Figure 12 a). However, in some other structures, molecules can also have positional order like in the columnar phases (typically formed by discotic molecules) and smectic phases (typically formed by some amphiphiles), as shown in Figure 12 b and 12 c, respectively.

Disk-like mesogens can form nematic phases and more commonly columnar phases, due to the stacking of disks. Additionally, columnar phases may also have hexagonal, tetragonal and oblique order between different columns (Figure 12 b).

Smectic phases are organized in planar layers (Figure 12 c). The positional order within the layers is of short range, as opposed to layers in solid crystals. If the order is long-ranged, the phases are no longer considered pure liquid crystals, but slightly disordered solids.\(^\text{111}\) The most simple smectic phase is the smectic A (SmA) and smectic C (SmC), where molecules are ordered in layers, but totally disordered in each plane, i.e. behaving like a liquid in the plane. However, molecules in the layer may also present positional order (e.g. SmB, SmI, SmF, SmE and SmH). These phases can be ordered by increasing degree of organization: (SmA) < (SmC) < (SmB) < (SmI) < (SmF) < (SmE) < (SmH). In the next page, the organization of the different smectic phases in the mesophase is described, also with reference to Figure 12c.\(^\text{120}\)
• **SmA**  No positional order in the layers; \( \hat{n} \) is perpendicular to the normal layer (\( \hat{k} \)).

• **SmC**  No position order in the layers; \( \hat{n} \) is tilted to the normal layer (\( \hat{k} \)).

• **SmB**  In-plane hexagonal organization; \( \hat{n} \) is perpendicular to the normal layer (\( \hat{k} \)).

• **SmI**  In-plane hexagonal organization; \( \hat{n} \) is tilted to the normal layer (\( \hat{k} \)); molecules are tilted towards the apex of the hexagonal unit cell.

• **SmF**  In-plane hexagonal organization; \( \hat{n} \) is tilted to the normal layer (\( \hat{k} \)); molecules are tilted towards the side of the hexagonal unit cell.

• **SmE**  Similar to SmB but with square organization in-plane.

• **SmH**  Similar to SmF but with square organization in-plane.

**Typically,** amphiphiles that commonly form smectic phases have a \( P_s \) close to 1 and the molecular shape is similar to a cylinder (e.g. double chained surfactants, gemini surfactants, bolaamphiphiles and catanionic surfactants).

In this thesis, the effect of the spacer length on the thermotropic behavior of the gemini 12-s-12 surfactants was investigated. The spacer length effect on gemini surfactants, which will change the \( P_s \) conferring a versatility that may be important for the choice of the liquid crystalline matrix to embed CNTs. This opens the door to a new hybrid material that will combine both the response of the LC and CNT to an external (magnetic, electric, chemical or mechanical) stimulus.
Figure 12. Schematic representation of thermotropic liquid crystal mesophases: (a) Nematic phase, where \( \hat{n} \) is the vector that points along the preferred average molecular orientation and \( \theta \) is the angle between the molecular axis of the mesogen and \( n \) is the bilayer director; (b) Stacking of disks forming an elongated rod and hexagonal columnar phases; (c) Smectic phases, where \( \hat{k} \) stands for the vector normal to be bilayer and \( \hat{n} \) is the bilayer director. Smectic phases B, I, F, E and H are shown as top views.
2. Experimental section

2.1. Methodology to prepare the CNTs dispersions

The CNT dispersions were prepared by first adding accurately a weighed amount of pristine nanotube powder to a vial, followed by the addition of (typically) 3 mL of dispersant solution. Exfoliation was then performed through a 3 mm tip sonicator, where the tip was immersed directly into the liquid, for a sufficiently long period (=10 min). Non dispersed material assumed to consist of large remaining grains of non-exfoliated nanotubes, amorphous carbon and other impurities were removed by centrifugation. The concentration of CNT dispersed in the supernatant was quantified by a combined TGA/UV-vis methodology outlined below.

Sonication

The exfoliation process of nanotubes in surfactant solutions is rather intricate. As a high amplitude ultrasonic pressure wave propagates through a liquid medium, cavitation bubbles are created and, above a critical size, collapse and hot spots (with few thousands degrees Celsius and pressures of several tens of MPa) are generated. If the bubble collapses near a surface, a hydrodynamic microjet is built up in the liquid. This high-speed microjet creates high shear forces in the surrounding liquid medium. On other hand, if the bubble is unperturbed by a surface, a shock wave is generated during a symmetric collapse. Nanotubes exfoliation is driven by the combination of both effects (shock waves and microjets), followed by the adsorption of dispersants that prevent CNT reaggregation (see unzipping mechanism Figure 5).

The effect of sonication on CNT dispersibility has been evaluated by several authors. Among other features, it was observed that a critical sonication threshold time exists for successfully opening all bundles and, provided that there is enough surfactant available, exfoliating all nanotubes. However, increasing the sonication time also increases CNT fragmentation. Indeed, some reports state that nanotube exfoliation cannot happen without nanotube fragmentation. Despite considerable effort, current knowledge on the most suitable and/or optimal experimental parameters, such as the time scale and energy density (i.e. the amount of acoustic energy transferred to a certain volume of liquid, herein expressed as J/mL) for de-bundling CNTs without considerable fragmentation, is still scarce. The difficulty to characterize the size distribution and homogeneity of dispersed CNT, together with difficulty to estimate the effective shear forces provided by sonication are the main causes for this shortcoming.

In this thesis, in order to make sonication conditions easier to reproduce, the total energy transferred to the system was estimated by a calorimetric method. There, we assumed that the heat generated by ultrasound is proportional to the acoustic energy dissipated from which the power $P$ transferred to the liquid was estimated as
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\[ P = m c_p \left( \frac{dT}{dt} \right) \quad (2.1) \]

where \( m \) is the mass of the water in our vial, \( c_p \) is the specific heat capacity of water and \( \left( \frac{dT}{dt} \right) \) is the rate of temperature increase as function of sonication time. For tip sonication, the power density \( P/V \) in the liquid was in the order of 1 W mL\(^{-1}\). We observed that, with our available equipment (see below), bath sonication (where ultrasonication is applied indirectly through the walls of the sample container) delivers only a few % of the power density delivered by the tip sonication. However, since the bath was used during much longer (≈20 times) time the energy density (J∙mL\(^{-1}\)) transferred to the liquid was in the same order of magnitude as the tip.

For tip sonication a Bandelin Sonoplus Vb 2070 and a Qsonica Q-500 equipped with a 3 mm microtip was used. During the sonication process, the tip was always carefully placed in the center of the vial, always at the same position from the bottom in order to maximize the reproducibility of the sonication conditions. The tip was frequently polished, and the amplitude of vibration of the tip was set to 20-30% of maximum, in order to minimize surface erosion. The sonication time used varied between 8.5 to 10 min. An external bath, in thermal equilibrium with the processing vial, was used to dissipate the heat produced during the sonication and keeping the sample temperature stable. For bath sonication, an Elma Sonic (model S10, 30W, 37 kHz) sonicator was employed.

**Centrifugation**

After sonication, a centrifugation step is used to sediment any non-dispersed material. Typically, after sonication the nanotubes are in the form of individual nanotubes, small bundles and non-exfoliated macro-bundles. These CNT states have slightly different densities \( \rho \) and highly different \( L/d \) aspect ratios, which allows CNT separation based on \( g \) force and/or centrifugation time. Indeed, using a density gradient ultracentrifugation it has been possible to separate nanotubes with different lengths.

Nevertheless, mild centrifugation conditions (1-10 x 10^3 g) are usually sufficient to remove the large bundles of non-dispersed CNTs and leave individual nanotubes and small bundles in the dispersion. In this thesis the centrifugation was carried out at 4000 g during 20-30 min. After the centrifugation step ≈ 50% of the supernatant (≈1.5 mm above the precipitate line) was collected with a pipette and used in subsequent experiments.

**CNT quantification**

The quantification of CNTs dispersed in water is based on a thermogravimetric-spectroscopic approach. In this methodology the exact concentration of the CNT dispersed in the liquid is quantified by thermogravimetric analysis (TGA) and
related to the optical density of the CNT dispersion. Because of the presence of CNT bundles with linear size comparable to wavelength, optical density may include both true absorbance and scattering.

In order to quantify the CNT concentration, an exact known volume $V_s$ of the supernatant was freeze-dried for 24 hours resulting in a dry powder of mass $m_s$, composed by CNT and dispersant. Data yielded by thermogravimetric measurements were then used to provide the CNT concentration as

$$c_{CNT} = \frac{m_s}{V_s} \times \left(1 - \frac{\phi_s}{\phi_d}\right)$$

(2.2)

where $\phi_s$ is the TGA mass loss fraction in the dry supernatant and the $\phi_d$ is TGA mass loss fraction in neat dry surfactant. Hence, the $\phi_s/\phi_d$ ratio accounts for incomplete surfactant decomposition in TGA. Measuring the optical density at $\lambda=660$ nm for same stock dispersion, one can estimate the apparent extinction coefficient $\varepsilon_{660}$. Once the $\varepsilon_{660}$ is known, the CNT concentration of the subsequent samples can be estimated quickly and simply from the optical density. In other words, TGA experiments were used to calibrate $\varepsilon_{660}$ to real CNT concentration. In order to ensure the maximum accuracy of the CNT concentration, a new calibration was performed every time that a different dispersant or new batch of nanotube was used.

### 2.2. Introduction to NMR

Nuclear magnetic resonance (NMR) spectroscopy is a noninvasive analytical technique used to obtain molecular information. It is a very versatile tool in terms of the methodology by which information is collected (e.g. chemical shift, spin relaxation, imaging, etc.) and type of systems that can be studied (e.g. hard and soft materials). In NMR spectroscopy, the signal from NMR-active nuclei is measured and processed in order to get insight into, for instance, molecular or macromolecular structure, molecular dynamics, distribution of molecules and properties in biological tissues synthetic materials, etc. In this thesis, NMR was mainly used to measure the translational diffusion of molecules and understand aspects of molecular structure and dynamics of amphiphiles in contact with CNT.

