Dipolar Coupling: Molecular-Level Mobility

D. Reichert and K. Saalwächter
Martin-Luther-Universität Halle-Wittenberg, Institut für Physik, Halle, Germany

1 INTRODUCTION

The majority of reported nuclear magnetic resonance (NMR) studies naturally aim at obtaining structural data, for the relevant NMR interactions like chemical shift and dipolar coupling primarily provide information on the chemical structure and spatial organization of the sample material. Limited dynamic information can be gained from such data only, for example, for conformational transitions that alter the values of the isotropic chemical shifts. However, the majority of the dynamic studies rely on anisotropic NMR interactions like the anisotropic chemical shift and the quadrupolar and—last but not least—the dipolar coupling (see Dipolar and Indirect Coupling Tensors in Solids). Soon after NMR was discovered and long before the discovery of the chemical shift and the J-coupling (which provide the basis of chemical applications), the relation between molecular dynamics and NMR relaxation parameters was elucidated (see Relaxation: An Introduction). Likewise, the broadening of the NMR lines due to the dipole–dipole coupling and the influence of molecular dynamic processes on this broadening were discovered early on: it was realized that the observed wide absorption lines were due to static dipolar interactions (see Polymer Dynamics and Order from Multidimensional Solid State NMR). In isotropic liquids, however, much narrower lines were detected and it was understood this is due to the averaging of static interactions. A stochastic reorientational motion (as it is the typical case for a thermally activated process in matter) can be described by the correlation function of motion, which correlates a dynamic variable at two points in time, say at \( t \) and \( t + \tau \), and averages over a sufficient number of different \( t \). For dipolar coupling, the simplest analytical expression reads

\[
C(\tau) = \frac{1}{r^3(t)} P_2(\cos \theta(t)) \times \frac{1}{r^3(t + \tau)} P_2(\cos \theta(t + \tau))
\]

where \( r \) is the internuclear distance and \( P_2(\cos \theta) = (3\cos^2 \theta - 1)/2 \) is the second-order Legendre polynomial (for simplicity, we here neglect the contributions of higher order Legendre polynomials/Wigner functions). For isotropic samples and fixed intermolecular vectors, equation (1) simplifies to

\[
C(\tau) = \frac{1}{2} \langle P_2(\cos \theta(0)) \cdot P_2(\cos \theta(\tau)) \rangle
\]

where \( \theta \) is the angle between the principal axis of the interaction tensor (the internuclear vector) and the applied magnetic field at time zero and \( \tau \). The meaning of equation 1 is demonstrated in Figure 1: for short \( \tau \), the value of the dynamic variable does not change and the product of the values of the dynamic variable is always positive and adds up on the average to a certain positive value (commonly normalized to 1); however, for long \( \tau \), the product of the dynamic variable at different points in time separated by \( \tau \) can be positive or negative, and thus averages to zero over the sample. The time average \( \langle P_2(\cos \theta) \rangle \) is zero when the orientation angle \( \theta \) follows an isotropic diffusion process; the correlation function of motion in this case becomes an exponential function that decays to zero

\[
C(\tau) = e^{-\frac{\tau}{\tau_c}}
\]

where \( \tau_c \) is the correlation time. If, however, the motion is fast but anisotropic, the averaging is incomplete, leaving an order parameter plateau, \( S^2 \propto \langle \omega_\parallel \rangle^2 \), related to a residual coupling \( \langle \omega_\parallel \rangle \) from which the geometry of the motional process can be concluded (see below)

\[
C(\tau) = (1 - S^2) \exp \left( -\frac{\tau}{\tau_c} \right) + S^2
\]
of 90° (rather at the magic angle),\(^3\) and the idea was later developed to what became known as magic angle spinning\(^4,5\) (see Magic Angle Spinning).

Any molecular reorientation leads to an alteration of the resonance frequencies and thus of the NMR data, and is therefore detectable. Parameters of molecular dynamics are quantified by the timescale as well as the geometry of the process that causes alterations of the orientation angle \(\theta\) of, in this case, the uniaxially symmetric dipolar interaction tensor with respect to the external magnetic field. The time dependence of the correlation function of motion (see Relaxation: An Introduction), in particular, the autocorrelation function of \(P_2(\cos \theta)\), contains the potentially available dynamic information. The shape of the correlation function can be as simple as a single exponential for an isotropic reorientation or as complicated as a multicomponent and nonexponential function for more complicated motions in larger and structured molecules. In most cases, this information is not completely accessible and approximations have to be made.

