Molecular Order and Dynamics in Nanostructured Materials by Solid-State NMR

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To my family
Abstract

Organic-inorganic nanostructured composites are nowadays integrated in the field of material science and technology. They are used as advanced materials directly or as precursors to novel composites with potential applications in optics, mechanics, energy, catalysis and medicine. Many properties of these complex materials depend on conformational rearrangements in their inherently dynamic organic parts. The focus of this thesis is on the study of the molecular mobility in ordered nanostructured composites and lyotropic mesophases and also on the development of relevant solid-state NMR methodologies.

In this work, a number of new experimental approaches were proposed for dipolar NMR spectroscopy for characterizing molecular dynamics with atomic-level resolution in complex solids and liquids. A new acquisition scheme for two-dimensional dipolar spectroscopy has been developed in order to expand the spectral window in the indirect dimension while using limited radio-frequency power. Selective decoupling of spin-1 nuclei for sign-sensitive determination of the heteronuclear dipolar coupling has been described. A new dipolar recoupling technique for rotating samples has been developed to achieve high dipolar resolution in a wide range of dipolar coupling strength. The experimental techniques developed herein are capable of delivering detailed model-independent information on molecular motional parameters that can be directly compared in different composites and their bulk analogs.

Solid-state NMR has been applied to study the local molecular dynamics of surfactant molecules in nanostructured organic-inorganic composites of different morphologies. On the basis of the experimental profiles of local order parameters, physical motional models for the confined surfactant molecules were put forward. In layered materials, a number of motional modes of surfactant molecules were observed depending on sample composition. These modes ranged from essentially immobilized rigid states to highly flexible and anisotropically tumbling states. In ordered hexagonal silica, highly dynamic conformationally disordered chains with restricted motion of the segments close to the head group have been found.

The results presented in this thesis provide a step towards the comprehensive characterization of the molecular states and
understanding the great variability of the molecular assemblies in advanced nanostructured organic–inorganic composite materials.

**Keywords:** mesoporous materials, organic-inorganic nanocomposites, surfactants, liquid crystals, MCM-41, clays, conformational dynamics, solid-state NMR, local field spectroscopy, dipolar coupling, dipolar recoupling, spin decoupling.
Sammanfattning

Idag är nanostrukturerade organiska-oorganiska kompositer ett vanligt förekommande inslag i materialvetenskap och materialteknologi. De används antingen direkt eller som startmaterial för nya avancerade material inom t.ex. optik, mekanik, katalys eller medicin. Många av dessa ämnens egenskaper beror på konformationsförändringar i de dynamiska organiska delarna. Denna avhandlings fokus ligger på studier av molekylers rörlighet i nanostrukturerade kompositer och lyotropa mesofaser samt på att utveckla relevanta metoder för fast-fas NMR-spektroskopii.

Ett antal nya experimentella tillvägagångssätt för att karakterisera molekylär dynamik med atomär upplösning i komplexa fasta och flytande material med dipolär NMR spektroskopii har utvecklats: (i) En ny pulssekvens för tvådimensionell dipolär spektroskopii gör det möjligt att utvidga det spektrala området trots begränsad effekt hos radiofrekvens pulser. (ii) Selektiv dekoppling av atomkärnor med spinkvantal 1, som ger möjligheten att mäta båda storleken och tecknet av dipolkopplingen mellan heteroatomer. (iii) En ny dipolär återkopplingsteknik för roterande prover, vilken uppnår en hög dipolär upplösning för en rad olika dipolära kopplingsstyrkor. Dessa utvecklade tekniker kan leverera detaljerad och modelloberoende information om molekylernas rörelse som direkt kan jämföras för molekyler i komplexa kompositmaterial och i enkla bulkssystem.

Fastfas-NMR har använts för att studera lokal molekylär dynamik hos ytaktiva ämnen inkorporerade i organiska-oorganiska nanostrukturerade kompositer med olika morfologi. För dessa ämnen har dynamikmodeller utvecklats baserade på de experimentellt erhållna ordningsparametrarna. För material uppbygga av olika skikt kunde ett antal olika rörelsemönster identifieras beroende på materialets sammansättning. Modellerna visar att dynamiken sträcker sig från helt orörliga tillstånd till fullt flexibel och isotrop rörelse. I hexagonalt strukturerad porös kiseldioxid kunde det påvisas att absorbentens huvudgrupp var minst rörlig medan kedjan uppvisade hög mobilitet.

Resultaten som presenteras i denna avhandling gör det möjligt att mer fullständigt karakterisera de molekylära tillstånden hos avancerade nanostrukturerade organiska-oorganiska kompositmaterial, samtidigt
som de ger en ökad förståelse för den stora variationen av olika molekylära tillstånd i dessa material.

**Nyckelord:** mesoporösa material, organiska-oorganiska nanokompositer, ytaktiva ämnen, flytande kristaller, MCM-41, leror, konformationsdynamik, fastfas-NMR, lokal fält spektroskopi, dipolär koppling, dipolär återkoppling, spinndekoppling.
List of papers

I Low rf power high resolution $^1$H-$^{13}$C-$^{14}$N separated local field spectroscopy in lyotropic mesophases
Kharkov, B. B.; Chizhik, V. I.; Dvinskikh, S. V.

II Sign-sensitive determination of heteronuclear dipolar coupling to spin-1 by selective decoupling
Kharkov, B. B.; Chizhik, V. I.; Dvinskikh, S. V.

III Probing molecular mobility in nanostructured composites by heteronuclear dipolar NMR spectroscopy
Kharkov, B. B.; Chizhik, V. I.; Dvinskikh, S. V.

IV Chain dynamics of surfactants in mesoporous silica
Kharkov, B. B.; Dvinskikh, S. V.

V Conformational Dynamics of Surfactant in a Mesolamellar Composite Studied by Local Field NMR Spectroscopy
Kharkov, B. B.; Dvinskikh, S. V.

VI Phase Transitions and Chain Dynamics of Surfactants Intercalated into the Galleries of Naturally Occurring Clay Mineral Magadiite
Kharkov, B. B.; Corkery, R. W.; Dvinskikh, S. V.
The author’s contribution to the appended papers is

I. Performed the NMR experiments and data analysis. Participated in writing the manuscript.

II. Formulated the research problem. Conducted most of the NMR experiments and performed the theoretical analysis and computer simulations of the novel method. Participated in writing the manuscript.

III. Prepared the samples. Performed the theoretical analysis and computer simulations of the pulse sequence. Participated in writing the manuscript.

IV. Prepared the samples. Performed most of the experiments. Participated in writing the manuscript.

V. Prepared the samples. Performed the experiments. Participated in writing the manuscript.

VI. Prepared the samples. Performed most of the experiments. Participated in writing the manuscript.

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**Introduction**

Nanostructured organic-inorganic composites have attracted much attention in material science and technology. Due to their unique surface, structural and bulk properties, these materials have found many important practical applications. They are used in catalysis,\(^6\)-\(^8\) as adsorbents for recyclable removal of organic pollutants in soil and water remediation,\(^9\),\(^10\) as nanocontainers for immobilization of macromolecules,\(^11\) as hosts for quantum structures,\(^12\) and in other industrial and academic applications.\(^13\)-\(^19\) Nowadays, among the approaches that have been suggested for producing hybrid composites, synthesis via surfactant self-assembly is the most widely employed method. In this technique, amphiphilic molecules serve as a structure-directing template. Microstructure and pore geometry of the resulting mesoporous solid are determined by the morphology of surfactant aggregates which become confined in the inorganic matrix that forms around them. A number of experimental and computational techniques have previously been employed to study the structure and dynamics of the organic components within mesoporous composites. The microstructure of the material is characterized by diffraction and scattering (XRD, SAXS) or electron and atomic force microscopy methods (SEM, TEM and AFM). However, no information on the dynamics of the template molecules is obtained by using these techniques. Information on dynamic molecular properties is of fundamental importance for understanding the molecular origin of the effects of confinement and surface interaction. NMR spectroscopy is capable of delivering detailed information with atomic-level resolution on the structure and dynamics of organic molecules assembled in the pores and confinements of hybrid materials.

Since the first successful observation of nuclear magnetic resonance by the groups of Purcell\(^20\) and Bloch\(^21\) in 1945, the number of diverse applications of this technique has been continuously increasing. From the first days, NMR found its place as one of the most powerful tools in the vast arsenal of methods applied by physicists and chemists. Nowadays, NMR spectroscopy is a method of choice for scientists in diverse fields such as chemistry, medicine, physics, material science etc. The method is based on measuring various intra- and intermolecular interactions providing valuable information on the organization of matter.
Compared to many other spectroscopic techniques, NMR has a significant drawback, namely poor sensitivity. Also, nuclear spin couplings are generally weak and challenging to register. However, a number of experimental and theoretical developments, such as high resolution NMR, pulsed Fourier-transform NMR, multidimensional spectroscopy, Average Hamiltonian Theory have transformed this shortcoming into an advantage. By applying short pulses of oscillating magnetic fields one can manipulate relatively weak internal spin couplings. This allows suppressing undesirable spin interactions and preserving those that are interesting, thus filtering the information obtained in experiments. Combining these achievements with magic angle spinning, MAS, which is a method of fast rotation of the sample during the course of experiment, provides the opportunity to investigate solids, liquid crystals, soft matter and other systems with restricted molecular dynamics. NMR studies of these materials are more challenging compared to isotropic liquids, largely due to the presence of anisotropic spin interactions.

Dipolar Separated Local Field (SLF) NMR spectroscopy has been proven to be a powerful tool for studying molecular mobility. The technique is based on the separation of nuclear interactions in a multidimensional experiment in such a way that anisotropic dipole-dipole couplings are correlated with chemical shifts. Residual dipolar couplings, sensitive to local molecular motion, are obtained for every resolved atomic position in a molecule, thus allowing studying overall and segmental conformational dynamics with atomic-level resolution.

This thesis focuses on structural and dynamic studies of ordered nanostructured organic-inorganic composites and lyotropic mesophases. A significant part of the work was also devoted to the development of relevant solid-state NMR methodology. Various SLF methods were employed to study conformational and overall molecular dynamics of surfactants in nano-confinement and nano-assembly. Local order parameters were compared for different materials of similar morphology that allowed us to study the effect of intermolecular interactions and confinement on the molecular mobility and macroscopic phase behavior.
1 Mesostructured materials

This chapter provides a brief description of the studied systems. The morphology and properties of liquid crystals are discussed with an emphasis on those of lyotropic mesophases. Mesoporous composite materials are introduced and various modes of molecular motion in these materials are described.

1.1 Liquid crystals

Liquid crystals are – in accordance to their name – a class of materials that simultaneously possess physical properties of two very distinct states of matter: isotropic liquids and solids. Being liquid-like with no long-range positional order and a high degree of translational freedom (though short-range positional order is possible in some phases) liquid crystals exhibit orientational order. Generally, the shape of molecules forming liquid crystals significantly deviates from spherical, causing the anisotropy of the material. The tendency to form liquid crystals is also prompted by the presence of large electric dipole moments or easily polarizable groups.