#### 2.2.1. NMR principles

Atoms are composed by a nucleus (made of protons and neutrons) embedded in a cloud of electrons. These particles (proton, neutron and electron) are, among other properties, characterized by an intrinsic angular momentum and an intrinsic magnetic moment that together are referred to as spin. Protons, neutrons and electrons are so-called fermions characterized by a spin quantum number $I = 1/2$. 


The combination of the neutron spins and proton spins and motion of those particles within nuclei results in a nuclear spin \( I \) that, depending on the isotope, may take the value \( I = 0, 1/2, 1, 3/2, 5/2 \) and higher. For instance, \(^1\text{H}, \(^{13}\text{C}, \(^{15}\text{N}, \(^{19}\text{F}, \(^{29}\text{Si}, \(^{31}\text{P}, \(^{207}\text{Pb}\) have \( I = 1/2; \(^2\text{H} \) and \(^{14}\text{N} I = 1; \(^{23}\text{Na} \) and \(^{35}\text{Cl} I = 3/2; \(^{17}\text{O} \) and \(^{27}\text{Al} I = 5/2 \) while \(^{12}\text{C} \) and \(^{16}\text{O} \) lack nuclear spin \( (I=0) \). Only nuclei with \( I \neq 0 \) are NMR-active, i.e. they interact with a magnetic field.\(^{12}\)

The discrete states a nuclear spin can take are indexed by the magnetic quantum number \( m = -I, -I+1...I-1, I \). In the absence of a magnetic field all spin states exhibit the same energy, that is, the system is degenerate. However, when an external magnetic field \( B_0 \) is applied, the degeneracy is lifted and the energy levels split. For a nuclear spin \( I = 1/2 \), two states are possible, \( m = -1/2 \) and \( m = 1/2 \). The energy associated with a spin state, \( E_m \), is related to the external magnetic field \( B_0 \) as

\[
E_m = -\mu_z B_0
\]

where \( \mu_z \) is the \( z \) component of the nuclear magnetic moment \( \mu \) of the nucleus:

\[
\mu_z = m \hbar \gamma
\]

where \( \hbar \) is the reduced Planck constant and \( \gamma \) is the gyromagnetic ratio, a parameter specific to each particular nucleus (element and isotope). It is this latter property that makes NMR element-specific. Combining equations 2.4 and 2.5, one can calculate the energy difference

\[
\Delta E = \hbar \gamma B_0
\]

between the two states \( m = \pm 1/2 \). Equation 2.6 shows that \( \Delta E \) is proportional to the strength of the external magnetic field, \( B_0 \).

In thermal equilibrium, the distribution of an ensemble of nuclear spins between the two allowed energy states follows the Boltzmann distribution

\[
\frac{N_{\text{high}}}{N_{\text{low}}} = e^{-\Delta E / k_B T}
\]

where \( N_{\text{high}} \) and \( N_{\text{low}} \) are the number of spins in the states with higher and lower energy, respectively, \( k_B \) the Boltzmann constant and \( T \) the absolute temperature. The Boltzmann distribution yields more spins at the lower energy level, and since in the two states the magnetic moments point oppositely to each other, the sample attains a net nuclear magnetization along the axis of the external magnetic field (\( z \)). The NMR signal is obtained by the perturbation of this net magnetization. Among other factors, the intensity of the NMR signal is proportional to the population difference \( (\Delta N = N_{\text{low}} - N_{\text{high}}) \) between the two energy states. For an ensemble of \(^1\text{H} \) spins at room temperature, and in a magnetic field with the strength of 11.7 T, the population difference, \( \Delta N \), is approximately 1 for every \( 10^4 \) spins. In other words, the net nuclear magnetization is very weak. It is for that reason that NMR is a very insensitive
technique hence requiring a large amount of sample (at least a few mg/mL) compared to other spectroscopic methods.

When the sample is affected by a time-dependent electromagnetic field characterized by a frequency

\[ \nu_o = \frac{\Delta E}{h} = \frac{\gamma B_0}{2\pi} \]  

(2.8)
one can create transitions between the different spin states. The frequency \( \nu_o \) at this resonant condition is known as the Larmor frequency. Due to typically small energy difference between the involved states, the Larmor frequency falls in the radio range.

Basic features of NMR are usually visualized using the vector model, where the thermal equilibrium state of nuclei is represented by a vector \( M \) pointing in the same direction (\( z \)) as the external field \( B_o \). For \( I = 1/2 \) nuclei that lack spin couplings, \( M \) depicting the net nuclear magnetization provides a suitable description, while for higher spins and with spin couplings, richer models may be needed. In the vector model, \( M \) is both (i) turned in different directions and (ii) is also left precessing around the direction of the external magnetic field. Regarding (i), it can be achieved by creating a circularly polarized magnetic field \( B_1 \) that oscillates with a frequency that matches the Larmor frequency. This requires a suitable coil placed around the sample. Having applied the magnetic field \( B_1 \) for a specific time period (summarized by the name radiofrequency or RF pulse), the magnetization vector \( M \) rotates away from its thermal equilibrium state along the \( z \) axis by a certain angle \( \alpha \). Specifically, if \( B_1 \) is applied as a pulse of duration \( \pi/2\gamma B_1 \), the magnetization \( M \) is turned by \( 90^\circ \), i.e. the vector \( M \) initially aligned with \( z \) is tilted to \( x-y \) plane (also called the transverse plane). The power level of the RF pulse characterizes the strength of \( B_1 \), which affects the \( 90^\circ \) pulse duration. The pulse duration is typically in the order of microseconds. Once the magnetization is tilted to the transverse plane, the magnetization is left precessing at the Larmor frequency around the direction of the field \( B_o \). The precession induces a voltage in the coil previously used to generate the RF pulse, which in turn generates the so-called time-domain NMR signal, often termed the free induction decay (FID). The Fourier transformation of the FID provides the frequency-domain NMR spectrum.132, 133

Thus far, we have considered the effect of a RF pulse with its frequency exactly at Larmor frequency. However, virtually the same effect is obtained at off-resonance conditions, provided that the frequency of the pulse is sufficiently close to \( \nu_o \). The condition for this involves the inverse of duration to the \( 90^\circ \) pulse. Hence, a short and strong \( 90^\circ \) RF pulse can turn nuclear magnetization for spins characterized by Larmor frequencies over a reasonable range. This is important because nuclei in matter indeed experience different magnetic fields, which then results in different Larmor frequencies. This feature arises because electrons around the nuclei have the
capacity to contribute to the magnetic field that may either augment or diminish $B_0$. As a result, the local field is expressed as

$$B_{\text{local}} = (1 - \sigma)B_0$$

(2.9)

where the dimensionless quantity $\sigma$ is called the shielding constant. These differences in shielding are expressed in terms of chemical shift, where shielding values for particular molecules and particular sites in them are related to that experienced in some reference compound.

After having tilted the magnetization $M$ to the x-y plane by a 90° RF pulse, the nuclear spins do not stay precessing there forever. Instead, the system returns to thermal equilibrium through a process called spin relaxation. There are two mutually independent relaxation processes involved, the longitudinal relaxation (characterized by a time constant $T_1$) and the transverse relaxation (with a time constant $T_2$). Longitudinal relaxation characterizes the return of the nuclear magnetization in the z direction (zero after a 90° RF pulse) to its thermal equilibrium value. Longitudinal relaxation is typically exponential with time $t$ as multiples of $T_1$ in the exponent, e.g. it takes almost $5 \times T_1$ for the magnetization to recover 99% of its equilibrium value.133

Transverse relaxation refers to the disappearance of magnetization in the x-y plane. Immediately, after the 90° RF pulse, the magnetization $M$ in the x-y plane is large because of the strong phase coherence among the precessing spins. However, spins interact with each other, and each spin will experience a local field generated by the nearby spin. In liquids, the temporally and randomly fluctuating local field generated by a spin acts like a pulse, which tilts the magnetic moment of the adjacent spins away from their original direction. Thus, spins precess at different and randomly assigned average speed and, consequently and over time, the spins lose coherence and the net transverse magnetization decreases. Since molecular motions produce fluctuations in spin interactions, relaxation processes may inform about molecular dynamics.133

On the other hand, if the local fields are constant over time, such as in case of having an inhomogeneous magnetic field over the sample volume, the resulting decay of the transverse magnetization could be reversed using a method called spin echo. Erwin Hahn introduced it, having demonstrated that — through the application of an additional 180° pulse, after a delay $\tau$ — a spontaneous refocusing of the magnetization occurred at time $2\tau$.134 A spin echo is analogous to a sound echo: the transverse magnetization is created by a RF 90° pulse, decays away, is reflected by a 180° pulse, and grows back to form an echo.4

Figure 1 displays the spin echo pulse sequence. A 90°x RF pulse tilts the magnetization to the y axis into the transverse plane (x-y) where the magnetization starts to precess. Due to the presence of static local fields, different spins precess at different Larmor frequencies — and, as a result, the spins start to dephase (that is,
loose coherence), represented as the fanning out in Figure 13 c. After a period \( \tau \), a 180\(^{\circ} \) RF pulse is applied that inverts all magnetization vectors in the x-y plane. The magnetization vectors of the slow spins are now in the position previously occupied by the faster ones and vice versa. As the spins continue to precess, the fast ones are now behind the slow ones. As a result, the fan starts to close up and the signal, that is proportional to the vector sum of all components, grows. At time 2\( \tau \), the vectors will all be aligned along the y axis and the signal reaches its maximum value, to decrease thereafter again.\(^4\)

![Figure 13](image)

Figure 13. Spin echo pulse sequence. (a) magnetization in thermal equilibrium aligned with the external magnetic field \( B_0 \); (b) magnetization flipped into the transverse plane; (c) Some spins are precessing faster and some slower than others, thereby the magnetization fans out; (d) The 180\(^{\circ} \) RF pulse inverts the magnetization vectors in the transverse plane and the spins end up in mirror image positions with respect to the yz-plane; (e) The magnetization is refocused.