Currently available dynamic solid-state NMR methods span a dynamic range of more than 10 orders of magnitude and also provide information about the geometry of the dynamic processes, i.e., about the amplitude of reorientations (detailed information of jump angles), the number of interchanging sites, or even the details of the correlation function of motion. The extraction of this information from the experimental NMR data often requires a simplified assumption of the correlation function of motion or a motional model for which the relation between relaxation time and correlation function has to be calculated or relies on the simulation of spectra or other NMR data and comparison with the experimental data. In a few cases of exchange-NMR experiments, the dynamic information can be extracted completely model-free. While the early experiments were mostly ‘low-resolution’ experiments on abundant nuclei (like \(^1\)H), the possibility of isotopic labeling as well as advances in line-narrowing approaches and multidimensional NMR provide an increased molecular resolution and sensitivity, making dynamic NMR a unique tool for the detailed investigation of dynamic processes in organic solids, and in which the dipolar coupling plays a major role.

2 BASICS

The cornerstone of all experiments and approaches described below is the dependence of the resonance frequency of a nucleus on the orientation of the internuclear vector versus the external magnetic field that is induced by the local field of a neighboring nucleus. In the static case, any NMR spectrum governed by dipolar coupling is the superposition of resonance lines located at the frequencies determined by the dipolar coupling constant and the orientation versus the external magnetic field, and is a superposition of all possible orientations that occur in the sample. From this, it is immediately apparent that the spectrum contains information about macroscopic orientations, too; however, henceforth we assume isotropic materials, that is, all molecular orientations present in a random statistical distribution. Also, we further consider \(^1\)H--\(^1\)H or \(^1\)H--X couplings only, since other couplings are more insensitive and often inconvenient to measure in organic solids. It should be noted that whenever isotopic labeling is feasible, one should consider \(^2\)H experiments since they provide the best tools for extracting dynamic information on all timescales (see Deuterium NMR in Solids).

Dynamic solid-state NMR spans a dynamic window from very fast processes with correlation times of nanoseconds down to very slow motions that occur on the timescale of seconds. Therefore, different experimental approaches have

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**Figure 1** Schematic illustration of the meaning of the correlation function of motion, \(C(\tau)\). The dynamic variable \(\sigma(t)\) can take two distinct values \(+a\) and \(-a\), which vary by a random dynamic process. For simplicity, \(C(\tau)\) is defined here as \(C(\tau) = \langle \sigma(t) \cdot \sigma(t + \tau) \rangle\). The two upper charts (a and b), \(\sigma(t)\) is shown. For illustration, the gray circles mark points in time at which the products \(\sigma(t) \cdot \sigma(t + \tau)\) are taken for two values of \(\tau\) (shown as bars) at four values of \(t\). Note that for short \(\tau\), the probability of finding \(\sigma(t)\) in the same state is high while for long \(\tau\), the probability of finding \(\sigma(t)\) in the one or in the other state is approximately equal. The averages of the products \(\sigma(t) \cdot \sigma(t + \tau)\) yield \(4a^2\) for the short \(\tau\) value (a) and \((a^2 - a^2 + a^2) = 0\) for the longer \(\tau\) value (b). The final correlation function of motion for this example is an exponential function (c), see equation (3).
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been developed. For dipolar coupling, one basically needs to
distinguish different time regimes that are defined by the ratio
of the rate of reorientation (that is inversely proportional to
the correlation time of motion, \( \tau_c \)) versus the dipolar coupling
constant \( \omega_D \):

A. slow motion: \( (\tau_c)^{-1} \ll \omega_D \)
B. intermediate motion: \( (\tau_c)^{-1} \simeq \omega_D \)
C. fast motion: \( (\tau_c)^{-1} \gg \omega_D \)

In turn, these conditions roughly translate into the relation
between the transverse relaxation time \( T_2^{\text{stat}} \) in the static case
and the inverse of the dynamic rate, i.e., \( \tau_c \):

A. slow motion: \( \tau_c \gg T_2^{\text{stat}} \)
B. intermediate motion: \( \tau_c \simeq T_2^{\text{stat}} \)
C. fast motion: \( \tau_c \ll T_2^{\text{stat}} \)