The orientational order implies that neighboring molecules or molecular aggregates preferably point in the same direction, which is called director. In general, the director of a LC is determined as the direction, with respect to which optical, electrical and magnetic properties of the material exhibit maximal anisotropy.

Liquid crystals can generally be divided into two groups according to their phase behavior. *Thermotropic* LCs can be considered as melts of crystalline solids and the phase transitions occur with changes in temperature or, sometimes, pressure. Another class, lyotropic LCs, consist of solutions of surfactants or polymers, though exotic examples, such as the suspension of tobacco mosaic virus in water,25 are also known. For lyotropic systems, the phase behavior is determined by many parameters, the principal ones are temperature and concentration. In multi-component systems, the concentration of surfactant in solution is replaced by the ratio of components.

A part of this PhD project was focused on the dynamics of surfactant molecules in concentrated solutions. Surfactants are a class of organic compounds whose molecules demonstrate amphiphilic properties i.e. one
part of the molecule is hydrophilic, while the other part is hydrophobic. Hydrophobicity does not mean that a part of the molecule repels water. It implies only that the water-water intermolecular interactions are more favorable than that between water and the hydrophobic part of the surfactant. This oversimplified explanation is nevertheless sufficient for a qualitative description of collective effects in surfactant solutions. Surfactants may be of various types such as ionic, non-ionic or zwitterionic. In this work, ionic surfactants were studied. The amphiphilic properties of surfactant molecules lead to aggregation (micellization, formation of a LC) and adsorption at interfaces that have been widely utilized in chemical engineering.

One of the most important concepts in physics of liquid crystals is the order parameter that characterizes and quantifies how anisotropic the material is. In general, the order parameter indicates how far from their average orientation molecules can deviate upon thermal motion.

To define the order parameter precisely, let us consider a one-component thermotropic mesophase composed of rigid rod-like molecules. A unit vector \( u^{(i)} \) parallel to the long molecular axis can be ascribed to each molecule. The distribution of the orientations of molecules in the sample may be characterized by the tensor quantity:

\[
S_{\alpha\beta} = \langle u_\alpha u_\beta - \frac{1}{3} \delta_{\alpha\beta} \rangle. \tag{1}
\]

\( u_\alpha \) and \( u_\beta \) are the components of the vector in a fixed frame, \( a, \beta = (x, y, z) \), and \( \delta_{\alpha\beta} \) is the Kronecker delta; angular brackets indicate average over the whole ensemble of molecules. Therefore \( S_{\alpha\beta} \) is a symmetric traceless tensor that vanishes only in ideally isotropic liquids.

Although the order parameter tensor is fully applicable for any anisotropic liquid (within the scope of the assumptions we made), it is difficult to use and a simpler related concept may be introduced. For the systems that possess at least three-fold symmetry, a scalar quantity defined as the second Legendre polynomial can be introduced:

\[
S = P_2(\cos \theta) = \frac{1}{2} (3 \cos^2 \theta - 1), \tag{2}
\]
where $\theta$ is the angle between long axis and the director of the phase. This definition disregards possible biaxiality of phase anisotropy, but due to its simplicity is more convenient and readily applicable.

**Phase behavior of lyotropic mesophases**

Liquid crystals exhibit complex phase behavior. A variety of structures of different order and geometry can be observed. In this section, the phases, typical for lyotropic liquid crystals, are discussed.

Figure 1 shows the so-called Fontell scheme, which depicts the approximate sequence of the structures that can be adopted by a solution upon changing of concentration. It should be emphasized that the scheme only demonstrate the general trend and neither all the phases shown on the scheme would realize for every surfactant solution nor all possible phases are present in the scheme.

For quantitative description, geometrical reasoning can be used to explain this trend. The critical packing parameter (CPP) is a useful concept defined as a ratio

$$CPP = \frac{v}{al} \quad (3)$$

of the volume $v$ per molecule in the aggregate, determined to a large extent by the volume occupied by the hydrophobic part, to the volume $al$ of a hypothetical cylinder, where $a$ and $l$ are the area of the molecular hydrophilic head group and length of the molecule, respectively. The effective packing parameter increases to the right in the Fontell scheme. For instance, CPP for the hexagonal phase is about $\frac{1}{2}$, for the lamellar phase it is close to 1, and it is greater than one for the inverse phases.

![Figure 1](Image)

Figure 1. The Fontell scheme connects the concentration of surfactant with the structure of the aggregates.
Thus, in accordance with the CPP concept, for changing the hexagonal phase to a lamellar one, one may either increase the hydrophobicity of the surfactant, for example by adding a co-surfactant, or reduce the effective head group area either by using an oppositely charged co-surfactant or by adding salt.

In the current work, this approach was used to induce the formation of a lamellar phase in the aqueous solution of cetyltrimethylammonium bromide at low concentrations. Hexanol was used as the co-surfactant, which allowed us to obtain the lamellar phase with ca. 2.5 times lower surfactant content than in absence of the co-surfactant, and drastically reduced viscosity.

**Magnetic alignment**

As prepared, a liquid-crystalline sample cannot be described with a single director for its whole volume. The sample is then inhomogeneous with respect to director orientation. In fact, the volume of the liquid crystal is divided into a number of small regions, domains, with homogeneous orientations of the molecules.

In NMR experiments, each domain in the volume of the liquid crystal is characterized by its director orientation with respect to the static magnetic field. Since intramolecular anisotropic interactions (dipole-dipole, chemical shift anisotropy (CSA), quadrupolar) are fixed in a molecular frame of reference, they vary from one domain to another. This distribution leads to inhomogeneous broadening of the NMR spectra. One of the approaches to avoid inhomogeneous broadening that reduces chemical resolution is magnetic alignment.\(^{35-40}\)

The LC domains of many phases, both lyotropic and thermotropic, align in the external magnetic field. The driving force for the alignment is the anisotropic diamagnetic susceptibility of LC molecules. For instance, hydrocarbon chains have negative diamagnetic anisotropy and therefore the energy of a molecule oriented perpendicular to a magnetic field is lower than energy of a molecule that is oriented parallel to the field. In lyotropic hexagonal mesophases, aliphatic chains of separate molecules form an angle of 90° to an axis of the long rod-like micelle. Thereby, the overall diamagnetic anisotropy of an aggregate is positive, and it aligns with the director of a phase parallel to the external field. Another situation is observed in lamellar mesophases, where the director of the phase is parallel to the molecules that form the aggregate. Therefore,
lamellar liquid crystals usually align with the director perpendicular to the static magnetic field.

Another moiety that may induce magnetic alignment is the aromatic ring. It has significant diamagnetic anisotropy and the plane of ring tends to orient parallel to a magnetic field. Sometimes LC molecules have aromatic rings and aliphatic chains. In this case the two described mechanisms of magnetic aligning compete, but, unless the hydrocarbon chain is very long, the magnetic anisotropy of the aromatic rings is stronger and their contribution is dominant.

Since LC mesophases are typically very viscous, not all of them orient spontaneously even in the strongest available magnetic fields. To address this problem one can align the mesophase using slow gradual cooling from high temperature isotropic phases usually characterized by low viscosity. In this case, the mesophase has enough time to align before the system becomes too viscous.\textsuperscript{1,41,42}

1.2 Mesostructured solids

Mesostructured composites are a fairly new type of materials that consist of two main components: an inorganic framework and an organic surfactant template. According to the IUPAC definition,\textsuperscript{43} the characteristic pore dimensions in mesoporous materials are between 2 and 50 nm. The organic component often serves as a structure-directing agent and, after the material has been prepared, removing the organic template leads to the formation of a porous solid structure.

Ordered mesoporous materials were discovered in the beginning of the 1990’s by the researchers of Mobile Oil Corporation. A series of mesoporous materials, MCM (which stands for Mobile Composite of Matter), with various composition and morphology was presented.\textsuperscript{44} In the following years, the number of works addressing various properties and applications of the ordered porous composites has increased dramatically. One of the characteristic features of the inorganic framework of a nanocomposite is its high porosity and large internal surface area. Pores in the nanocomposites are monodisperse and the structure is regular on the crystallographic scale. Mesostructured materials can adopt different structures that generally correspond to the structures typical for various lyotropic liquid crystals. This can be explained by the fact that the most widely used protocol for synthesis of mesocomposites is via supramolecular assembly, which is discussed
further below. The pore size can be tuned in a wide range by adjusting the template composition or, for some surfactants, the temperature of synthesis. Varying surfactant molecule length modulates the pore diameter in the range of several nanometers.\textsuperscript{44-47} Employing triblock co-polymers of the \textit{Pluronic} family as template agents has led to a significant extension of accessible pore sizes up to 30 nm. This class of materials is called SBA-15.\textsuperscript{46-48}

Another strategy that allows increasing the pore size is to use different swelling agents to inject an additional hydrophobic component into the aggregates. The size and the degree of hydrophobicity of the swelling agent influence the location of the molecule within the template micelle. The smaller and more hydrophobic additives penetrate into the core of the surfactant aggregate resulting in its extension.\textsuperscript{44,46,49} Thermal treatment during synthesis has also been successfully utilized for pore size control.\textsuperscript{50}

For further applications, such as separation processes and catalysis, the internal surface of a composite is functionalized with various organic modifiers.\textsuperscript{13,51} This can be done in two ways. The first one, often called post-functionalization, involves covalent grafting of the organic functionalities on the internal surface of a composite.\textsuperscript{52-54} The second way is to introduce the organic modifier into the initial precursor solution that leads to embedding the functionalities in the inorganic framework of a porous material.\textsuperscript{55,56} The second route typically gives higher degree of functionalization compared to the grafting method.

**Synthesis routes**

Organic-inorganic hybrid materials are produced by employing so-called bottom-up processes that imply the formation of the well-ordered pattern of the material from smaller, initially non-linked elements. In the current work, we used two main implementations of that paradigm: synthesis via supramolecular assembly and block assembly.

The two methods are illustrated in Figure 2. In the first method, surfactant is used as a structure directing agent that drives the formation of porous solid of desired geometry. Nowadays, this is the most common way to synthesize hybrid mesocomposites. In this method, organic amphiphilic molecules and inorganic components are dissolved in the initial precursor solution(s). The inorganic precursor interacts with the surfactant forming molecular aggregates providing the basis for the
mesostructure of the resultant product. At the low concentrations typically used for this kind of synthesis, the lyotropic liquid crystalline phases do not form in the whole solution volume. Nevertheless, it is commonly assumed that the LC phase forms in the self-assembly process prior the polymerization of the inorganic component. In case of ionic surfactants, the driving force for the self-assembly processes is the Coulomb interaction between charged species dissolved in solution. For oppositely charged amphiphiles and inorganic precursors, direct co-assembly may be considered, while for organic and inorganic species with the charges of the same sign, assembly mediated by counter-ions is assumed.\textsuperscript{57,58} Neutral templating has been suggested to be mediated by hydrogen bonding in case of non-ionic surfactants and a neutral inorganic component.\textsuperscript{59,60}

![Diagram](image.png)

Figure 2. Schematic representation of two strategies used for synthesis of nanostructured organic-inorganic silica-based materials containing cationic surfactants.\textsuperscript{61} (Reproduced from Ref. 61 with permission of The Royal Society of Chemistry.)