2.2.2. Diffusion NMR

Self-diffusion is the net result of the random thermally-induced motion of molecules or atoms in space. Translational diffusion is the basic mechanism by which molecules are distributed in solution and it plays a role in chemical reactions since the species have to meet before a reaction occurs. The probability of finding a molecule, initially at position \( r_0 \), at a position \( r \) after a time \( t \) follows a Gaussian distribution. In a homogeneous isotropic system, the width of this distribution is characterized by the self-diffusion coefficient \( D \).\(^{135, 136}\)

Considering a system without concentration or thermal gradients, the average displacement of the entities is zero. However, the mean square displacement \( \langle r^2 \rangle \) for any individual entity over time \( t \) is not zero, but is given:

\[
\langle r^2 \rangle = 6Dt
\]

(2.10)
which can be obtained after having considered random-walk statistics. For instance, water self-diffusion coefficient is in the order of $10^{-9} \text{ m}^2\text{s}^{-1}$; hence the root mean square displacement $\sqrt{\langle r^2 \rangle}$ for water molecules during one second is only tens of microns. The self-diffusion coefficient is closely related to molecular size by the Stokes-Einstein equation:

$$D = \frac{k_B T}{6 \pi \eta r_s}$$

where $T$ the absolute temperature, $\eta$ is the (micro)viscosity of the solvent and $r_s$ is the Stokes (or hydrodynamic) radius. Therefore, the self-diffusion coefficient $D$ is a parameter that provides information about the diffusing species and their surroundings, such as molecular interactions or self-assembly. In addition, studying the dependence of the displacement spectrum on the diffusion time permits one to extract information about the structure of the system (e.g. porous systems, liquid crystals, etc.) through the effect of spatial limitations that those structures set for diffusing molecules. For some other systems, the diffusion time dependence allows one to follow the exchange between two sites with different diffusion coefficients (e.g. ligand binding to a macromolecule). Because of its noninvasive nature, NMR spectroscopy is an excellent tool for studying molecular dynamics in chemical and biological systems.\textsuperscript{136}

Erwin Hahn, in his pioneering work about spin echo, pointed out that the echo amplitude would be influenced by the translational diffusion because of the resulting fluctuations of local magnetic field.\textsuperscript{134} In the early times, the spin echo amplitude was measured in the presence of a static magnetic gradient in the $B_0$ field to measure diffusion. The limitations imposed by static gradients have been circumvented by Stejskal and Tanner\textsuperscript{137} through the application of magnetic gradients as pulses in the spin echo sequence — yielding Pulsed Gradient Spin-Echo (PGSE) NMR.

![Figure 14](image.png)

**Figure 14.** The principle of Pulsed Gradient Spin-Echo (PGSE) NMR experiments. (a) The spins are spatially labeled with a Larmor frequency that changes linearly with the magnitude of magnetic field; (b) The spin-echo based PGSE pulse sequence.
PGSE-NMR (Figure 14 b) is the most common pulse sequence used to measure translational diffusion. It employs two magnetic field gradient pulses during the dephasing and rephasing periods of a spin echo experiment. The magnetic field gradient is defined as $g_i = \partial B_z / \partial i$ where $i$ indexes the possible spatial directions $x$, $y$, and $z$; typically, one works with a linearly varying field that implies a constant magnetic field gradient along the sample. Usually, it is the gradient $g_z$ that is explored, which implies that along the $z$ axis the Larmor frequency of the spins changes linearly (Figure 14 a). The effect of the gradient during precession can be depicted as if the magnetization is twisted in a helix with axis $z$, where the precession angle of spins changes along the $z$ axis according to the magnitude of the gradient or the duration of the gradient pulse. The initial 90° RF pulse turns the magnetization to the transverse plane. During the first $\tau$ period and at time $t_1$, a gradient pulse of duration $\delta$ and magnitude $g$ is applied. After the end of the first $\tau$ period, a 180° RF pulse is applied that has the effect of reversing the sign of the precession; in effect, it reverts the handedness of the helix mentioned above. At time $t_1 + \Delta$, a second gradient pulse of equal magnitude and duration is applied. If the spins maintain their positions during the $\Delta$ period and thereby maintain also their Larmor frequency, the effects of the two applied gradient pulses cancel and all magnetization refocuses completely and provides maximum signal. On the other hand, if the spins have undergone some translational diffusion which changes their position during the time $\Delta$, their Larmor frequency at the time of the two gradient pulses differ, which yields incomplete refocusing and an attenuation of the signal.

In the pulsed gradient stimulated echo (PGSTE) pulse sequence, during the diffusion time $\Delta$, the magnetization is stored along the $z$ axis (Figure 15). The new concept of this pulse sequence is that the signal decay due to diffusion competes with longitudinal, rather than transverse relaxation. The use of this pulse sequence is particular advantageous for the study of the translational diffusion of larger molecules and aggregates, for which $T_2$ can be much shorter than $T_1$.135, 138
The attenuation of the NMR signal $S$ due to the translational diffusion depends on three variables: the magnitude of the magnetic field gradient $g$, the pulse duration $\delta$ and the diffusion time $\Delta$ as summarized by the so-called Stejskal-Tanner equation \[^{37}\]

$$
\frac{S}{S_o} = e^{[-D/jg(\delta^2 \Delta - \delta/3)]} 
$$

(2.12)

where $S_o$ is the signal without any gradient applied. Typically, translational diffusion is measured by recording the signal attenuation $(S/S_o)$ as field $g$ is increased. The diffusion time $\Delta$ can also be manipulated in order to observe the time dependence of diffusion, e.g. to study the restricted diffusion inside porous material or to follow exchange between sites.\[^{36}\]

**Experimental aspects**

The majority of the $^1$H NMR diffusometry experiments were carried out in Bruker Avance III spectrometer equipped with a standard-bore magnet providing a 500 MHz resonance for $^1$H nuclei and a z-gradient probe Bruker DIFF30. The gradient pulses were provided by a Bruker GREAT 60 gradient amplifier. All the measurements were carried out at 20.0 °C and the gradient strength was calibrated by measuring the diffusion of $^1$HDO in D$_2$O $(1.63 \times 10^{-9}$ m$^2$·s$^{-1}$) at 20 °C. In order to be able to measure low volumes, Shigemi tubes were used.
2.3. **Additional characterization techniques**

2.3.1. **Microscopy**

**Polarized light microscopy**

For common observations of colloidal aggregates, regular non-polarized light is used. However, when anisotropic materials like liquid crystals are observed, one can exploit birefringence as a source of extra contrast. This requires linearly polarized light. Polarization is achieved by placing a polarizer filter along the optical path where the highly aligned structure of the filter interferes with the electric component of the electromagnetic radiation, and permits only waves with the electric field vector along one particular direction (polarization axis). When polarized light propagates through an anisotropic material, this direction is altered which can be evaluated by a second polarizer placed between the sample and the eyepiece of the microscope, typically in a way that the polarization axis is at 90º with respect to that of the first polarizer. Hence, the only light that crosses must have propagated in a region containing anisotropic and optically transparent material.\(^{139}\)

Liquid crystalline phases are birefringent, and when analyzed in a microscope using polarized light, characteristic optical textures are observed. These textures arise from the birefringence phenomenon resulting from structural defects in the liquid crystalline phase. Because the defects are intrinsic to the nature of the liquid crystalline phase, the texture observed is characteristic of that particular phase. Thus, through comparison of the observed image with a known characteristic texture, it is possible to assess a liquid crystalline phase. Figure 16 displays the fan shaped textures which enable the assignment of smectic phases A and C, respectively.

![Figure 16](image)

Figure 16. Optical textures observed in polarized light microscopy. (a) fan-shaped SmA texture; (b) Same sample area as (a), showing the transition to the broken fan-shaped texture with helix lines of the SmC phase. Reprinted with permission from Wiley-VCH.\(^{120}\)
**Differential interference contrast**

The microscopic observation of some aggregates is sometimes not possible using simple light microscopy because of the lack of contrast between the aggregate and the surrounding medium (water). This problem can be circumvented by using the technique of differential interference contrast (DIC), that enhances the contrast. DIC is based on the principle of interferometry to gain information about the length of particular optical path. To do this, polarized light is manipulated to provide contrast between parts of the sample with different composition but similar refractive index or different thickness.\(^{139}\)

In the DIC experiment, a polarized beam is split by the use of a Nomarski prims into two perpendicularly polarized mutually coherent beams which are spatially displaced at the sample plane, and recombined by a second Nomarski prism before observation. The orthogonal beams cross the sample in different regions, thereby they will experience different propagation conditions that influences their transmission. When the second Nomarski prism recombines the beams into one, interference will appear. This produces the appearance of a 3-D physical relief which corresponds to the variation of the optical density of the sample.

**Experimental aspects**

The microscopic observations were carried out using an Olympus BX51 polarized light microscope equipped with a differential interface contrast system. For the study of the thermotropic behavior of gemini surfactants, a Linkam TMHS heating stage controlled by a TP94 unit was used. For the observation of microscopic aggregates formed by nanotubes, the differential interface contrast mode was used together with an Olympus C-5060 Wide Zoom digital camera.

**Cryo-Transmission Electron Microscopy**

Electron microscopy allows direct observation of nanostructures due to its subnanometer compared to micrometer resolution in light microscopy. The limiting condition in light microscopy lies on the wavelength of visible light, but this obstacle can be overcome by using accelerated electrons instead of photons to visualize the sample. In order to control both focusing and magnification, the conventional optical lens system is replaced by electromagnetic lenses.\(^{140}\) High-resolution electron microscopy requires high vacuum inside the microscopic chamber \((p < 10^{-5} - 10^{-6}\) Pa\) in order to avoid interferences with the electron beam that interacts with the sample, which is a drawback for hydrated samples. Therefore, samples need to be either dried or vitrified (ultra-fast cooling) to reduce their vapor pressure. Drying is not an option in colloidal systems in which the liquid is essential for the formation of the structures (e.g., micelles or vesicles). Moreover, to prevent structural modification due to slow cooling (and subsequently formation of ice crystals) of
samples, (Figure 17) the sample is cooled extremely rapidly (1×10⁵ K/s) and thereby vitrified, i.e., remains in amorphous state.

Cryo-TEM is an excellent tool to visualize nanostructures in liquid samples, provided that those can be properly vitrified.