Since \( T_2^{\text{stat}} \) approximately equals the lifetime of the NMR
signal (length of the free induction decay, (FID) time),
the different regimes correspond to the following: (A) The FID
decays faster as compared to the average lifetime of a certain
molecular orientation, (C) the rate of reorientation is faster
as compared to any frequency component of the FID, or
(B) an appreciable number of reorientations happens during
the lifetime of the FID. Fast processes in the range of the
inverse Larmor frequency efficiently stimulate transitions of
spins between their Zeeman levels and drive NMR relaxation.
Thus, these experiments provide accurate information about
fast motions with correlation times on the order of the inverse
Larmor frequency, while in the absence of molecular dynamic
processes, only spin dynamics like spin diffusion that do not
contain information about the molecular dynamics contribute
substantially to the relaxation data and make a faithful
determination of molecular dynamic parameters difficult. Since
there are excellent texts on NMR relaxation, we will not deal
with such experiments here (see Relaxation: An Introduc-
tion). Also, these fast processes lead to an averaging of the
experimentally determined dipolar coupling that provides
dynamic information, see below. Slower motion, however,
can be either investigated by relaxation experiments in
lower effective fields or one can make use of the fact that
processes with correlation times on the order of the lifetime
of the solid-state NMR signal, i.e., microseconds, have an
effect on the appearance of the NMR spectrum due to a
modulation of the resonance frequencies or interference with
external perturbations. Even slower processes are the domain
of exchange experiments that basically provide access to
to processes with correlation times as long as the relaxation
life \( T_1 \).

Historically, the first ‘dipolar’ experiments were carried
out on abundant spins with large gyromagnetic ratio, i.e.,
\(^1\text{H}\) and \(^{19}\text{F}\). In particular for \(^1\text{H}\), the dominant interaction is
the homonuclear \(^1\text{H}–^1\text{H}\) interaction that leads to an overall
spectral width of about 40 kHz in a typical organic solid, in
contrast to the chemical shift effects that are as small as a
few tens of hertz at the external field strengths used in those
days. Basically, it is possible to calculate the effects of a
molecular reorientation on the experimental dipolar spectrum
using standard procedures like exchange theory,\(^6\) however, for
the case of dipolar interaction in solids, this is strictly true
only for isolated spins forming a spin pair. The problem in

Figure 2 Theoretical line shapes for a dipolar-coupled nuclear spin
pair with like spins \( I = 1/2 \) when stationary and when in motion about
an axis perpendicular to the internuclear axis. (Reproduced from Ref.
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real systems is that many closely spaced protons interact with
each other; there are hardly any isolated \(^1\text{H}–^1\text{H}\) pairs that
would yield spectra that match theory and enable a quantitative
calculation of the line shape. Though theoretical attempts were
made to increase the number of spins in the calculation,
the usual approach was to convolute the theoretical two-
spin spectrum with a broad Gaussian or Lorentzian function
that results in a rather featureless broad line\(^7\) (see Figure
2) from which in most cases the second moment of the
line shape was extracted. In Figure 3, temperature-dependent
dipolar spectra and the extracted linewidth are shown for
hexamethylbenzene.\(^8\) The ‘onset’ of the ring rotation, i.e.,
the temperature at which the inverse correlation time of the
rotation becomes similar to the dipolar coupling constant and
a substantial line narrowing happens, is also detected in the DSC
trace. The application of temperature-dependent line shapes
and the measurements of second moment in more complex
organic solids like polymers followed soon after\(^9,10\) (see
Polymer Dynamics and Order from Multidimensional Solid
State NMR). In these temperature-dependent experiments,
this line is narrowed down close to a temperature when the
motional rate of the thermally activated process approaches
and eventually exceeds the dipolar coupling constant; however,
this basically provides a single data point in the activation
diagram. In addition, the transition from the static line shape
to the narrow line happens over a certain temperature range,
so the accuracy in both temperature and rate is fairly limited.
No detailed information about the geometry of the process is
available either, except a rough estimate about the anisotropy
of the reorientation: if the dynamic process happens to be
isotropic, the limit is the natural linewidth related to the applied
external field, while for anisotropic motions, a larger linewidth
is obtained. Qualitatively, the smaller the amplitude of the
reorientation, the closer the fast-limit linewidth to that of the
rigid limit.

It should be noted that there is experimental evidence that
dynamic parameters can be obtained not only by recording
spectra at different temperatures (and thus motional rates of
thermally activated processes) but also by changing parameters
of the NMR experiment like the decoupling efficiency,
inducing an ‘exchange narrowing’ analogous to the classical
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Figure 3  (a) $^1$H Resonance line derivate for hexamethylbenzene (HMB). (b) Variation with temperature of the resonance linewidth and of the specific heat for HMB. The drop of linewidth between 150 and 200 K is due to the sixfold rotation of the molecule, which is also visible in the DSC trace by the hump between 135 and 165 K. The peak at 108 K is due to a structural change of the crystal lattice, which is unobservable by NMR. (Reproduced from Ref. 8. © American Institute of Physics, 1950)