In the method discussed above, inorganic species were involved in the self-assembly process. It has been shown that under certain experimental conditions, the surfactant self-assembly process may be decoupled from the inorganic species. In this synthesis strategy, the actual liquid crystalline phase forms at high surfactant concentration. The inorganic precursor is dissolved in an aqueous phase of the liquid crystal. The structure of the mesophase determines the morphology of the composite to be made. After preparation of the initial silica-surfactant liquid crystal,
one initiates polymerization by changing one of the synthesis conditions, i.e. the pH of the solution. As a result, a solid inorganic network is formed with LC aggregates trapped within. The geometry of the resultant mesoporous solid may be tuned by changing the composition of the template. It has been shown that using the described technique one can produce mesocomposites with the pores aligned on a macroscopic scale. As mentioned above, liquid crystals tend to align when immersed in a strong magnetic field. If one induces polymerization with the precursor LC oriented, the resulting solid will retain the pore alignment pattern in the whole sample.

Another approach for mesocomposite production is the so-called block-assembly (Figure 2). This method makes use of already formed nanosized building blocks such as nano-layers of naturally occurring clay minerals e.g., magadiite, kanemite etc. Surfactant molecules penetrate into the galleries of the swollen layered mineral and attach to the walls. Coulomb interactions with the surface of nano-layers and surfactant self-aggregation interactions control the formation of the periodic arrangement of this type of composite. A variety of structures, including monolayers, bilayers, paraffin-like assemblies, may be formed by the surfactant molecules confined within the pores – depending on the adsorption density, synthesis conditions and the length of the surfactant alkyl chain.

### 1.3 Molecular mobility in mesostructured materials

In mesostructured composites, the organic component of the material exhibits different kinds of motion. Complex segmental mobility of a surfactant molecule can be decomposed into several motional modes that roughly may be divided in two main classes: the motion of the whole molecule as a solid body and the internal dynamics of different segments of a molecule in the molecular frame of reference. The first class of motional modes includes translational dynamics and various types of rotation; the second type of modes regards the conformational motion. Investigation of the overall mobility of surfactant in nanocomposites provides information on the details of the organization of the material on a molecular scale and gives fundamental insight on the effects of nanoconfinement on the intermolecular interactions and phase behavior of surfactant aggregates.
In the current work, the interatomic bond order parameter concept was used for quantitative description of the molecular mobility. In the forthcoming discussion we assume C-H bonds in methylene or methyl groups, but in general the concept can be extended to any kind of interatomic vector. The bond order parameter is defined in analogy to the concept of order parameter of liquid crystals (See Eqs. (1), (2)). It is a tensor quantity that, however, in most cases may be replaced by a scalar. Numerically, the order parameter is defined as follows:

\[ S_{CH} = \frac{1}{2} (3 \cos^2 \theta_{CH} - 1), \]

and its value indicates how far from its average orientation an internuclear bond may deviate upon its thermal motion. Subscript \( CH \) is used in order not to confuse bond order parameters with the order parameter defined for liquid crystals. The angle \( \theta_{CH} \) determines the deviation of the instantaneous position of the C-H bond from its average position. It is readily seen that for the two extreme cases of a rigid bond and an isotopically tumbling bond the order parameter equals to 1 and 0, respectively.

Let us consider different types of molecular dynamics and their influences on the bond order parameter. Translational motion generally can be divided in two cases: parallel shift without reorientation of the molecule and movement on a curved trajectory. The former obviously does not lead to a change in order parameters, while the latter type of motion decreases \( S_{CH} \). Movement on a surface of a cylinder is of particular practical interest, since it describes the behavior of a molecule in hexagonal LC phases and in hexagonal mesocomposites. This kind of motion, when considered in terms of molecular orientation, is identical to rotation of a molecule around the axis of a cylinder. When this motion is accompanied by rotating a molecule around its long axis, which, in turn, is usually perpendicular to the cylinder axis, the order parameters are additionally scaled down by the factor of \(-1/2\).

Rotation of a molecule around a molecular axis is an important kind of motion in mesostructured solids and liquid crystals. It is always present in liquid crystals and often observed in composite solids. When it is not accompanied by significant conformational dynamics, this dynamical state is called the rotator phase. Since a C-H vector in a methylene group in an all-trans alkyl chain points at the angle of 90° with
respect to the molecular axis, fast rotation of the molecule leads to the scaling of all C-H order parameters by the factor of $-1/2$. For this kind of motion, taking into account that the order parameter is in fact a tensor quantity, one can show that the effective average orientation, or simply the main principal axis of the tensor, is parallel to the axis of rotation.

Conformational dynamics can also be studied in terms of segmental order parameters. For long molecules, mobility of a segment depends on its position in the molecular chain. For example, in lyotropic mesophases, the hydrophilic head group of the amphiphilic molecule is immersed in the water phase, while the tail is left free inside the aggregates. This arrangement leads to gradual reduction in the order parameters towards the end of the chain. This motional gradient characterizes the intensity of the steric repulsion experienced by the molecular tail. The more conformational freedom the molecule has in the aggregate, the faster decreases $S_{CH}$. 
2 Experimental

This chapter introduces the NMR technique and provides the reader with the underlying quantum mechanical description. Such concepts as wave function, density operator and Hamiltonian are described briefly along with the mathematical formalism required for the analysis of modern NMR experiments.

2.1 Introduction to NMR

In quantum mechanics, the concept of wave function is used for describing the state of a particle. In general, for a particle having spin, the wave function depends on both the position of the particle and the orientation of its spin. However, for atomic nuclei, spin and spatial components of the wave function are independent of each other for all practical purposes and, since in NMR one is concerned only with the orientation of nuclear magnetization, the spatial part of the wave function can be safely omitted. The wave function for a spin-$1/2$ particle can be written as follows:

$$|\psi\rangle = c_\alpha |\alpha\rangle + c_\beta |\beta\rangle,$$

where $|\alpha\rangle$ and $|\beta\rangle$ are the eigenfunctions for operator $I_z$ and hence also for Zeeman term in nuclear spin Hamiltonian.

In a big ensemble of particles in thermal equilibrium, the state of a certain spin cannot be specified precisely. The only thing to be asserted is the probability of realization of one of the infinite number of possible quantum states characterized by a set of complex coefficients, $c_\alpha$ and $c_\beta$. Such “insufficiently determined” states of the quantum system, also called “mixed” states, can be defined using the formalism of density operator $\rho(t)$:

$$\rho(t) = \sum_i \sum_j \overline{c_i(t)c_j^*(t)} |i\rangle\langle j|,$$

where the bar denotes ensemble average and $|i\rangle$ and $|j\rangle$ can be $|\alpha\rangle$ or $|\beta\rangle$ for an ensemble of spins-$1/2$.

The time evolution of a quantum system is governed by the Liouville – von Neumann equation:
\[
\frac{d}{dt} \rho(t) = -i[H(t), \rho(t)],
\]
where \( H(t) \) denotes the Hamiltonian that includes all spin couplings within the system as well as interactions with external magnetic fields. Eq. (7) has a formal solution:

\[
\rho(t) = U(t)\rho(0)U^\dagger(t),
\]
where \( U(t) \) is the propagator, i.e. the operator that affects the density operator and governs the way the state of the system will change. The propagator is given as

\[
U(t) = D e^{-\int_0^t H(t)\,dt}.
\]

Here, \( D \) is the Dyson time ordering operator which is crucial when the Hamiltonian does not commute with itself at different time points. According to Eq. (9), the propagator \( U(t) \) is a unitary operator that describes rotations in the subspaces isomorphic to a subspace \( \{I_x, I_y, I_z\} \).

Knowing the density matrix one can calculate any experimentally measurable quantity, e.g. the transverse magnetization

\[
S(t) = Tr[\rho(t)I^\dagger],
\]
where the raising operator is defined as \( I^\dagger = I_x + iI_y \).

### 2.2 Spin interactions

To calculate the evolution of the macroscopic magnetization one needs to know, besides the initial state of the spin ensemble \( \rho(0) \), the Hamiltonian that accounts for all spin interactions that cause changes in the state of the system. The Hamiltonian includes internal nuclear couplings such as chemical shift, dipole-dipole interaction, \( J \)-coupling etc., and the interactions with the external magnetic fields introduced by the researcher according to the scheme of the experiment. In this section, the internal couplings that are relevant to the current work will be discussed.
Chemical shift

A chemical shift (CS) appears as a reaction of electron cloud to the external magnetic field $B_0$. Currents induced in the electron system surrounding atomic nuclei produce a magnetic field. The $z$-component of this field in most cases points in the opposite direction to the field $B_0$, reducing the effective field experienced by the nucleus. Being a function of the configuration of molecular electron orbitals, the chemical shift thus depends on the structure of a molecule.

The field induced by the electron shell is given by\footnote{73}

$$B^{\text{ind}} = \begin{pmatrix} B^{\text{ind}}_x \\ B^{\text{ind}}_y \\ B^{\text{ind}}_z \end{pmatrix} = \delta \cdot B_0 = \begin{pmatrix} \delta_{xx} & \delta_{xy} & \delta_{xz} \\ \delta_{yx} & \delta_{yy} & \delta_{yz} \\ \delta_{zx} & \delta_{zy} & \delta_{zz} \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix}. \quad (11)$$

The chemical shift tensor $\delta$ is not necessarily symmetric with respect to the main diagonal, but as long as relaxation is not considered we can disregard the asymmetry. The resonance frequency shift is caused by the $z$-component of $B^{\text{ind}}$. Two other components correspond to non-secular terms in the CS Hamiltonian (operators $I_x$ and $I_y$), and hence can be neglected.

The effective field experienced by the nucleus becomes

$$B_{\text{eff}} = (1 + \delta_{zz})B_0, \quad (12)$$

and the Hamiltonian containing Zeeman and CS terms is given by

$$H_{0+\text{cs}} = -\gamma(1 + \delta_{zz})B_0 I_z, \quad (13)$$

where $\gamma$ is the gyromagnetic ratio for the given sort of nuclei. The definition of the chemical shift in this form takes into account that for most diamagnetic materials, the induced field causes the reduction of resonance frequency and thus $\delta_{zz}$ is the negative quantity. In practice, the origin of the chemical shift scale $\delta=0$ is set with respect to a reference sample.