![Figure 17. Schematic representation of the vitrification method used in cryo-TEM sample preparation. A drop (≈4 μL) of the sample is placed in a copper grid (represented as the black dashed region); the excess of liquid is blotted way, flowed by vitrification in liquid ethane. The sample is transferred to the TEM and visualized.](image)

**Experimental aspects**

The sample support in cryo-TEM experiments is typically a copper grid, covered with a lacy polymer film. The specimens are prepared by dropping an aliquot (≈4 μL) of solution on the grid. Excess solution is blotted away with filter paper, resulting in a film that spans the holes of the polymer support, and whose thickness (>200nm) allows both a high cooling rate and a high transmission of the electron beam. The sample is then plunged into liquid ethane (≈92 K) in order to rapidly vitrify and then stored in to liquid nitrogen (< 77 K) before being transferred to a TEM (Tecnai 12, FEI) using a Gatan workstation and cryo-holder for imaging at 98K. The microscope was operated at 120 kV in low electron dose mode (to reduce radiation damage) and with a few micrometers under-focus to increase phase contrast. Images were recorded on a Gatan 794 CCD camera.

**Cryo-Scanning Electron Microscopy**

Scanning Electron Microscopy (SEM) produces images of a sample by scanning it with a high energy beam of electrons (primary beam). The interaction of electrons with the atoms in the sample yields secondary electrons that arise from those regions that are close to the sample surface. The secondary electrons are ejected from the valence shell of atoms. For these reasons, SEM provides information about sample topography and composition. The images obtained with SEM have a three dimensional appearance due to lateral and depth resolution, which is particularly useful to understand the morphology of any nano- or micro-structures present.
**Experimental aspects**

The vitrification process for SEM is carried out by the immersion of the sample in nitrogen slush. The sample is fractured *in situ* and the solvent is sublimated, exposing the bulk structural details. If the sample is not electrically conductive, it needs to be sputter-coated with a thin conductive film (e.g. Au/Pd alloy) to drain the charge transferred by the primary electron beam. The images were acquired using a JEOL JSM 6301F SEM microscope equipped with a Gatan Alto 2500 cryo-preparation chamber.

2.3.2. **X-ray diffraction**

X-ray diffraction (XRD) is one of the most used techniques to characterize the structure of crystalline and liquid-crystalline materials. In common XRD diffractometers, X-ray are generated in a cathode ray tube where electrons are accelerated to bombard a metal target. As electrons plunge in the metal, they decelerate and generate a radiation with a continuous range of wavelengths called Bremsstrahlung. In addition, collision with an electron from the inner shell of the metal atom may eject an electron from the shell. Another electron of higher energy drops then into the vacancy, emitting the excess of energy as an X-ray photon of well-defined wavelength. If the electron falls into a K shell, the X-rays are classified as K-radiation. The most common equipment uses copper as metal target, with CuKα monochromatic radiation with a wavelength of $\lambda = 0.154$ nm. These X-rays are collimated and directed onto the sample. Electrons in the sample scatter the incoming X-rays in all directions. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. Depending in the structure of the sample, at certain angles constructive interference of the scattered X-rays occurs and a diffraction peak is observed.

Crystal materials are characterized by a periodic repetition of a structural unit. Figure 18 shows the representation of Bragg’s law for a simple lattice crystal modulated as stacks of parallel planes of separation $d$. When wave 1 hits the point D on the surface of the plane, the extra path length traveled by wave 2 at a scattering angle $\theta$ is given by:

$$AC + BC = 2d \sin \theta$$

(2.13)
Figure 18. Schematic representation of Bragg’s law of diffraction for parallel planes. $d$ is the distance between the planes, $\theta$ is the diffraction angle and A, B, C and D are the points used to calculate the path length.

Constructive interference occurs (i.e. scattered waves are in phase) when the path length difference between the two waves is equal to an integer of the wavelength $\lambda$, i.e. $(AC+BC )=n\lambda$. Thus, equation 2.13 becomes:

$$n\lambda = 2d \sin \theta$$  \hspace{1cm} (2.14)

The equation above is known as Bragg’s law. An XRD diffractogram usually presents the diffracted intensity, $I$, as a function of the scattering angle $2\theta$. Bragg reflection peaks occur when at certain angles the scattered waves are in phase. Bragg’s law can also be expressed in terms of the modulus of the scattering vector $q$ by

$$q = n\frac{2\pi}{d}$$  \hspace{1cm} (2.15)

where $n$ is the order of the scattering peak. For the case of parallel planes, such as thermotropic smectic phases or lyotropic lamellar phases, $n$ is a series of integers (1:2:3:4:5). Table 1 presents the ratios of $q$ values of the peaks in the diffractogram and the structural organization of the most common lyotropic liquid crystalline phases.\(^{14}\)

<table>
<thead>
<tr>
<th>n</th>
<th>Lamellar</th>
<th>Hexagonal</th>
<th>Cubic (primitive)</th>
<th>Cubic Pn3m</th>
<th>Cubic Fd3m</th>
<th>Cubic Lm3m</th>
<th>Cubic la3d</th>
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<td>$\sqrt{11}$</td>
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<td>$\sqrt{19}$</td>
<td>$\sqrt{12}$</td>
<td>$\sqrt{22}$</td>
</tr>
</tbody>
</table>
Experimental aspects
The X-ray powder diffraction spectra of the solid state gemini compounds were recorded at room temperature with a PANalytical X’Pert MPD diffractometer using the $\lambda = 0.154$ nm $K\alpha$ line of a Cu anode (Bragg–Brentano geometry) equipped with a X’Celerator detector. The spectra were obtained from 10 to 95° (2$\theta$), using a step of 0.017° and 100 s/step.

2.3.3. Differential scanning calorimetry (DSC)
Differential scanning calorimetry (DSC) is a widely used technique for the thermal analysis of materials. This technique allows the quantification of the heat absorbed or released during a given physical or chemical process. The designation differential is due to the fact that the behavior of a sample is compared with a reference material which does not undergo any chemical or physical change during the analysis. The term scanning comes from the fact that the temperature of the sample and reference is increased or decreased in a controlled manner, to enable continuous measurement over a range of pre-determined temperatures.\textsuperscript{144, 145}

![Figure 19. Representation of a thermogram with a first order transition and its parameters. Reprinted with permission from Springer.\textsuperscript{114}]

This technique provides a thermogram (Figure 19), which is usually a plot of the heat flow (or differential heat capacity) as function of temperature (or time). The thermogram analysis allows the determination of the enthalpy change during a physical process, e.g. a phase transition.\textsuperscript{144, 145}

Experimental aspects
DSC scans were performed using a Setaram DSC141 differential calorimeter. The equipment was previously calibrated, both for temperature and energy, using benzoic acid, indium and tin as reference compounds. A mass of 6–12 mg of solid compound was weighed to Al crucibles, and an empty crucible was used as a reference. The heating-cooling cycles were performed at a scanning rate of 3 K min\textsuperscript{-1}
in a temperature range of 20-250 °C, with nitrogen (p = 0.3 bar) used as sweeping fluid. Five independent essays were typically run for each compound, with at least one heating-cooling scan for each sample.

2.3.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is an experimental technique in which the mass of a sample is measured as a function of temperature or time. Typically the sample is heated at a constant rate or held at a constant temperature (isothermal measurement). The temperature range of the analysis will depend on the type of information required about the sample. Moreover, the atmosphere used in the TGA experiment plays an important role and can be reactive or inert. Changes of the atmosphere during the measurement are also possible. Mass changes occur when the sample loses material or reacts with the surrounding atmosphere.

![Thermogram](image)

Figure 20. Thermogram obtained from a thermogravimetric analysis.

The output data from TGA is a thermogram (Figure 20), where the variation of mass is represented as a function of temperature (or time). Typically, when a thermogravimetric analysis of a mixture of different components is carried out, the most volatile components start to evaporate/sublimate or thermally decompose in gaseous products (if the products are not in the gas state no mass variation is detected). Therefore, if the components decompose at different temperatures with well-defined mass variations (steps), the composition of the mixture is easily determined. The measurements can be carried out in air, nitrogen or other gases.

**Experimental aspects**

TGA measurements were carried out in a Mettler Toledo Star System (Mettler TGA/STDA851) under N\(_2\) atmosphere at flow rate of 50 ml/min, for a heating rate of 10 °C/min from 100 to 430 °C. Aluminium crucibles of 100 µL of volume were used.
2.3.5. UV-vis

Ultraviolet-visible spectroscopy (UV-vis) refers to the absorption of electromagnetic radiation in the ultraviolet-visible spectral region. This type of spectroscopy corresponds to the electronic transitions of electrons in the molecular orbitals, which falls in the UV-vis region of electromagnetic spectrum. Molecules which contain π and non-bonding electrons can absorb photons with a given energy (i.e. wavelength in the UV-vis region) that matches the energy difference between the electron states. A spectrometer records the wavelength at which absorption occurs, together with the absorbance at each wavelength.

Because absorbance is proportional to concentration of absorbing molecules it is possible to carry out quantitative measurements of different analytes. Carbon nanotubes absorb in the UV-vis region as mentioned in the section 1.1.1 and shown in Figure 21. Because nanotubes may also scatter light, the term optical density (or apparent absorbance) is preferably used within this thesis instead of absorbance.

Figure 21. UV-Vis spectrum of a SWNT dispersion, stabilized by Pluronic F127 in water.

The Beer-Lambert law, which relates the apparent absorbance $A$ of a liquid medium, having an optical path $b$ and a extinction coefficient $e$, with the concentration $c$ according to

$$A = -\log T = \log \frac{I_0}{I} = abc$$

(2.16)

where $T$ is the transmittance, $I_0$ is the intensity of the incident light and $I$ is the transmitted intensity. The amount of CNT dispersed in a given sample is determined by measuring the absorbance in relation to that of an aqueous dispersion with a known CNT concentration. Combining the TGA results with the UV-vis it is possible to calibrate the apparent extinction coefficient to mass.

**Experimental aspects**

The spectra were obtained using double beam (U- 2001 and Varian Cary 300 Bio) spectrometers. The dispersions were properly diluted to keep the apparent absorbance in a measurable range and absorbance was then recorded at $\lambda = 660$ nm.
Chapter 3. Dispersibility and binding dynamics: high molecular-weight dispersants

3. Summary of the research

In this chapter, a summary of the main results of this thesis is presented. We first explored the dispersibility of CNTs using high molecular-weight dispersants (namely, an amphiphilic polymer and a protein) where the exchange dynamics, the surface dynamics of the polymer onto the CNT surface, and the competitive adsorption of protein/polymer dispersants to the surface of nanotube were addressed (paper I and II). Additionally, a systematic study of the dispersibility of CNTs using low molecular-weight dispersants (surfactants) was investigated (paper III). The relative binding strength of the surfactant dispersants, and the effect of mechanical agitation on the dispersed CNTs were also subject to investigation (paper IV and V, respectively). In another study, the dispersibility of CNTs was evaluated using gemini surfactants, where the effect of the hydrophobicity of the surfactant (chain and spacer length) was explored (paper VI). Investigations on liquid crystal/CNT interactions were also attempted in this thesis. The thermotropic behavior of gemini surfactants in the absence of nanotubes was addressed (paper VII), and some exploratory work on gemini surfactant-CNT interactions was carried out.

3.1. Dispersibility and binding dynamics: high molecular-weight dispersants

In order to get a deeper insight into polymer-assisted CNT dispersions, we must follow the dynamics established between the dispersant and the nanotube at equilibrium. To fulfil this goal, NMR diffusometry was used, which allowed to quantify the fraction of dispersant adsorbed, to detect the surface displacement of dispersant on the CNT surface, and to assess the relative binding strength of polymer and protein (competitive adsorption) to the nanotube surface, as depicted in Figure 22.

Figure 22. Main findings obtained for the dynamics established between the dispersant and the CNT by NMR diffusometry: (a) lateral diffusion of a triblock copolymer (Pluronics F127) onto the nanotube surface and the residence time; (b) competitive adsorption of dispersants onto the CNT surface where the relative binding strength is assessed.
3.1.1. Slow exchange and adsorbed polymer amount

The behavior of a triblock copolymer, Pluronics F127 \((\text{PEO})_{97}(\text{PPO})_{69}(\text{PEO})_{97}\), on the SWNT surface was evaluated by NMR diffusometry. The diffusional decay of \(^1\text{H}\) NMR methylene signal of F127 was found to be not single exponential, but instead have a more complex profile. Changing the diffusion time \(\Delta\) allowed to conclude that F127 unimers were in slow exchange (within the NMR experimental time scale, \(\Delta\)) between a slow- and a fast-diffusing site.

The two diffusing sites were identified as follows: 1) the fast decay corresponds to the free F127 unimer in solution and 2) the slow decay is assigned to the F127 bound to the SWNT surface. In order to extract the residence time, \(\tau_{\text{bound}}\), and the fraction of F127 adsorbed on the SWNT, fits of the diffusional decays at different \(\Delta\) using the Kärger model were attempted.\(^{147, 148}\) The data could not be fitted together, as shown in Figure 23 a, indicating the possibility of a distribution of residence times on the SWNT surface. The data were then fitted pairwise (Figure 23 b,c,d), by using those with shortest available diffusion times (\(\Delta = 10\) and 20 ms) and those with the longer diffusion times (\(\Delta = 100, 200\) and 500 ms). It was then possible to observe that the fitted residence times, \(\tau_{\text{bound}}\), get longer with the increasing diffusion times, with a distribution between 100 to 400 ms. In addition, the fraction of F127 adsorbed on nanotube is merely 6 – 8 % of the total F127 in the dispersion.

Figure 23. (a) Fitting the Kärger model simultaneously to all diffusion data collected with diffusion times ranging from 10 to 500 ms. In (b-d), the fits are to the data collected on one hand at the shortest diffusion times (\(\Delta = 10\) ms, black symbols and \(\Delta = 20\) ms, red symbols) and on the other hand to data collected at one of the longer diffusion time (b) \(\Delta = 100\) ms, green (c) \(\Delta = 250\) ms, blue and (d) \(\Delta = 500\) ms, magenta.
3.1.2. Lateral diffusion and the wrapping/non-wrapping picture

Although the milliseconds time scale may be perceived as short in some context, it is still long as concerning conformational dynamics of the polymer. In particular, PEO and PPO chains are known to possess high flexibility and fast internal dynamics. This internal dynamics should permit the polymer to change its conformation also in relation to CNT, thus providing a mechanism for molecular displacement on the CNT surface. Therefore, the slow component in the diffusional decay is assigned to the polymer molecules diffusing on the nanotube surface. Taking into consideration that the lateral diffusion of polymer on nanotube axis is essentially one dimensional, the decay was fitted to 1-D isotropic diffusion. Despite some complications that can arise due to the orientation of nanotubes with the magnetic field, a lateral diffusion coefficient could be estimated, $D_{\text{lateral}} = (3-8) \times 10^{-12}$ m$^2$·s$^{-1}$. The depicted molecular picture (Figure 22 a), in this case, is consistent with a nonwrapping mode for the polymer-nanotube interaction.

3.1.3. Surface coverage and competitive binding between polymer and protein

The binding affinity of dispersants to the CNT surface is closely related with the dispersibility and the kinetic stability of nanotubes in water. NMR diffusometry was used to assess the relative binding strength of different dispersants to SWNT surface, where F127-SWNT is used as a reference system. Diffusion NMR enables the quantification of the fraction of F127 that is bound to the SWNT and the fraction that is free in the bulk. Therefore, by adding a second dispersant to the system one can monitor how the fraction of adsorbed F127 changes. One can compare directly the binding strength of the second added dispersant, and check 1) if that dispersant replaces or not F127, 2) to which extent it does so (if at all) and 3) how the replacement changes with concentration. Therefore, we can compare a series of dispersants and quantify the extent to which the dispersants can replace F127 on the SWNT surface. We firstly analyze a protein, leaving the case for low molecular weight dispersants for §3.2.2.

The protein Bovine Serum Albumin (BSA) is known to be a good dispersant of CNTs. Moreover, the use of BSA as dispersant is both important to 1) potentially enhance the CNT biocompatibility and 2) to use it as a model for CNT–biomolecules interactions. Understanding the binding competition between BSA and synthetic polymers is also important for drug formulations (were CNT acts as a drug carrier) or to mimic the mammalian body where albumins are present and would interact with CNTs.

In the light of this, we performed a study where BSA was added to a F127–SWNT dispersion (and conversely F127 to BSA-SWNT) to evaluate the relative binding strength and observe if one of the dispersants can replace the other (paper II). In order to assess and understand the effect of adding BSA to the F127-
SWNT dispersion, we started with a simpler scenario by adding a small aliquot of a F127 concentrated solution to the original SWNT dispersion. Figure 24a presents the diffusional decay of the oxyethylene signal after having increased by Δc_{F127} the concentration of F127 in the dispersion. Fitting the diffusional signal decay to a two-site model, it is possible to extract the fraction f_{F127} that is adsorbed to the nanotube surface. The obtained f_{F127} (Figure 24 b) shows that upon addition of F127 the relative population of F127 adsorbed to the nanotube decreases monotonically, indicating that the SWNT surface is saturated and the adding of F127 only increases the fraction of free F127.

![Figure 24](image.png)

Figure 24. The diffusional decay of the 1H NMR signal from the F127 oxyethylene peak as function of Δc_{F127}, the amount of F127 added to an F127-SWNT dispersion. The lines are two-component exponential where the amplitudes of the two components provide the populations of the free aqueous (fast component) ad surface-adsorbed (slow component) F127 populations

Since we know both the total concentration of F127 (c_{F127}) and the total amount of SWNT (c_{SWNT}), the surface coverage of the nanotube (σ) is obtained by

\[ σ_{F127} = (f_{127} \times c_{F127}) / c_{SWNT} \] (3.1)

As figure 24 b shows, this apparent surface coverage remains constant (within the data uncertainty), or at best slightly increases, despite the fact that c_{F127} increased twofold.

Since we had previously established that the exchange time between these dispersants is below 1 s, a few minutes are expected to be enough to establish equilibrium between both dispersants and the nanotube surface. The dispersant with higher binding affinity should have a higher surface concentration. The effect of adding BSA to the F127-SWNT dispersion is shown in Figure 25. As is clear, adding BSA does not decrease significantly the apparent surface coverage of SWNTs by F127 (σ_{F127}). The most straightforward explanation for this behavior is that the binding strength of BSA to the SWNT surface is significantly lower than that of F127.
Chapter 3. Dispersibility and binding dynamics: high molecular-weight dispersants

Figure 25. (a) The diffusional decay of the 1H NMR signal from the F127 oxyethylene peak as a function of BSA added to a F127-SWNT dispersion. The lines are two-component exponential fits; (b) The population fraction of F127 ($f_{F127}$) adsorbed on the SWNT surface and the corresponding apparent surface coverage $\sigma_{F127}$ by F127 molecules. The dashed lines are linear fits.

The reverse effect (i.e. adding F127 to the BSA-SWNT dispersion) was also tested in order to confirm the stronger binding strength of F127 to SWNT surface. Figure 26 presents the diffusional NMR decays of F127 added to BSA-SWNT dispersion. It is observed that part of the F127 molecules added to the dispersion adsorb to the nanotube surface, as evidenced by the appearance of the slow diffusion component in the decay. Figure 26 shows that with the increasing of F127 concentration, the fraction of polymer adsorbed to SWNT surface decreases. However, the apparent surface coverage increases with the increase of F127 concentration.

Figure 26. The diffusional decay of the 1H NMR signal from the F127 oxyethylene peak as a function of F127 added to a BSA-SWNT dispersion. The lines are two-component fits.
A comparison of Figure 25 and 26 can be most-easily interpreted as F127 binding to the CNT surface more strongly than BSA. Hence, in a system with dynamic equilibrium with continuously exchanging molecules, the CNT surface becomes preferentially covered by F127 even if it was originally covered by BSA. Conversely, an initial F127 coverage on the SWNT surface is kept, despite BSA having been added to the solution.