Since the CS is a tensor quantity and the orientation of the tensor is connected to the molecular frame, the observed value of $\delta_{zz}$ varies with
the changes in molecular orientation. This effect is important in solids and anisotropic liquids, where the observed CS may differ significantly from its isotropic value.

When the three principal values of the chemical shift tensor are not equal, the CS interaction is said to be anisotropic and the chemical shift anisotropy (CSA) is often considered as a separate coupling. CSA for a given nucleus is characterized by two numbers:

\[
\delta_{\text{aniso}} = \delta_{zz} - \delta_{\text{iso}}, \\
\eta = \frac{\delta_{yy} - \delta_{xx}}{\delta_{\text{aniso}}}
\]

\(\delta_{\text{aniso}}\) is the amplitude of the CSA coupling; \(\eta\) is the asymmetry parameter also called the biaxiality parameter. In solids and liquid crystals, CSA results in reduction of chemical resolution in NMR spectra. Since CSA produces inhomogeneous broadening, it may be suppressed by MAS that is discussed below.

In liquids, molecular motion results in averaging of the chemical shift tensor. The isotropic value observed in liquids is calculated as follows

\[
\delta_{\text{iso}} = \frac{1}{3} Tr(\delta) = \frac{1}{3} (\delta_{xx} + \delta_{yy} + \delta_{zz}).
\]

**Dipolar coupling**

Every nucleus with non-zero spin possesses an intrinsic magnetic moment. The magnetic dipole generates a magnetic field in the surrounding space which affects other dipoles. Thus, nuclear spins can “feel” each other and mutually influence the Larmor frequency of each other. This interaction is called through-space or direct dipole-dipole coupling in contrast to indirect dipolar interaction, also called \(J\)-coupling. \(J\)-coupling is an interaction of dipoles that is mediated via molecular electron system.

The dipolar Hamiltonian in tensor notation is given by

\[
H_{dd} = I_i D_{ij} I_j.
\]
Here, $D_{ij}$ is a traceless symmetric tensor and $I_i$ and $I_j$ are the spin operators of the coupled nuclei. Components of the tensor $D_{ij}$ can be calculated from the conventional expression\textsuperscript{72,73}

$$H_{dd} = b_{ij}(3(I_i \cdot e_{ij})(I_j \cdot e_{ij}) - I_i \cdot I_j).$$

(18)

$$b_{ij} = -\frac{\mu_0 \gamma_i \gamma_j h}{4\pi r_{ij}^3}.$$  

(19)

Here, $\mu_0$ is the vacuum permeability, $\gamma_i$ and $\gamma_j$ are the gyromagnetic ratios for the coupled nuclei and $r_{ij}$ is the internuclear distance.

The unit vector $e_{ij}$ is parallel to the line connecting the coupled nuclei; the dots represent scalar product operation.

There are a number of possible ways to express the full dipolar Hamiltonian in different bases. Let us consider one of them called the dipolar alphabet. Expressing Eq. (18) in terms of the operator $l_z$ and the so-called shift operators, $l_+$ and $l_-$,\textsuperscript{73} one obtains\textsuperscript{72}

$$H_{dd} = b_{ij}(A + B + C + D + E + F);$$

(20)

$$A = l_z l_z (3 \cos^2 \theta_{ij} - 1);$$

(21 a)

$$B = -\frac{1}{4} (l_+ l_- + l_- l_+)(3 \cos^2 \theta_{ij} - 1);$$

(21 b)

$$C = \frac{3}{2} (l_+ l_z + l_z l_+)(\sin \theta_{ij} \cos \theta_{ij} e^{-i\phi_{ij}});$$

(21 c)

$$D = \frac{3}{2} (l_- l_z + l_z l_-)(\sin \theta_{ij} \cos \theta_{ij} e^{i\phi_{ij}});$$

(21 d)

$$E = \frac{3}{4} (l_+ l_+)(\sin^2 \theta_{ij} e^{-2i\phi_{ij}});$$

(21 e)

$$F = \frac{3}{4} (l_- l_-)(\sin^2 \theta_{ij} e^{2i\phi_{ij}});$$

(21 f)

This notation is convenient because different terms are separated in accordance to how they change the projection of the full spin of the system. For instance, the so-called flip-flop term $B$ is a zero quantum term.
term, since it does not change the full projection of the spin. Similarly, terms $C$ and $D$ are called single-quantum, whereas $E$ and $F$ double-quantum.

As long as relaxation is disregarded, the spectral shape is determined solely by the terms $A$ and $B$. In fact, in case of heteronuclear interaction, only term $A$ commutes with the Zeeman Hamiltonian. For homonuclear coupling, both of them, $A$ and $B$, become secular and influence the NMR spectra.

Since tensor $D_{ij}$ in Eq. (17) is traceless, rapid molecular motion averages dipolar interaction to zero and in NMR of isotropic liquids this interaction cannot be measured directly. $J$-coupling, in contrast, has a finite trace of the tensor and thus can in principle be assessed in all states of matter.

**Quadrupolar coupling**

Nuclei with spin quantum number greater than $\frac{1}{2}$ possess electric quadrupole moment, which characterizes how much the shape of a nucleus deviates from spherical. The quadrupole moment interacts with the gradient of electric field surrounding the nucleus. Hence, various orientations of a nucleus with respect to the gradient have different energies. In a strong magnetic field, quadrupolar interaction acts as a perturbation and makes correction to the Zeeman system of energy levels.

The quadrupolar coupling may be very strong, up to several tens of megahertz or even higher in some exotic cases. This makes this interaction rather difficult to treat, since the secular high field approximation is not always applicable. In this case, a more detailed consideration including higher order terms of quadrupolar Hamiltonian is necessary, but these matters are beyond the scope of this introduction.

The quadrupolar Hamiltonian is given for spin $I$ by

\[
H_Q = \frac{eQ}{2I(2I-1)\hbar} I \cdot V_q \cdot I. \tag{22}
\]

Here, $V_q$ is the electric field gradient tensor, $Q$ is the nuclear quadrupole moment, and $e$ is the elementary charge.

The first-order (secular) quadrupolar Hamiltonian can be written as follows:
\begin{equation}
H_Q = \omega_Q^{(1)} \frac{1}{6} (3I_z^2 - I(I + 1))E,
\end{equation}

where \( E \) is the identity operator and \( \omega_Q^{(1)} \) is the first-order quadrupolar coupling constant given by

\begin{equation}
\omega_Q^{(1)} = \frac{3eQV_{zz}}{2I(2I-1)\hbar}.
\end{equation}

The quadrupolar nuclei that we dealt with in this work were \(^{14}\text{N}\) and \(^2\text{H} – \text{spin-1} \) nuclei. In oriented samples, in the presence of moderate electric field gradients, spectra of these nuclei appear as symmetrical doublets with splitting equal to \( 2\omega_Q^{(1)} \). In powder samples, a Pake powder pattern\(^{75}\) is observed.

### 2.3 Average Hamiltonian Theory

Eqs. (8) and (9) give an exact solution of the quantum mechanical equation of motion. They are readily applicable when the spin Hamiltonian is independent of time. However, usually spin interactions vary in time. Internal nuclear couplings change due to molecular dynamics or sample spinning. Moreover, external fields that are used according to the scheme of an experiment to excite the spin system, decouple undesirable interactions or recouple suppressed ones vary in time as well. This makes it difficult to apply Eqs. (8) and (9). Several approaches have been developed to address this problem.

One possible solution is to split the time interval of the Hamiltonian into segments and consider the Hamiltonian during each segment as being time-independent. An important condition to be fulfilled for this approximation is that the segments must be short enough to reduce simulation errors. This method is employed in modern NMR simulation software like SIMPSON\(^{76}\) and SpinEvolution\(^{77}\).

Another customary approach involves the formalism of the Average Hamiltonian Theory, AHT, developed by Haeberlen and Waugh.\(^{78}\) This theory is particularly useful for the analysis of periodic pulse sequences and cyclic perturbations such as MAS. In principle, it is always possible to find a time-independent Hamiltonian \( \bar{H} \) which affects the spin ensemble in exactly the same way as a given time-dependent Hamiltonian \( H(t) \). In general, the average Hamiltonian depends on the integration interval.
The average Hamiltonian (AHT) is calculated over the interval $t_1 < t < t_2$ over which it is being averaged. This makes AHT difficult to apply for non-periodic sequences. In contrast, in case of a periodic interaction-frame Hamiltonian, the average Hamiltonian is the same when calculated over any number of periods.

For calculation of the effective average Hamiltonian one may use the Magnus expansion

$$\bar{H}(\tau_c) = \bar{H}^{(1)} + \bar{H}^{(2)} + \bar{H}^{(3)} + \cdots,$$

where the first two terms are

$$\bar{H}^{(1)} = \frac{1}{\tau_c} \int_0^{\tau_c} H(t) \, dt,$$  \hspace{1cm} (26a)

$$\bar{H}^{(2)} = \frac{-i}{2\tau_c} \int_0^{\tau_c} \int_0^{\tau_c} \{H(t_2),H(t_1)\} \, dt_1 \, dt_2,$$  \hspace{1cm} (26b)

and $\tau_c$ is the period length.

Due to the periodicity of the Hamiltonian, the sampling pattern must also be periodic, since the effect of the average Hamiltonian is equal to the effect of the Hamiltonian that is being averaged at certain points in time $t = t_0 + n\tau_c$, $n \in N_0$:

$$U(n\tau_c) = D e^{-i \int_0^{n\tau_c} H(t) \, dt} = e^{-i \bar{H} n\tau_c}.$$  \hspace{1cm} (27)

We can see from Eq. (26) that in case of an inhomogeneous interaction, when the Hamiltonian commutes with itself at different points in time, 2nd and higher order terms vanish.

The convergence conditions of the series in Eq. (25) were not elucidated precisely. One of the conservative conditions can be expressed as

$$\|H(t)\| \tau_c \ll 1,$$  \hspace{1cm} (28)

where the norm of the Hamiltonian is defined as

$$\|H(t)\| = (Tr\{H(t)^2\})^{\frac{1}{2}}.$$  \hspace{1cm} (29)
2.4 Frames of reference

The AHT is usually applied in problems where relatively small internuclear couplings bearing useful information are influenced by strong external rf irradiation. In this case, the full spin Hamiltonian can be written as

\[ H(t) = H_{\text{ext}}(t) + H_{\text{int}}(t). \]  

(30)

To calculate the effect of external impact on the \( H_{\text{int}}(t) \) one should transfer to the frame of reference associated with \( H_{\text{ext}}(t) \). In the new frame of reference, called the interaction frame, the Hamiltonian of internal couplings \( H_{\text{int}}(t) \) changes according to following expression

\[ \tilde{H}_{\text{int}} = U_{\text{ext}}^\dagger(t)H_{\text{int}}U_{\text{ext}}(t) - i U_{\text{ext}}^\dagger(t) \frac{d}{dt} U_{\text{ext}}(t), \]  

(31)

where

\[ U_{\text{ext}}(t) = De^{-i \int_0^t H_{\text{ext}}(t) dt}. \]  

(32)

The first term in Eq. (31) describes how internal couplings transform due to the external manipulation. The second term ensures that in the frame associated with certain interaction this interaction does not manifest itself. For instance, there is no external static magnetic field in the rotating frame.

Additionally, we can see that the propagator of the external perturbation appears explicitly in the expression for \( \tilde{H}_{\text{int}} \). This is undesirable if one is interested in measuring the internal couplings with no effect from strong external irradiation. Therefore, periodic pulse sequences that leave the state of the spin system unchanged over the period

\[ U_{\text{ext}}(\tau_c) = 1 \]  

(33)

are of great practical interest.
Rotating frame of reference and the secular approximation

An example of the interaction frame is the rotating frame of reference, associated with the Zeeman interaction.

Let us consider first term of Eq. (31) with $U_{\text{ext}} = \exp(-i\omega_0 l_Z t)$ and neglecting the second term:

$$\tilde{H}_{\text{int}} = e^{i\omega_0 l_Z t}H_{\text{int}}e^{-i\omega_0 l_Z t}. \tag{34}$$

We can separate $H_{\text{int}}(t)$ into two parts that contain secular and non-secular terms that, respectively, commute and do not commute with the Zeeman Hamiltonian.

$$H_{\text{int}}(t) = H_{\text{int}}^{\sec}(t) + H_{\text{int}}^{\text{nonsec}}(t), \tag{35}$$

$$[H_{\text{int}}^{\sec}(t), I_Z] = 0, \tag{36}$$

$$[H_{\text{int}}^{\text{nonsec}}(t), I_Z] \neq 0. \tag{37}$$

Since Eq. (34) describes rotation in spin subspaces (compare to Eq. (8)), all non-secular terms of the internal Hamiltonian rapidly oscillate about the external field $B_0$ and thus can be neglected. In contrast, secular terms do not acquire any additional time-dependence and are preserved in the rotating frame.

2.5 Single transition (ST) operator formalism

The single transition (ST) operator formalism allows treating different pairs of energy states in a multi-level system separately. Such multi-level systems appear, for instance, when one deals with the ensembles of particles with spin-1 or higher. The ST operator formalism\textsuperscript{79-81} has been used in the analysis of spin dynamics in multi-quantum spectroscopy and decoupling, selective excitation etc. In this work, we used this formalism to analytically study selective decoupling of spin-1 nuclei (Paper II) for experimental determination of the sign of dipolar coupling constants.

The ST operators can be written in a matrix form:
Experimental

All omitted components are equal to zero. These are three operators analogous for Cartesian spin projection operators of spin-1/2. They connect the eigenstates |1⟩ and |2⟩. The Pauli matrices can be recognized in the operators of higher dimensionality. Similarly, one can write operators connecting any pair of eigenstates as well as define single-transition shift or projection operators.\textsuperscript{73}

For ST operators connecting the same pair of levels the usual commutation relation is valid:

\[ [I_x^{rs}, I_y^{rs}] = iI_z^{rs}. \] (41)

In contrast, operators for unconnected transitions always commute:

\[ [I_x^{rs}, I_y^{tu}] = 0, \] (42)

where \( \alpha \) and \( \beta \) denote x, y or z.

The complete definition of ST operators and some useful commutation relations can be found in Refs. \textsuperscript{79-81}. 

\[ I_z^{1-2} = \begin{pmatrix} \frac{1}{2} & 0 & \vdots \\ 0 & -\frac{1}{2} & \vdots \\ \vdots & \vdots & \ddots \end{pmatrix}, \] (38)

\[ I_x^{1-2} = \begin{pmatrix} 0 & \frac{1}{2} & \vdots \\ \frac{1}{2} & 0 & \vdots \\ \vdots & \vdots & \ddots \end{pmatrix}, \] (39)

\[ I_y^{1-2} = \begin{pmatrix} 0 & -\frac{i}{2} & \vdots \\ \frac{i}{2} & 0 & \vdots \\ \vdots & \vdots & \ddots \end{pmatrix}. \] (40)
2.6 Local field spectroscopy

In this chapter, the general scheme of the separated local field spectroscopy (SLF) experiment is discussed. Various implementations of dipolar spectroscopy to different systems are described. The consideration is restricted to the techniques that have been used in the current work and do not cover all the vast diversity of SLF methods.

Residual dipolar couplings

By their nature, dipolar couplings have well-established orientational and distance dependence that makes them convenient and informative probe for different kinds of dynamic processes. As discussed in Chapter 1, surfactants in mesoporous materials and lyotropic liquid crystals exhibit a wide range of motional modes from translational and rotational diffusion of the whole molecule to conformational dynamics of molecular segments. In most cases, couplings measured with dipolar spectroscopy are of intramolecular nature and typically between neighboring nuclei. Hence, the dominant cause for scaling of dipolar interactions is the changes in the orientation of an internuclear bond rather than variation in internuclear distance.

Scheme of experiment

Let us consider the general scheme of an SLF experiment for measuring heteronuclear dipolar couplings. Spin systems containing nuclei of different sorts, $I$ and $S$, will be discussed. Usually, $I$ denotes abundant nuclei like protons, while $S$ is a rare spin like $^{13}$C or $^{15}$N, though any combination is possible.

![Figure 3. The principal scheme of a 2D SLF experiment. Carbon or proton magnetization evolves under the influence of dipolar spin couplings during the evolution period $t_1$. During the detection period $t_2$, magnetization is registered on the nuclei with high chemical resolution, such as $^{13}$C and $^{15}$N.](image-url)
In a typical dipolar spectroscopy experiment, two main structural blocks or time periods may be distinguished. These are the evolution period $t_1$ and the detection period $t_2$. During the first period, the nuclear magnetization evolves under the influence of the dipolar couplings that are being measured in the experiment. This magnetization belongs either to spin $I$ or spin $S$. It depends on the type of experiment and both possibilities will be discussed further below. In the second period, the magnetization bearing the information on the dipolar couplings is detected in form of a free induction decay (FID) on $S$ channel. Herewith, chemical resolution is gained, since the CS range of rare nuclei is usually much wider than that of protons. This scheme allows separating different interactions in a 2D spectrum with dipolar doublets correlated to the chemical shift of $S$ spins (Figure 4).

![Figure 4](image)

Figure 4. Schematic representation of a 2D dipolar spectrum. The CS axis is usually called the direct dimension of the spectrum; the heteronuclear dipolar couplings (HDC) are encoded in the dipolar or indirect dimension.

Depending on the type of experiment and the studied system, various additional blocks may be added. For instance, a prepolarization block, which is used for the enhancement of magnetization before the evolution period,$^{82}$ or a polarization transfer pulse sequence inserted between $t_1$ and
which is essential for Proton Detected Local Field (PDLF) spectroscopy. 

In general, the idea that underlines the design of various SLF techniques is that all the principal elements of an experiment can be changed to others with similar functionality adjusting the experiment to solving a particular problem.

Evolution period. A great number of different types of pulse sequences for the \( t_1 \) period have been developed in recent years. All of them can generally be divided in two groups depending on which part of the dipolar Hamiltonian is active in the \( t_1 \) period. As discussed previously, the dipolar Hamiltonian consists of a number of terms, two of which are directly accessible in NMR spectroscopy. Hence, the two types of experiments are:

- those that assess the static term, \( l_{ix}l_{jx} \);
- methods focused on measuring the flip-flop (exchange) dipolar term (Eq. (21 b)).

In SLF spectroscopy, one aims at measuring the heteronuclear dipolar coupling, while all the other interactions present in the system should be suppressed. For example, a variety of decoupling sequences has been designed to selectively remove homonuclear interaction while (partly) preserving heteronuclear coupling. The CS effect can be eliminated by applying refocusing pulses. MAS is also widely used for suppressing anisotropic interactions but in SLF spectroscopy it must be accompanied by one of the heteronuclear recoupling techniques.

The SLF without MAS is difficult to apply to unoriented powder samples because the CSA interaction limits the resolution of the spectrum in the direct dimension. Hence, the main target for this method is oriented samples. In our work, this approach was applied to magnetically aligned lyotropic mesophases.

Under MAS conditions, dipolar recoupling, the technique that prevents heteronuclear interactions from being averaged by MAS, is required. A number of pulse sequences have been designed for that purpose. For example, symmetry based R- and C-type recoupling sequences introduced by Levitt et al. are frequently used.

The dipolar SLF experiments of the second type are designed to measure the flip-flop term of the dipolar Hamiltonian. However, for unlike spins the flip-flop term is ineffective, because the quantum of energy released upon flipping one spin is not equal to the quantum that could be absorbed by the other spin. That is due to a large difference in
the gyromagnetic ratios. In other words, it is the conservation of energy law that forbids the flip-flop transitions in the case of unlike nuclei. To activate this mechanism of dipolar interaction one needs to provide conditions under which the two spins have the same precession frequency. This can be done using the cross-polarization (CP) technique.

**Polarization transfer.** This structural block of an SLF sequence follows the evolution period. It is used in the experiments where dipolar evolution encoded in the magnetization of abundant spins (e.g. $^1$H) needs to be transferred to rare spins with a wide CS range (e.g. $^{13}$C). The choice of polarization transfer method is based on the molecular mobility and spin couplings present in the system. For instance, in solids the most common technique for polarization transfer is the CP,$^{97,98}$ which is efficient in the systems with large residual dipolar couplings.

Methods, exploiting $J$-coupling, such as INEPT, DEPT, and their modifications$^{83-85,99,100}$ are less common in solids. That is because of a short spin-spin relaxation time, $T_2$, in the presence of the strong static homonuclear spin interaction. Techniques such as PRESTO$^{95}$ and INEPT-FSLG,$^83$ incorporating homonuclear spin decoupling$^{101-105}$ for increasing the transfer efficiency have been introduced.

**Detection and heteronuclear decoupling.** Evolution and polarization transfer blocks are followed by the detection period $t_2$. During this block, the magnetization that carries information about dipolar couplings is being detected using the nuclei with high CS range.

Spin couplings may cause reduction of chemical resolution in the direct dimension. If carbon-$^{13}$ spins are detected, one may disregard homonuclear dipolar interaction because of low natural abundance of the $^{13}$C isotope. In the case of isotopically enriched samples one would need to apply homonuclear decoupling.$^{106-113}$ The CSA and heteronuclear dipolar couplings may also cause severe broadening of the spectral line. The later is especially relevant for compounds with high content of protons i.e. for most organic compounds. The CSA coupling for carbons causes inhomogeneous line broadening of the range up to 200 ppm. This broadening may be averaged out by fast MAS.