3.2. Dispersibility and binding dynamics: low molecular-weight dispersants

In this section a systematic study of the ability of low molecular-weight dispersants (herein, ionic surfactants) to disperse SWNTs and MWNTs is presented. The dispersed CNT concentration ($c_{CNT}$) in water was estimated using calibration curves (apparent extinction coefficient) obtained from thermogravimetric analysis combined with UV-vis spectroscopy. Two main types of surfactant, single-chained surfactants and gemini surfactants, were explored. For single-chained surfactants, the effects of 1) the presence of aromatic rings in the chemical structure, 2) alkyl chain length, 3) the head group charge and 4) morphology of CNTs (SWNT vs. MWNT) were assessed. The relative binding strength of some dispersants and the vortex mixing effect in the aggregation of nanotubes is also presented. Lastly, the dispersibility of CNTs using gemini surfactants, where the effect of the spacer and the hydrophobic chain length was evaluated, is presented.

3.2.1. Single-chained ionic surfactants: systematic studies and molecular insight

In Paper III the dispersion ability of several ionic surfactants (SDS, STS, SDBS, CPyCl, DTAB, TTAB and CTAB) to disperse CNTs was assessed. Both bath and tip sonication were employed to disperse CNTs and compared in terms of reproducibility of the obtained dispersions. Our main observations show that, even though the energy density transferred to the liquid is in the same order or magnitude, the tip is far more reproducible than the bath. Converting the energy density to shear stress both the sonication methods apply shear stress enough to exfoliate and fragment the CNTs. However, converting the power density to stress rate, the tip delivers much higher average stress rate. This stress rates can be related with the number of cavitation bubbles imploding per time, i.e. for tip sonication the implosions/s is much higher. Considering the kinetics effect of: 1) the rate of exposing a new CNT surface, 2) the rate of reattaching the exposed surface and 3) the rate of the surfactant to adsorb in the nanotube to avoid reaggregation; we can infer that the higher rates produced by the tip seem to be needed in order to assure a kind of "steady-state" to maintain the reproducibility of the data.
Figure 27 presents the dispersion curves, where the effect of varying $c_s$ (surfactant concentration initially present in the dispersion, before sonication-centrifugation) on $c_{CNT}$ dispersed is evaluated. All the dispersion curves show a sigmoidal profile. Several new metrics (presented for the first time) were extracted from dispersion curves after appropriate fittings to the data (Figure 27 d). The $c_s$ required to effectively start dispersing CNTs is designated by us as the critical dispersibility concentration ($cdc$). After this point (i.e $cdc$), $c_{CNT}$ increases rapidly until a maximum value, $c_{CNT,max}$, is attained at the surfactant concentration denoted as $c_{s,max}$. In addition, two other metrics were introduced: the dispersion effectiveness, $\eta$, and the dispersion efficiency $\eta^*$. All these metrics were used to evaluate and compare the dispersion ability of the surfactants and rationalize it in the light of the chemical structure (presence of aromatic rings, alkyl chain length and polar head group).

The effect of nanotube morphology (MWNT vs. SWNT) on the nanotube dispersibility was evaluated Figure 27 (a and c). It is observed that the $cdc$ and $c_{s,max}$ are always lower for MWNT than for SWNT. As concerning the dispersion effectiveness, $\eta$, and efficiency $\eta^*$, the studied surfactants are more effective dispersing MWNT (on a mass basis). However, we can analyze this result accounting the differences of the specific surface area (SSA) between SWNT and MWNT. We estimated that the SSA of SWNTs is $\approx$4 times that for MWNTs. Using that relation in the SSA, one can calculate the amount of surfactant $c_{s,max}$ at the $c_{CNT,max}$, which results in a surface concentration of 10 $\mu$mol·m$^{-2}$, that is $\approx$ 5 molecule·nm$^{-2}$ for both SWNT and MWNT. Thus, the surface concentration at saturation is similar for MWNT and SWNT pointing that adsorption of surfactant is not appreciably affected by the nanotube curvature.

The presence of the aromatic ring in the surfactant structure is assessed comparing the dispersibility of the pairs SDS vs. SDBS and CTAB vs. CPyCl. We observed that SDBS is the most efficient dispersant (both on mass and surface basis) for SWNT and MWNT. On the other hand, CPyCl that also possesses an aromatic pyridinium ring in the chemical structure does not present a significantly superior performance when compared with CTAB.

Analyzing the surfactant chain length effect, the dispersion effectiveness, $\eta$ and efficiency $\eta^*$ increases with the number of C atoms (nC) in the alkyl chain length. The zeta potential measurements also follow this trend. Since the zeta potential measurements were carried out at fixed $c_s$ and $c_{CNT}$ the increase in $\zeta$ is proportional to the increase of the surface charge, it seems reasonable to conclude that surfactants with higher nC adsorb more extensively, which is presumably related with a higher $\eta$ and $\eta^*$. 

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Due to the adsorption of surfactants onto CNTs surface, the presence of small bundles or individual nanotubes in a surfactant solution will shift the \( \text{cmc} \) to 10-50\% higher values. However, before exfoliation, the nanotube powder is typically sedimented and we can assume that the fraction of the surfactant adsorbed on the powder has a minor effect on the \( \text{cmc} \). Thus, it is valid use the \( \text{cmc} \) of neat surfactant to assess the role of micelles in the dispersibility of CNTs. During the exfoliation process two simple situations can happen: 1) micelles help as full aggregates in the exfoliation or 2) just act as a reservoir of unimer. In order to elucidate which of the situations are more favorable to the CNT exfoliation, we tried to find patterns in the dispersion curves correlating the \( \text{cdc} \) and the \( c_{\text{s,max}} \) with the \( \text{cmc} \). For the systems studied, no clear trends were observed in the metrics. Therefore, the presence of micelles does not seem to play any important role in the exfoliation process.
3.2.2. Surface coverage and competitive binding between polymer and surfactant

In paper IV the same methodology used to investigate the competing binding between the F127 and BSA was extended to ionic surfactants in order to assess the relative binding strength and correlate with other parameters such as dispersion efficiency and colloidal stability of nanotube dispersions.

For a given SWNT-F127 dispersion the surface coverage was calculated using equation 3.1. The addition of a second dispersant, the fraction of F127 adsorbed in the SWNT decreases. The replacement of F127 by DTAB, TTAB, CTAB, sodium cholate (SC), SDS, SDBS and CPyCl at different concentrations was evaluated. Figure 28 presents the relative capability of surfactants to displace the F127 from the SWNT surface. The results are correlated with the relative binding strength of each surfactant.

Clearly we can observe that DTAB has a limited capability to bind to the SWNT surface as compared to the other dispersants. On the other hand, SDBS is the surfactant with the highest relative adsorption strength. At lower concentration (0.5 mg mL\(^{-1}\)) CPyCl and S. cholate are the surfactants with higher affinity to the SWNT. As the concentration of surfactant is increased, SDS and SDBS are the surfactants with higher binding strength.

Within each class of (anionic and cationic) surfactants, those with aromatic rings present a higher relative binding strength to the SWNT surface. However, as concerning the charge of the polar head group, anionic surfactants present a relative higher binding strength.

Apparently the increase of the number of carbons in the chain length increases the binding affinity to the SWNT. Clearly DTAB has lower affinity to the surface than surfactants with higher number of carbons. However, comparing CTAB and TTAB the conclusions are not straightforward, and at higher concentration CTAB removes less F127 from the surface. However, we should have in mind that the measurements were carried out at 20 °C (to avoid micellization of F127). Clearly this temperature is lower than the Krafft temperature of CTAB. The precipitation of CTAB was not detected by NMR, however, we cannot exclude the possibility that a small amount of CTAB is crystalized and thereby is not actively replacing the F127 on the SWNT surface.

In Figure 29 we tried to correlate the relative binding strength with the metric \(cdc\) obtained for the dispersants in paper III. The concentration unit was rescaled in units of \(cdc\). We observe that all the data fall in a in a universal curve where at \(cdc\) all surfactants displace ca half of the F127 originally at the CNT surface. This finding provides us with a new hypothesis as concerning the origin of \(cdc\) – namely, dispersing by cleavage requires a particular threshold coverage that is characteristic for the nanotube.
Figure 28. Normalized surface coverage as function of ionic surfactant addition. The lines are a visual guide.

Figure 29. The change in surface coverage by F127 molecules (data as in Figure 28, except that for sodium cholate) with surfactants concentration normalized by the critical dispersion concentration, cdc. The cdc data was taken from paper III.
3.2.3. Aggregation of pre-dispersed CNTs induced by mechanical agitation

Vortex-shaking is typically used to fragment and disperse insoluble materials in a solvent. However, we observed an aggregation process of pre-dispersed CNTs that, contrary to expectation, is induced by vortexing. The vortex mixer produces a turbulent regime flow that enhances the collisions between the dispersed CNTs in water nanotubes, forming micron-sized loose structures.

In paper V the effect of the vortex mixing is evaluated for several SWNT—dispersants (cationic: DTAB, CTAB; anionic: SDS, SDBS; and nonionic: F127, F68 and TX-100). It was observed that the aggregates display an irregular morphology similar to a fractal. These aggregates are noncompact and are easily redispersed by bath sonication. Therefore, we designate them as loose aggregates.

![Figure 30. Dependence of average loose aggregate size with the vortex time for different surfactants. The $c_{SWNT}$ was kept constant in all the studied systems.](image)

The aggregates were visualized using video-enhanced light microscopy (VELM) and the size of the aggregate was characterized by the length ($L_a$) of the higher axis. In Figure 30, we present the average length $<L_a>$ of the loose aggregates as function of vortexing time for different the dispersant-SWNT systems. Clearly, some trends in the average size can be observed. Vortexing induces aggregation for all the surfactant—CNT systems, with $<L_a>$ increasing with vortexing time. However, there are significant differences in the average size $<L_a>$ for the different SWNT-surfactant systems. SDBS and F127 take longer time to form visible aggregates, experience a slower rate of growth and form the smallest ones ($<L_a>$ = 20–40 μm). On the other extreme, F68 and DTAB form the largest aggregates ($<L_a>$ = 40–140 μm) and undergo a sharper growth rate.

For the two block copolymers used (F127 and F68), we observed two extreme behaviors. On one hand for F127 (PEO)$_{97}$–(PPO)$_{69}$–(PEO)$_{97}$ the aggregates are quite
small, on other hand F68 (PEO)_{76}-(PPO)_{29}-(PEO)_{76} display larger aggregates. Both the polymer and nanotube concentration are identical, thus we can argue that the main difference is due to the effective steric repulsion exerted by each polymer. Indeed, the longer hydrophobic block of F127 (=69 PPO monomers), which provides a stronger anchoring to the nanotube, combined with a bigger PEO block (=97 PEO monomers) is the cause for this difference between the two polymers. Not surprisingly, F127 shields more efficiently the CNT, which results in much smaller aggregates.

SDBS is a good dispersant of nanotubes (as shown in paper III), mainly due the \(\pi-\pi\) interactions established with the CNT surface. Therefore, it is expected that it will also be a good shielding surfactant, which will reflect on smaller aggregate size. Indeed, this is the case. Analyzing other surfactant with aromatic ring in the hydrophobic region, Tx-100, we observe that it is not as efficient as SDSB in shielding the nanotubes, hence producing bigger aggregates. This can be explained by the smaller (and branched) hydrophobic tail of Tx-100 (as compared with SDBS) which will perhaps result in a lower adsorption to the nanotube (less coating). In addition, TX-100 stabilizes the nanotubes by steric repulsion. The headgroup is an oxyethylene block (PEO)_{10} composed by \(\approx 10\) monomers, but quite small when compared to the F127 or F68, and thus the steric repulsion is also weaker. The surfactant DTAB, which is not a very good dispersant as we pointed in paper III, not surprisingly also presents quite big aggregates suggesting that the shielding is weak. Conversely, CTAB, a surfactant with higher \(n_C\) and observed to be a good dispersant in paper III, also presents a quite good shielding effect. Analyzing the behavior of SDS aggregates, one observes an intermediate behavior - slightly better in shielding than DTAB at shorter vortexing times.

The effect of relative centrifugation force, \(g\), was also assessed in the formation and growth of aggregates. The vortexing time effect was tested for a SDS-SWNT dispersion centrifuged at four different \(g\)-grades - \([2, 4, 10, 30] \times 10^3\) g. As presented in paper V, it was observed that for higher \(g\) values more vortexing time was necessary to induce the growth of the aggregates. At higher \(g\), bigger bundles are sedimented in the precipitate. Thus, if bundles have a role similar to a nucleation process, i.e. the presence of bigger bundles are favorable to the formation and growth of aggregates, it is expected that for higher \(g\) forces more time will be necessary to grow the aggregates.

Different concentrations of SWNTs were also tested (at constant \(4 \times 10^3\) g). The general observation was that as \(c_{\text{SWNT}}\) increases \(<L_a>\) also increases. This effect seems to be related with the higher amount of nanotubes which results in high frequency of collisions, originating a larger mesh structure.
**Mechanism of aggregation**

Molecular dynamics simulations have shown that the surfactant coating is more vulnerable for a pair of perpendicular tubes – i.e. shielding that prevents nanotube aggregation is less effective if nanotubes collide perpendicularly. Therefore, we can assume the same happens when nanotubes collide at more favorable angles. Additionally, if the nanotube is not totally coated and possess free areas, these areas can act as bridging points. Vortexing induces the collision of the nanotubes, creating bridging points that originate a network. In Figure 31, the microstructure of the aggregates can be observed at different scales. Clearly, an aggregate is observed using VELM. In the Cryo-SEM, an entangled structure of nanotubes is observed. By increasing the magnification (in the cryo-TEM), we can see several nanotubes linked forming a mesh-like network, which supports our molecular model (Figure 31 d).

![Figure 31](image_url)

**Figure 31.** Imaging of the vortex-induced aggregates at different size scales: a) VELM shows the loose structure of the floc. It is also possible to discern dark particles (< 1 µm) inside the aggregate. b) Cryo-SEM magnification showing a network of entangled CNTs. c) Cryo-TEM showing individual CNTs, but also 200-300 nm dark regions d) Schematic view of the CNT cross-binding. Perpendicular junctions should be favored.
3.2.4. Gemini surfactant-assisted dispersions: spacer length and hydrophobicity effects

In paper VI, the dispersibility of multiwalled carbon nanotubes (MWNTs) using a set of bis-quat dicationic gemini surfactants of the n-s-n type was investigated. Both the lengths of the covalent spacer (s)—bridging the two cationic headgroups—and of the tail (n) were systematically varied. Hence, 12-s-12 gemini with s = 2, 6, and 12 were studied together with 16-s-16 (s = 2 and 12). In addition, the single-tailed homologues DTAB (n = 12) and CTAB (n = 16) were also used for direct comparison.

![Graph](image_url)

**Figure 32.** Concentration of dispersed MWNTs vs. surfactant concentration (log scale): (a) for the 12-s-12 gemini, including DTAB for comparison; (b) for the 16-s-16 gemini, including CTAB for comparison; (c) comparison of chain length effects for homologues 12-2-12/16-2-12, 12-12-12/16-12-16 (shown as an inset) and DTAB/CTAB.

Similar to the previous study for single chained ionic surfactants (paper III), high precision dispersion curves (Figure 32) were obtained through a well-controlled sonication/centrifugation procedure and accurate determination of MWNT concentration by a combined thermogravimetry/UV-vis spectroscopy method. This allowed us to extract some reliable metrics for each surfactant, for proper comparisons, namely the critical dispersibility concentration ($c_{dc}$), the maximum dispersed CNT concentration ($c_{CNT,max}$) and respective surfactant concentration at that point ($c_{s,max}$), and the dispersion effectiveness ($\eta$) and efficiency ($\eta^*$).
All gemini surfactant showed a relatively modest capacity to disperse the nanotubes (about 20 %), comparable to that of DTAB, but strikingly inferior to that of CTAB. However, long spacer surfactants like 12-12-12 and 16-12-16 were found to be much more efficient that CTAB. Comparing only the gemini compounds, we found that spacer length has a more significant influence than tail length on the ability to disperse MWNTs. The effectiveness remains basically insensitive to both spacer and tail variation; however, the efficiency is clearly increased as the spacer length increases.

As one of the most important observations, we have noticed that \( c_{s,\text{max}} \), the ratio \( c_{s,\text{max}}/c_{\text{CNT,\max}} \) and the surfactant amount per CNT area at \( c_{s,\text{max}} \) all decrease linearly with spacer length. This suggests that the adsorption of gemini surfactants to the MWNT surface, even though governed principally by hydrophobicity, is rather different from the bulk micellization process, for which the \( \text{cmc} \) is well known to vary non-monotonically with spacer length. Moreover, our data also indicate that the presence of surfactant micelles in the exfoliation process does not seem to play any decisive role in the final dispersibility, in line with our observations for the common single-tailed surfactants (paper III). In conclusion, the broader picture that emerges from these observations is that of an adsorption mechanism that does not involve the formation of micelle-like aggregates on the MWNT surface, but rather a loose surfactant binding.

3.3. Carbon nanotube-liquid crystal interactions

3.3.1. Overview

The incorporation of CNTs in liquid crystals allows their orientation along the director axis of the liquid-crystalline phase, where the mesophase acts as a host\(^{152-154}\). The development of nanocomposites made by CNTs, where the thermotropic liquid crystal acts as the host has, however, been quite limited due to the poor dispersibility of CNTs directly in the liquid crystal\(^{155}\). Here, our goal was to circumvent this limitation by dispersing the nanotubes in gemini surfactant solutions, and by simple drying to obtain a nanocomposite film. In order to assess and rationalize the molecular interactions between CNTs and surfactants, it is important to know the phase behavior of neat surfactants. In the next section, we present the thermotropic phase behavior of gemini surfactants in the absence of nanotubes. Additionally, a very exploratory work of SWNT-thermotropic liquid crystals interactions, using gemini surfactants as dispersants, is presented.
3.3.2. Thermotropic liquid-crystalline behavior of gemini surfactants

Paper VII presents a systematic study on the thermotropic phase behavior of dimeric or gemini surfactant, based on differential scanning calorimetry, polarized light microscopy and X-ray diffraction. The compounds consist of a series of dimeric amphiphiles designated as 12-s-12, with covalent spacer lengths s=2, 3, 4, 5, 6, 8, 10 and 12. Such compounds display a structure-property versatility that may prove useful for the choice of liquid-crystalline matrices for the incorporation of CNTs.

The DSC thermograms for all the compounds show a strong effect on the thermal behavior produced by the increment of the spacer length, at constant tail length. All the compounds show several thermotropic phase transitions denoting a complex melting process. Inspection of the thermograms allows us to infer that the main peak corresponds to partial melting of the chains. Therefore, the phase formed on heating immediately after the strongest peak is considered as a (partially ordered) mesophase or a soft-crystalline phase, most likely with the headgroups positions fixed by the strong ionic interactions and with only partially molten alkyl chains.

The thermotropic behavior was characterized by combining the thermograms and direct PLM observations of birefringent defective structures. Below the main peak temperature, the 12-s-12 compounds exhibit a solid phase, which shows as birefringent crystallites. Although solid-solid transitions appear on the thermograms for some compounds, the PLM textures remain practically unchanged.

Figure 33. Different textures for the SmA liquid crystals of 12-s-12 amphiphile compounds: s = 2, oily streak; s = 3, oily streaks and focal conics; s = 4, narrow flake; s=8, feather-like flake; s = 10, mosaics; and s = 12, mosaics.
The mesophase textures depend on the spacer length of the gemini surfactant. Typical textures of mosaics and fan-shaped appear for the lower-temperature phases, while the upper-temperature more fluid mesophases appear as oily streaks and focal conics. Some of the textures only become better defined in the polarized light microscope upon several controlled heating-cooling cycles or the application of a small shearing force. Figure 33 shows some examples of textures: 12-2-12, oily streaks and fan-shaped textures; 12-3-12, oily streaks and focal conics; 12-4-12, narrow flakes; 12-8-12, feather-like flakes; 12-10-12, mosaic and fan-shapes; and 12-12-12, mosaics. Upon cooling the isotropic liquid of the four 12-s-12 surfactants with s=2, 8, 10, and 12, hysteresis effects are observed between the liquid and mesophases.