Heteronuclear dipolar coupling to protons that was being measured in the first part of the experiment complicates the spectrum in the detection period and have to be decoupled. A great number of decoupling techniques have been proposed. In principle, heteronuclear interaction produces inhomogeneous broadening and should be averaged by MAS as
well as CSA. However, in the systems with strong proton-proton interactions, these homonuclear couplings interfere with heteronuclear carbon-proton interactions which, as a result, exhibit properties of a homogeneous interaction. In other words, in a molecule with dense proton network, carbon-proton couplings cannot be completely averaged out by MAS. Hence, active heteronuclear decoupling is necessary. Some common decoupling methods in solid-state NMR are TPPM\textsuperscript{114} and SPINAL\textsuperscript{115}.

**MAS and dipolar recoupling**

Magic angle sample spinning is used to suppress anisotropic interactions such as CSA and dipolar couplings. The secular parts of anisotropic couplings are proportional to the second Legendre polynomial $P_2(\cos \theta) = \frac{1}{2}(3 \cos^2 \theta - 1)$. For such interactions, spinning of a sample around the axis at the angle $\beta = \arctg \sqrt{2} \approx 54.7^\circ$ (the so-called magic angle) with respect to the external magnetic field $B_0$ averages out these couplings to first order. This reduces line broadening and therefore improves spectral resolution. Nowadays, this technique is routinely employed in solid-state NMR.

However, anisotropic interactions contain valuable information about the structure of a molecule and its mobility. Selective recovering of spin interactions averaged by MAS can be achieved by specially designed pulse sequences. This technique is called *recoupling*, with additional specification of what kind of interaction is recoupled.

In our work, dipolar recoupling has been used as a key element of dipolar SLF spectroscopy in unoriented samples.

**Proton Detected (Encoded) SLF spectroscopy**

Indirect detection (encoding) of the magnetization of the abundant spins (protons) instead of rare spins can significantly simplify the dipolar spectral shape. Figure 5 demonstrates a scheme of three-spin systems with homonuclear and heteronuclear dipolar couplings. During the PDLF experiment, I-I interaction is suppressed by homonuclear spin decoupling, while information about heteronuclear couplings is encoded in the spin-I magnetization. Each I-S pair behaves as an isolated two-spin system and the dipolar Hamiltonians $I_{1z}S_z$ and $I_{2z}S_z$ commute. The
dipolar spectrum in this case consists of two doublets corresponding to couplings within different spin pairs.

![Scheme of dipolar couplings in a three-spin system. Couplings registered in a PDLF experiment are S-I₁ and S-I₂.](image)

**Figure 5.** Scheme of dipolar couplings in a three-spin system. Couplings registered in a PDLF experiment are S-I₁ and S-I₂.

**PDLF. Oriented samples**

Figure 6 shows one of the possible implementations of the PDLF technique applicable to oriented liquid crystals. In powder samples, the isotropic distribution of CSA tensor orientations leads to line broadening. In contrast, in oriented samples only one main tensor orientation with respect to external magnetic field $B_0$ is present. This is valid not only for the CSA tensor but also for all anisotropic interactions e.g., dipolar and quadrupolar couplings.

To ensure that only the heteronuclear dipolar $I_zS_z$ term is active during the evolution period, homonuclear decoupling should be applied. For the static PDLF experiment we used BLEW-48, a sequence of 48 90°-pulses with alternated phase. The advantage of this sequence is high tolerance to various possible experimental imperfections. On the other hand, the length of the BLEW-48 block can be significant in the case of low decoupling rf power. This increases the sampling interval and correspondingly reduces the spectral window in the indirect dimension. This problem has been addressed in Paper I, where a new incremental scheme for the evolution period has been proposed. For details, see Section 3.

The effective field of the BLEW-48 sequence lies along the $y$-axis and magnetization rotates around the effective field with the nutation
frequency $k \omega_{15}$. Here, $k = 0.42$ is the scaling factor of the BLEW-48 sequence; $\omega_{15}$ is the heteronuclear coupling magnitude.

A high power $180^\circ$ pulse is applied in proton channel in the middle of the evolution period to refocus evolution by proton CS. This pulse alone would refocus also the heteronuclear dipole-dipole couplings and, to avoid this, the second $180^\circ$ pulse is added in the carbon channel.

The information encoded in the amplitude of proton magnetization is transferred to the carbon channel in the cross-polarization block and subsequently detected. The heteronuclear decoupling scheme TPPM\textsuperscript{114} or SPINAL\textsuperscript{115} have been utilized to enhance resolution in the direct dimension.

Figure 6. A PDLF method, presented in Paper I, designed for static heat-sensitive samples. The proton magnetization is encoded as it evolves under the effect of $^1\text{H}-^{13}\text{C}$ couplings. The applied rf field strength of the central BLEW-48 cycle is alternated between two levels in order to decrease the sampling time (as discussed in the text). At the end of the evolution period, the magnetization is transferred via CP to $^{13}\text{C}$ spins and detected in the presence of $^1\text{H}$ heteronuclear TPPM decoupling (Reprinted from Ref. 1 with permission from Elsevier).

Since the $J$-coupling Hamiltonian $J l_z S_z$ has the same form as the dipolar Hamiltonian term $\omega_{15} l_z S_z$, these two interactions cannot be separated in an SLF experiment. The splittings obtained in the indirect dimension contain contribution from both couplings:\textsuperscript{1,117}

$$\Delta v = \left| k \left( C_{\text{geom}} S_{\text{CH}} D_{\text{CH}}^{\text{static}} + J_{\text{CH}} \right) \right|. \quad (43)$$

$C_{\text{geom}}$ is a constant that depends on the molecular aggregate geometry, $S_{\text{CH}}$ is a C–H bond order parameter and $D_{\text{CH}}^{\text{static}}$ is the dipolar coupling
constant for an immobile C–H bond. The parameter $S_{CH}$ can be estimated from experimental splittings using Eq. (43).

**PDLF. Powder samples under MAS**

Powder samples usually exhibit poor resolution in static NMR spectra due to the distribution of CSA tensor orientations. MAS is routinely applied in solid-state NMR for averaging out the CSA and other anisotropic interactions.

Figure 7 presents a scheme of an R-PDLF experiment under MAS conditions. During the evolution period $t_1$, a symmetry based $R18^7_1$ recoupling sequence is applied to restore heteronuclear couplings. $R18^7_1$ is a rotor-synchronized pulse sequence that consists of nine $180^\circ_{70}180^\circ_{70}$ blocks that span one rotor revolution period. This implies that the recoupling rf field strength should be 9 times the spinning frequency. Besides heteronuclear recoupling, this R-sequence provides homonuclear decoupling making this method applicable to relatively immobile solid systems with strong residual homonuclear couplings.

Just as in the PDLF experiment on a static sample, after the evolution period, the magnetization is transferred via the CP block and the NMR signal is detected as it evolves under $^{13}C$ chemical shift interaction and TPPM decoupling.

![Figure 7. R-PDLF pulse sequence. An R-type recoupling sequence is applied during the evolution period $t_1$ to restore heteronuclear interactions averaged by MAS and suppress homonuclear dipolar couplings among protons. At the end of the evolution period $t_1$, the magnetization is transferred via CP to carbons and detected in the presence of heteronuclear spin decoupling.](image_url)
Chemical bond order parameters $S_{\text{CH}}$ are calculated from experimental splittings\(^{85}\)

$$\Delta v = |k S_{\text{CH}} D_{\text{CH}}^{\text{static}}|.$$ \hfill (44)

For R18\(^7\), the scaling factor $k = 0.315$. Active homonuclear decoupling and relatively low scaling factor make the R-PDLF spectroscopy particularly suitable for studies of the systems with low molecular mobility.

**SLF spectroscopy based on cross-polarization**

Figure 8 schematically illustrates active spin-spin couplings in an SLF experiment based on cross-polarization. The goal of the experiment is to register flip-flop term of the largest of the $S-I_1$ and $S-I_2$ couplings, while strong homonuclear proton-proton interaction is suppressed.

In the CP sequence, nuclei of both sorts are irradiated to fulfill the Hartman-Hahn conditions:\(^{97,98}\)

$$\gamma_S B_{1S} - \gamma_I B_{1I} = n \omega_r, \quad n = \pm 1, \pm 2.$$ \hfill (45)

Here, $\omega_r$ is the spinning frequency. Eq. (45) is valid also for static experiments. In this case, $\omega_r = 0$ and the Hartman-Hahn condition implies that nutation frequencies for both spins are equal.

![Figure 8. Scheme of dipolar couplings in a three-spin system. Couplings registered in a CP-based SLF experiment are denoted with brown arrows.](image)
Under CP irradiation, the flip-flop operator $S_+I_-$ is the leading term in the dipolar Hamiltonian. For an isolated two-spin system $I-S$ the magnetization of spin S (the same is valid for spin I) oscillates with the frequency $k\omega_{IS}$, where scaling factor $k$ depends on the specific implementation of the method.

In CP-based techniques, unlike that in PDLF spectroscopy, couplings of connected spin pairs cannot be separated. That is because the flip-flop Hamiltonians for $S-I_i$ and $S-I_j$ pairs do not commute. However, in multiple spin systems, a resolution enhancement is achieved due to efficient truncation of the weak coupling terms in the presence of a strong one. If, for instance, for the spin system of Fig. 8, the $S-I_2$ interaction is much weaker than the $S-I_i$, then the former is partly suppressed by the later and the resultant dipolar splitting is proportional to $\sqrt{\omega_{S1}^2 + \omega_{S2}^2} \approx \omega_{S1}^2$.

In case of highly mobile systems, residual homonuclear couplings are weak and can be suppressed by MAS. For less mobile systems, different active decoupling methods have been incorporated in the CP blocks during $t_1$.2,83

**APM-CP**

An example of CP-based SLF technique is shown in Figure 9. The method called Amplitude and Phase Modulated Cross-Polarization spectroscopy82,84,118 has been developed for measuring relatively weak dipolar couplings.

The evolution period is preceded by the prepolarization block that utilizes CP to enhance the initial magnetization in the carbon spin subsystem at the expense of proton magnetization. Then, during the $t_1$ period, a modified CP sequence is employed. The important feature of this pulse sequence is amplitude and phase modulation of the rf-fields. The phase modulation provides compensation of various experimental errors and imperfections but at the same time it causes changing the sign of the parameter $n$ of the Hartman-Hahn condition (See Eq. (45)). Careful inspection of the spin dynamics underlying CP transfer shows that, for a successful experiment, the Hartman-Hahn condition should not change during the course of the experiment. This is provided by alternating the carbon irradiation amplitude by $2\omega_r$ every time the phase is inverted.
Figure 9. The APM-CP pulse sequence. After the CP signal enhancement, the spin evolution is initiated by inverting the phase of the proton spin-lock field. The phases and amplitudes of the applied rf fields are alternated to achieve the heteronuclear decoupling. After the evolution period, the carbon magnetization is detected in the presence of heteronuclear decoupling. (Ref. 3 – Reproduced by permission of the PCCP Owner Societies)

In contrast to PDLF spectroscopy, in the APM-CP method it is the carbon magnetization that is encoded and, therefore, no polarization transfer block is needed before the acquisition period $t_2$. Order parameters can be estimated from dipolar splittings using Eq. (44).\textsuperscript{85}

APM-CP has the scaling factor $k = 1$ for methylene groups. This makes this pulse sequence especially appropriate for highly mobile systems with low residual couplings, since in these systems homonuclear proton interactions are also scaled down and can be averaged out by MAS.
3 Summary of research

In this chapter, a brief summary of new methodological developments of dipolar NMR spectroscopy (papers I, II and III) and new experimental data on molecular structure and dynamics of mesostructured composites (papers III, IV, V and VI) and mesophases (papers I and II) is presented.

3.1 Methodology

PDLF spectroscopy for heat-sensitive samples

Paper I describes a new experimental approach, PDLF with variable rf power, for studying the conformational dynamics of surfactant molecules in an aligned lyotropic mesophase.

In concentrated solutions of ionic surfactants, applying strong rf irradiation may induce severe heating of the sample. In extreme cases, sample heating can even induce phase transitions. Also, this heating causes frequency shift due to the temperature dependence of the carbon chemical shift. This reduces spectral resolution and makes 2D experiments difficult to implement.

In a 2D experiment, the spectral window in the indirect dimension is inversely proportional to the dwell time (sampling interval) during the evolution period \( t_1 \). In the conventional implementation of PDLF sequence, the dwell time is determined by the length of rf cycle of the homonuclear decoupling sequence. Thus, the spectral width is dependent on the rf pulse length – and consequently – on the rf strength during homonuclear decoupling. Since the spectral width should be higher than the range of dipolar couplings, strong rf pulses must be applied.

In Paper I, we addressed the problem of rf-induced heating of the sample and suggested a new incremental scheme that allows reduction of the applied rf power while keeping the spectral width constant. In contrast to the conventional incremental scheme where the number of decoupling blocks is incremented in consecutive scans, in the proposed scheme the changing of the pulse train duration is achieved by either incrementing the number of decoupling blocks or changing the duration of some blocks. This provides an opportunity to arbitrarily decrease the dwell time without increasing the rf power level.
One possible implementation of this method for PDLF spectroscopy with BLEW-48 homonuclear decoupling is schematically illustrated in Figure 10.

![Figure 10](image)

Figure 10. Incremental scheme for BLEW-48 decoupling sequence based on the alternation of rf amplitude in some of the decoupling blocks. The first six incremental steps are shown.

Each rectangle in the scheme depicted in Figure 10 is a BLEW-48 decoupling block. The duration of a block and the rf strength is proportional to the width and height of the rectangle, respectively. Longer BLEW-48 elements with reduced rf power are used in the odd increments of the scheme in such a way that the effective dwell time of the sequence is a factor of two shorter than in conventional experiment. The first increment does not follow the described pattern. Instead, half of the BLEW-48 block is applied. While the BLEW-24 sub-cycle is not well compensated for rf errors, its effect on the resulted spectral shape is negligible.

**Selective decoupling of spin-1**

The symmetry properties of dipolar interactions lead to symmetrical patterns of dipole multiplets. Due to that fact, the information available from dipolar spectra is limited to the magnitude of the interaction, while the sign of the coupling is not accessible. Knowing the sign of a coupling can often help to remove ambiguities in the molecular structure.

In Paper II, we investigated the possibility to break the internal symmetry of dipolar multiplets obtained for a spin-1/2 coupled to one or several spins-1 in static oriented liquid crystals. In aligned samples, NMR spectra of quadrupolar spin-1 are doublets with the splitting proportional to the quadrupolar coupling constant. The dipolar spectra of spin-1/2 coupled to spin-1 are symmetric triplets. Selective irradiation of one line
in the quadrupolar doublet of spin-1 mixes two of three eigenstates for spin-1 that results in collapsing of the two neighboring lines to a single peak. Which pair of lines collapses is dependent on the sign of dipolar interaction.

Using the described technique, in addition to the magnitude, the sign of the dipole-dipole coupling or, in case when the sign of the quadrupolar coupling is unknown, the relation between signs of quadrupolar and dipolar couplings may be established.

A detailed quantum mechanical analysis of the selective decoupling using the Average Hamiltonian Theory formalism is given in Paper II, where the more complex case of three-spin systems is considered. It is demonstrated that employing the different spin-operator bases may significantly simplify the analysis of spin dynamics. For instance, the single-transition operator formalism allows expressing the effective average Hamiltonian in its simplest form, while calculation of the density operator evolution is most conveniently described on the basis of projection operators. Theoretical results are complemented with numerical spin dynamics simulations and experimental results on model samples.

**Dipolar recoupling based on APM-CP and magic echo homonuclear decoupling**

The organic components of nanostructured composite materials exhibit a great variety in the local molecular mobility, which, in turn, results in a wide range of dipolar coupling values. It is difficult to find a comprehensive NMR tool for measuring dynamics in these systems, because, in general, different methods are sensitive to different dynamical modes. For instance, as discussed above, the R-PDLF experiment is better suited for studying relatively rigid immobile systems, while the APM-CP method performs best when applied to highly mobile less ordered materials. Thereby, it has been a significant challenge to find a general approach that would work throughout the whole range of dynamical states.

In **Paper III**, a novel method for studying the molecular mobility in mesostructured solids is presented. The approach, which combines amplitude- and phase-modulated cross-polarization recoupling with magic echo homonuclear decoupling, is shown in Figure 11.
For a pair of spins, the polarization in the evolution period $t_1$ oscillates between carbons and protons at the frequency $(2/3)(b/2\sqrt{2})\sin 2\beta$. Here, $b$ is the dipolar constant (see Eq. (19)) and $\beta$ is the polar angle determining the orientation of the internuclear bond in the rotor frame of reference. Hence, the splitting in the dipolar powder spectrum (Figure 12) is given by

$$\Delta \omega = \frac{2}{3} \frac{b}{\sqrt{2}} S_{CH}.$$  

(46)

The order parameter $S_{CH}$ takes into account the molecular mobility. The scaling factor of $2/3$ originates from the fact that cross-polarization works only during the $2/3$ of the total pulse sequence length. For a three-spin system of a methylene group, the coupling of two equivalent protons to a single carbon nucleus results in a higher dipolar splitting by the factor of $\sqrt{2}$.

![Figure 11](image-url)  

**Figure 11** Rf pulse sequence for 2D dipolar spectroscopy in rotating solids. The technique is based on the combination of the APM-CP sequence with magic-echo based homonuclear decoupling sandwiches (Paper III). After initial signal enhancement, the carbon magnetization evolves under the effect of scaled heteronuclear couplings. After the evolution period $t_1$, the carbon magnetization is detected during the $t_2$ period in the presence of TPPM heteronuclear decoupling (Reprinted with permission from Ref. 2. Copyright © 2014 American Chemical Society.)

Previously, magic echo was used in SLF spectroscopy of static samples. Under MAS condition, however, dipolar interactions are averaged out by fast sample rotation and dipolar recoupling is necessary to restore the desired spin interactions. In this technique, dipolar
recoupling is achieved by implementation of the recently developed amplitude- and phase-modulated cross-polarization,\textsuperscript{82,118}

The significant advantage over conventional APM-CP is that in ME-CP the proton-proton couplings are suppressed by the magic-echo sandwiches embedded into the pulse sequence.\textsuperscript{119,120} In contrast to FSLG-CP,\textsuperscript{121} a dipolar spectroscopy technique with off-resonance Lee-Goldburg homonuclear decoupling, magic-echo based sequences are less dependent on frequency offset and chemical shift terms. Additionally, the phase alternating scheme adopted from the APM-CP method makes the pulse sequence less sensitive to rf imperfections.

![Figure 12. Simulated $^{13}$C–H dipolar recoupled spectra of (a) CH and (b) methylene CH$_2$ groups. Experimental spectra of (c) the CH group in l-alanine and (d) the CH$_2$ group in α-glycine are compared to respective simulated shapes. (Reprinted with permission from Ref. 2. Copyright © 2014 American Chemical Society.)](image)

In contrast to many NMR recoupling methods, the synchronization of the ME-CP pulse sequence with rotor spinning is not necessary. In addition, the pulse sequence is $\gamma$-encoded\textsuperscript{92,122} that partly eliminates the signal interference due to spatial distribution of internuclear vector in powder samples.

### 3.2 Conformational dynamics in lyotropic LCs

The conformational dynamics of surfactant molecules in lyotropic lamellar and hexagonal mesophases is discussed in Paper I. Additionally, order parameter profiles for various liquid crystalline
phases in comparison to those for surfactants in organic-inorganic mesocomposites are presented in Papers IV, V and VI.

It has been shown that measuring the C-H bond order parameter profiles is a convenient and informative approach for characterizing conformational mobility of flexible molecules. Figure 13 compares the order parameters profiles for hexagonal CTAB/D$_2$O and lamellar CTAB/hexanol/D$_2$O mesophases. The order parameters of the first seven segments of the CTAB molecule are higher in a lamellar phase than in a hexagonal phase. This can be explained taking into account the internal structure of molecular aggregates in different phases. The difference in composition leads to changes in molecular assembly and molecular aggregate structure. In the lamellar phase, molecules of hexanol are integrated into the aggregates. They are located close to the head groups of the CTAB molecules and, by steric interactions restrict the mobility of the first several segments of the hydrocarbon chains.

![Figure 13](image_url)

Figure 13. Order parameters profiles for hexagonal (circles) and lamellar (squares) lyotropic mesophases obtained from PDLF experiments in oriented samples of CTAB/D$_2$O and CTAB/Hexanol/D$_2$O.

High spectral resolution, both in dipolar and CS dimension, has been achieved in these experiments. Since the experiments were conducted in magnetically aligned samples, lines in carbon CS spectrum are shifted with respect to their isotropic positions. Due to this additional shift and separation of the spectral lines in two dimensions, it became possible to resolve all non-equivalent carbons in the CTAB molecule.
3.3 Surfactant mobility in nanostructured solids

Surfactant dynamics in MCM-41

Molecular dynamics and the aggregate structure of surfactants are greatly affected by confinement effects and surface interactions in mesostructured composites. The material MCM-41, one of the first discovered silica-based mesostructured solids, has been extensively studied and has found important applications in chemical industry.

Figure 14. C-H bond order parameter profiles for CTAB molecules in the CTAB/MCM-41 (circles) and the CTAB/D$_2$O (squares) samples. (Ref. 3 – Reproduced by permission of the PCCP Owner Societies).