Gemini surfactants with spacer s=5 and 6 do not seem to show any fluid mesophases with oily streaks or focal conics below 200 °C but change instead into a brownish color. Thus, it is likely that they undergo decomposition before or concomitantly with isotropization. 12-3-12 and 12-4-12 exhibit fluid LCs but no isotropic liquid formation also because of decomposition.

Smectic structures are amongst the most frequently encountered liquid crystals when studying the thermotropic behavior of amphiphiles. Because of the structural asymmetry between hydrophilic headgroups and hydrophobic chains in the gemini compounds herein investigated, the smectic liquid crystal structure should possess a double layer with end-to-end or interdigitated chain arrangements. With respect to the relation between the director of the molecules and the bilayer plane, the long chains may be perpendicular to the plane (SmA phase) or tilted (SmC phase).

Combining the DSC and PLM studies, only briefly described here, it is possible to present a global thermal phase diagram (Figure 34), in which the effect of the spacer length on the thermotropic behavior of the gemini surfactants is apparent. The proposed assignment of the mesophases (soft crystals, ordered and disordered smectic liquid crystals) is shown in the phase diagram.
Figure 34. Thermal phase behavior of 12-s-12 gemini compounds. Notations are: Cr, crystalline solid phase region; M1, mesophase 1; M2, mesophase 2; M3, mesophase 3; SmA, smectic A liquid crystalline phase; SmB, smectic C liquid crystalline phase; I isotropic liquid phase.

Figure 35. Possible packing configurations for the smectic layers in the 12-s-12 gemini, based on a cis (A) or trans (B) conformation for the tails. For A arrangements: A1, upright tails with no interdigitation (tail to tail); A2, tilted tails with no interdigitation; A3, upright tails with full interdigitation (tail to head); A4, tilted tails with full interdigitation. For B arrangements: B1, upright tails with no interdigitation (tail to tail); B2, upright tails full interdigitation (tail to head); B3, tilted tails with full interdigitation (tail to head).

Relating the information above with the $d_{001}$ spacing obtained from X-ray diffraction, some possibilities for the molecular packing could be put forth. XRD
data for the solid phases agree qualitatively with the trends observed in thermal behavior. Essentially two different types of packing were proposed (Figure 35).

### 3.3.3. Exploratory investigations

Considering that the thermotropic behavior of gemini surfactants was previously assessed, some preliminary attempts were carried out in order to create a hybrid material – i.e. a nanocomposite. Chiral SWNT (6,5) were dispersed using a dicationic gemini surfactant, with the tail length \((n = 12)\), and spacer length \((s = 12)\), i.e. gemini 12-12-12 (a good dispersant according to paper VI). After quantification of the SWNT dispersed, additional gemini surfactant was added to the dispersion in order to tune the proportion SWNT/surfactant. The solvent (water) is removed by vacuum-oven \((40^\circ C)\) drying and a SWNT-surfactant film was formed on the wall of the vial. During the drying process, the surfactant solid can undergo phase transitions to multiple liquid-crystalline phases until total remove of water. The crystal lattice of the surfactant can work as a template for SWNT alignment. However, the SWNT will also induce changes in the local organization of the surfactant lattice crystal. Our goal was to investigate the extent to which the inclusion of the SWNT in the crystal lattice changes the thermotropic behavior of the neat gemini surfactant.

![Figure 36. Polarized light microscopy images obtained at room temperature: (a) birefringent crystallites of the solid powder of gemini 12-12-12 surfactant; (b) texture of the 0.5 wt% SWNT–12-12-12 film nanocomposite - oily streaks domains seems to appear.](image)

Several ratios of SWNT-surfactant were attempted, but samples with more than 0.5 wt% (in proportion to the surfactant mass) of nanotube resulted in a less uniform film. In Figure 36 we can observe textures, obtained under polarized light microscopy, for the gemini surfactant 12-12-12 powder and the nanocomposite SWNT–12-12-12. Birefringent crystallites are observed for the neat surfactant, whereas oily streaks textures seem to appear for nanocomposite. Additional observations are needed to full characterize the obtained nanocomposite.
In addition, X-ray analysis was performed on the film, and two $d$-spacing domains could be observed in the pattern (Figure 37). In summary, some attempts were made to produce a SWNT-gemini composite. Tuning the relative proportion of SWNT to surfactant resulted in different morphology of the film deposited. Further work, such as thermal behavior, can be performed in order to characterize and explore this type of nanocomposites.
4. Concluding remarks

In this work, aqueous dispersions of carbon nanotubes were studied by resorting to several characterization methods, namely NMR diffusometry, light and electron microscopy, UV-vis spectroscopy and TGA. The results allowed us to obtain molecular-level information on the dispersant-nanotube interactions, and rationalize them in light of the chemical structure of the dispersants. Additionally, it was shown that NMR diffusometry can be a versatile, non-invasive and valuable technique to assess the dynamics of the dispersant adsorbed onto the CNTs.

The exchange time between free and bound F127, a polymeric dispersant, onto the SWNT surface was found to be in the time scale of NMR diffusometry (1–10^3 ms), which in turn allowed estimating the residence time of F127 on the CNT surface, the fraction adsorbed, and the lateral displacement of this dispersant on the CNT surface—observations in line with a non-wrapping model. Moreover, the amount of F127 adsorbed onto CNT detected by diffusion NMR permitted to carry out surface coverage and competitive adsorption studies of several types of dispersants (F127, BSA and ionic surfactants) onto SWNTs. It was shown that BSA is not able to replace F127 on the nanotube surface. However, the addition of ionic surfactants was found to cause displacement of F127 from the nanotube surface, which allowed gauging the relative binding strength of ionic surfactants to SWNTs.

Dispersibility studies of CNTs in water as a function of the concentration of dispersant (namely ionic surfactants) were carried out. The effect of the molecular properties of the surfactants were assessed and rationalized according to objective metrics obtained from the sigmoidal profile of the dispersibility curves. Among the most relevant results, we found that a minimum dispersant concentration, designated as critical dispersibility concentration (cdc), is needed to start dispersing CNTs. Additionally, the concentration of surfactant required to attain maximal dispersibility depends linearly on alkyl chain length for a series of homologue surfactants, which indicates that the CNT-surfactant association, although hydrophobic in nature, is rather different from a micellization process.

An interesting and somewhat counterintuitive result obtained was the effect of mechanical agitation, through vortex shaking, on SWNT dispersions, namely the formation of weakly bound micron-sized aggregates, which can be easily redispersed by mild sonication. The effect of vortexing time on the size of the aggregates was investigated and significant differences were found between different dispersants. The results were rationalized in terms of vortex-driven tube-tube contacts and the shielding effect of dispersants, which in turn were related to factors such as surface coverage and binding strength of the dispersants.

For dicationic gemini surfactants of the n-s-n type, with alkyl spacer length s and alkyl tail length n, it was observed that the spacer length has a more significant influence than tail length on the dispersibility of MWNTs. The overall data pointed
further to an adsorption mechanism that does not involve the formation of aggregates on the MWNT surface, and suggested that the hydrocarbon tails (in contrast to the spacer) do not take active part in the binding process. In addition, the data also indicated that the presence of surfactant micelles does not play any decisive role in the exfoliation process and in the final dispersibility, in line with a pattern observed for the single-tailed surfactants previously explored.

With the prospective goal of incorporating nanotubes in liquid crystalline (LC) phases to prepare nanocomposites, the effect of the spacer length on the thermotropic behavior of the gemini 12-s-12 surfactant was explored. The spacer length (s) on the 12-s-12 gemini was found to present a sharp and non-monotonous effect on the thermotropic behavior of these compounds. This was related to differences in packing in the solid state caused by variations in spacer length, and some packing models were presented on the basis of XRD data. Some exploratory work was attempted concerning the imbedding of SWNTs on the surfactant solids and birefringent films were obtained. This work opened the possibility of future investigations, exploring the structure and thermal behavior of the nanocomposites formed.
List of abbreviations

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<th>Full Form</th>
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<tr>
<td>BSA</td>
<td>Bovine Serum Albumin</td>
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<td>cdc</td>
<td>critical dispersibility concentration</td>
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<td>cmc</td>
<td>critical micelle concentration</td>
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<tr>
<td>CoMoCAT</td>
<td>Cobalt-Molybdenum Catalysis process</td>
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<td>CPyCl</td>
<td>Cetylpyridinium Chloride</td>
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<tr>
<td>Cryo-SEM</td>
<td>Cryo-Scanning Electron Microscopy</td>
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<td>Cryo-TEM</td>
<td>Cryo-Transmission Electron Microscopy</td>
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<td>CTAB</td>
<td>Cetyltrimethylammonium Bromide</td>
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<td>CVD</td>
<td>Chemical Vapor Deposition</td>
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<td>Dimethylformamide</td>
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<td>LC</td>
<td>Liquid Crystalline</td>
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<td>MWNT</td>
<td>Multiwalled Carbon Nanotubes</td>
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<td>NMP</td>
<td>N-methyl-2-pyrrolidone</td>
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<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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<td>PEO</td>
<td>Poly(ethylene oxide)</td>
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<td>PGSE</td>
<td>Pulsed Gradient Spin-Echo</td>
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<td>PGSTE</td>
<td>Pulsed Gradient Stimulated-Echo</td>
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<td>PPO</td>
<td>Poly(propylene oxide)</td>
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<td>RF</td>
<td>Radio Frequency</td>
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<td>SANS</td>
<td>Small-Angle Neutron Scattering</td>
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<td>SDBS</td>
<td>Sodium Dodecyl Benzene Sulfonate</td>
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<td>Specific Surface Area</td>
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<td>SWNT</td>
<td>Single-Walled Carbon Nanotube</td>
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<td>TGA</td>
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<td>Video-Enhanced Light Microscopy</td>
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<td>XRD</td>
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