In Paper IV, a study of conformational dynamics of surfactant in the hexagonally ordered pores of MCM-41 using conventional 1D $^{13}$C NMR and dipolar $^1$H-$^{13}$C SLF spectroscopy is presented. The analysis of CS data shows that the molecules in cylindrical pores are in a conformationally disordered state. CTAB molecules in CTAB-templated MCM-41 mesoporous silica exhibit essentially the same CS values as in lyotropic CTAB/D$_2$O mesophases and isotropic micellar solutions. This suggests that CTAB molecules in MCM-41 are highly mobile with significant conformational dynamics. This was confirmed by dipolar NMR
spectroscopic measurement in Paper IV. Moreover, it was possible to quantitatively characterize conformational dynamics of surfactant in mesopores. The segmental mobility of the surfactant in the solid hexagonal mesoporous framework exhibited essentially the same fast decrease of $S_{CH}$ parameters towards the end of the chain as has been found in the fluid hexagonal mesophase (Figure 14). However, a strong motional gradient of the chain segments close to the wall of the material was observed for CTAB in MCM-41. The higher order parameters for the initial groups in the alkyl chains indicated significant mobility restriction due to electrostatic interaction of the surfactants with the charged solid silica interface.

Our results proved the presence of high molecular dynamics of surfactant molecules confined in mesocomposites with hexagonal geometry and provided for the first time the detailed quantitative characterization of the molecular dynamics with atomic level resolution.

**Template mobility in AlPO/CTAC lamellar composites**

Surfactant conformational dynamics in the mesolamellar composite AlPO/CTAC (Aluminium phosphate/Cetyltrimethylammonium chloride) has been studied in Paper V using 1D carbon-13 NMR and advanced 2D dipolar SLF spectroscopy. The 1D carbon spectra show that the majority of the CTAC molecules are in all-trans conformation at room temperature, as observed also for the crystalline bulk surfactant. At elevated temperatures (80 °C), a significant change in the chain conformational dynamics is observed. The chemical shift values suggest a great increase of the population of gauche conformers in the alkyl chains. However, this data do not deliver quantitative information on the dynamic processes in the composite.

In contrast, rather detailed quantitative information on molecular mobility is obtained by measuring bond order parameters by SLF spectroscopy (Figure 15). At room temperature, order parameters of 0.5 were observed for all methylene groups in the surfactant alkyl chains. This information, combined with the data about all-trans conformation of surfactant molecules, suggests the presence of the so-called rotator phase, with the CTAC molecules undergoing free rotation about their molecular axis. Upon heating, a phase transition accompanied by a significant reduction in the order parameters for most of the alkyl segments was observed. Finally, in the high temperature phase, the
chains become much less ordered and significant motional gradient towards the chain end was detected.

Figure 15. C-H bond order parameter profiles for mesolamellar aluminophosphate CTAC/AlPO at 25 (solid circles) and 80 °C (squares) and in CTAC/D$_2$O lamellar lyotropic mesophase at 40 °C (open circles). (Reprinted with permission from Ref. 4. Copyright © 2013 American Chemical Society.)

The comparison of the order parameters profile in the high temperature phase of the solid composite with the profile for a lamellar LC sample reveals similar degree of conformational mobility for a large part of the hydrocarbon chain. In fact, the amplitude of molecular motion is slightly higher in the mesocomposite material. This may be explained by lower packing density in the mesocomposite, which is restricted by the density of surface charges on the walls of the material. Despite the high overall conformational dynamics of the CTAC chains, a strong anchoring effect at the solid interface was observed for the first four methylene groups. Order parameter for the C1 carbon is as high as 0.4 that is only slightly lower than that in the room temperature rotator phase. This indicates strong Coulomb interaction between the surfactant and the aluminophosphate interface.
Phase behaviour of surfactant intercalated into magadiite

The lamellar composite studied in Paper VI is based on the natural layered clay mineral magadiite in contrast to purely synthetic lamellar material described in previous section. Intercalation of surfactants in clays is widely used to prepare polymer/clay composites for various industrial applications. The molecular mobility of the functionalizing surfactant layer is one of the factors promoting the penetration of the macromolecules into the clay galleries. Transitions between highly ordered immobile states to the disordered “molten” phases in surfactant/clay composites have been demonstrated previously.124–127

We investigated the phase transitions and associated changes in molecular dynamics in the CTAB/magadiite system by dipolar SLF spectroscopy. Order parameter profiles were used as motional signatures of the particular dynamical modes. It was possible to detect broad phase transitions not observable by other spectroscopic techniques or by DSC.

The study showed that at room temperature the intercalated surfactant molecules are in all-trans conformations with no large angle reorientations. The obtained order parameters of ca. 0.9 for all methylene carbons indicated that the C-H bond vectors undergo minor wobbling about the long molecular axis with approximate angular amplitude of ~15° (Figure 16). Upon heating the sample to 70 °C, the surfactant molecules transform to a different dynamical state. The fraction of gauche bonds in the surfactant molecules slightly increases and is accompanied by a reduction of the order parameters for all methylenes. This motional mode was identified as the rotator phase with a small fraction of gauche bonds. Conformational dynamics, although present, is negligible and the molecules may be described as nearly rigid rotating bodies.

The second phase transition at about 110 °C is associated with the so-called “chain melting” transition observed, for example, in lipid bilayers.71 In the high temperature state, order parameters for different segments were in the range 0.04±0.15 and lower than those for the corresponding lyotropic mesophase. Such high mobility of surfactant molecules may be explained by the lower packing density of template molecules in mesocomposites. In contrast to what was concluded for the ALPO/CTAC composite in Paper V, no significant anchoring effect by Coulomb interactions with the solid interface was observed in
intercalated magadiite. This suggested that the surfactant molecules in the high-temperature phase in magadiite gain translational mobility.

![Graph](image)

Figure 16. (a) C-H bond order parameter profiles for CTA+/magadiite sample at 22, 75 and 110 °C (circles, triangles and diamonds, respectively) and order parameter profile for the bulk CTAB at room temperature (squares). (b) Comparison of the CTA/magadiite composite at 110 °C (diamonds) and CTAB/D$_2$O lamellar lyotropic mesophase at 70 °C (circles). (Reprinted with permission from Ref. 5. Copyright © 2014 American Chemical Society.)

Another indirect evidence of translational diffusion was provided by an observation of vanishing intermolecular dipolar couplings. These spin-spin connections cannot be fully averaged out by conformational dynamics. Fast translational motion of the molecules with respect to each other, however, would break the coupling. Thereby, we concluded that a
smectic-like liquid crystalline phase is formed within the layers of nanocomposite materials.
Concluding remarks

In this work, molecular dynamics in ordered mesostructured composites and lyotropic mesophases have been studied and relevant NMR methodology has been developed.

New experimental approaches that address the limitations of the existing SLF methodology have been proposed. A method of reducing the rf power in dipolar spectroscopy experiments in heat-sensitive samples was introduced. A method for sign-sensitive determination of dipolar couplings to spin-1 has been demonstrated. A new recoupling technique for studying samples under MAS conditions has been developed to achieve a high dipolar resolution in a wide range of the dipolar coupling magnitudes. Theoretical analysis, computer simulations and experiments on model samples have demonstrated that the developed experimental techniques deliver detailed model-independent information on the molecular motional parameters of flexible molecules.

It has been shown that the separated local field spectroscopy is capable of delivering detailed quantitative information on the molecular dynamics and aggregate structure in ordered mesostructured composite materials. This advanced spectroscopic technique allows direct measurement of residual dipolar couplings in anisotropic systems with high chemical resolution. Order parameters profiles that were established allowed the accurate description of molecular dynamics in these complex materials. Comparison of dynamic data for the ordered mesostructured solids and lyotropic liquid crystals of similar morphology provided experimental insights to the effect of confinement and surface interaction on molecular mobility and aggregate structure. The phase behavior of surfactants intercalated into the pores of ordered mesocomposites has been studied. On the basis of NMR data, different dynamical modes of surfactant molecules in nano-assemblies were described.

Analysis of the local order parameters profiles provides a basis for developing physical motional models of the molecular assemblies in confinement. It is anticipated that the results of this work will improve the understanding of the dynamic processes in mesostructured composites and contribute to the design of these advanced materials with improved properties.
# List of abbreviations

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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<tr>
<td>AHT</td>
<td>Average Hamiltonian Theory</td>
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<td>APM-CP</td>
<td>Amplitude- and Phase-Modulated Cross-Polarization</td>
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<td>BLEW</td>
<td>Burum, Linder, Ernst Windowless decoupling</td>
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<tr>
<td>CP</td>
<td>Cross-Polarization</td>
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<td>CPP</td>
<td>Critical packing parameter</td>
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<td>CS</td>
<td>Chemical shift</td>
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<td>CSA</td>
<td>Chemical shift anisotropy</td>
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<td>CTAB</td>
<td>Cetyltrimethylammonium bromide</td>
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<td>CTAC</td>
<td>Cetyltrimethylammonium chloride</td>
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<tr>
<td>DEPT</td>
<td>Distortionless Enhancement by Polarization Transfer</td>
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<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
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<td>FID</td>
<td>Free induction decay</td>
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<tr>
<td>FSLG-CP</td>
<td>Frequency Switched Lee-Goldburg Cross-Polarization</td>
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<td>HDC</td>
<td>Heteronuclear Dipolar Coupling</td>
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<td>INEPT</td>
<td>Insensitive Nuclei Enhancement by Polarization Transfer</td>
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<tr>
<td>INEPT-FSLG</td>
<td>Insensitive Nuclei Enhancement by Polarization Transfer with Frequency Switched Lee-Goldburg decoupling</td>
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<tr>
<td>LC</td>
<td>Liquid crystal</td>
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<td>MAS</td>
<td>Magic angle spinning</td>
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<td>ME-CP</td>
<td>Magic Echo Cross-Polarization</td>
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<td>NMR</td>
<td>Nuclear magnetic resonance</td>
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<tr>
<td>PDLF</td>
<td>Proton Detected (Encoded) Local Field (spectroscopy)</td>
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<tr>
<td>PRESTO</td>
<td>Phase-shifted Recoupling Effects a Smooth Transfer of Order</td>
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<tr>
<td>R-PDLF</td>
<td>R-based Proton Detected Local Field (spectroscopy)</td>
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<td>SAXS</td>
<td>Small Angle X-Ray Scattering</td>
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<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>SLF</td>
<td>Separated Local Field (spectroscopy)</td>
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<tr>
<td>SPINAL</td>
<td>Small Phase Incremental Alternation decoupling</td>
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<td>ST</td>
<td>Single-transition (operator)</td>
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<tr>
<td>TEM</td>
<td>Tunneling Electron Microscopy</td>
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<tr>
<td>TPPM</td>
<td>Two Pulse Phase Modulation</td>
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<td>XRD</td>
<td>X-Ray Diffraction</td>
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