Figure 4  Dependence of the order parameter of motion, $S$, equation 5, on the topology (angle $\delta$) of the molecular motion. (a) Sketches of the jump geometries. (1) Jumps about an angle $\delta$ between two equivalent sites. (2) Jumps about angles $\delta$ between three sites at the corners of an equilateral triangle. (3) Diffusion on an arc with the opening angle $\delta$. (4) Diffusion inside a cone with the opening angle $2 \cdot \delta$. (5) Diffusion on a cone with the opening angle $2 \cdot \delta$. (b) Dependence of $S$ versus $\delta$. Note that for the case (2), $\delta$ is only defined between 0 and 120° where complete transverse isotropy is achieved ($S = -1/2$).

However, this approach does not seem to have found applications in real systems.

3 AVERAGED DIPOLAR COUPLINGS—FAST MOTIONS

The most common quantitative approach is to apply a general model (see also model-free approach$^{13,14}$) that defines a so-called dynamic order parameter $S$ as the ratio of the averaged versus the full dipolar coupling

$$S = \langle P_2 (\cos \theta) \rangle = \frac{\langle \omega_D \rangle}{\omega_D}$$

where $\langle ... \rangle$ means the time average and $\omega_D$ is the dipolar frequency. $S$ is a measure of the anisotropy of the molecular reorientation and ranges from one for a completely rigid system (or a vanishing reorientation angle), passing zero for an isotropic motion down to $-1/2$ for transverse isotropy,
i.e., the motion occurs in a plane perpendicular to the reference orientation. For special topologies of motion, a quantitative relation between the reorientation angle and $S$ can be drawn$^{15,16}$ as shown in Figure 4 where this relation is displayed for two- and three-site jump motions as well as planar diffusion and diffusion within a cone and on a cone, respectively. If such models are not applicable, at least anisotropic jump motions can be distinguished from rotational diffusions or relative information, comparing different samples, etc., can be obtained. However, it should be noted that from averaged dipolar couplings measured in the fast limit, no information about the timescale of the motion can be obtained.

4 DYNAMIC LINEShape–INTERMEDIATE MOTIONS

If the rate of the process does not satisfy the condition for a fast process, i.e., if there are motionally induced frequency alterations during the lifetime of the FID, equation 5 cannot be applied anymore and, therefore, easy determination of dynamic parameters is not possible. However, the experimental parameters like the dipolar spectrum now contain information about the topology of the process and additionally about the timescale of the process. In principle, the NMR time-domain signal ($fid$) can now be written as

$$fid(t) = M_0 \exp \left( i \int_0^t \omega(t') \, dt' \right)$$

where in a dynamic system, the resonance frequency $\omega$ that is determined by anisotropic interactions now is a random function of time as a result of the motion. For single spin pairs, and in particular the related case of $^2$H NMR experiments with models relying on jumps between a limited number of sites, theoretical solutions based on exchange matrices are straightforward and well established in the literature.$^{17}$ More generally, following the well-known Anderson and Weiss (A–W) approach$^{18}$ of 'random frequency modulation', approximate and rather simple analytical solutions are possible. The theory is based on a Gaussian resonance frequency distribution, which is due to the distribution of the dipolar local fields, and requires that the resonance frequency varies in time due to a random thermal process. The simplest model usually adopted is isotropic rotational diffusion, which has a particularly simple, monoexponential correlation function. While the Gaussian frequency distribution naturally arises for the multiplet scenario of a proton system, it turns out that the short-time behavior of just a spin pair (Pake-like frequency distribution) performing N-site jumps can still reasonably well be described by such an ansatz.$^{19}$ Details are addressed below. The A–W approach is an underestimated and powerful tool, as it provides simple analytical equations to describe frequency or time-domain data$^{20}$ and even the time dependence in MAS experiments can be accommodated.$^{21}$ There are a number of extensions to the model$^{22–24}$ and applications to extract dynamic parameters from organic solids, in particular rubbery materials and of adsorbed molecules.$^{24–35}$

5 SITE-RESOLVED HETERONUCLEAR AND HOMONUCLEAR DIPOLAR COUPLINGS

In addition to the disturbing multispin effects described above, experiments on abundant nuclei (like $^1$H) in typical organic solids are often too unselective: one of the powers of NMR: its chemical selectivity thus molecular resolution, is lost due to the unfavorable ratio of the strong dipolar interaction between the spins that broadens the spectra and the small chemical shift that provides the spectral resolution. It is therefore generally desirable to separate the information from structure (chemical shift) and dynamics (dipolar coupling) in a two-dimensional manner.$^{36}$ For organic solids at natural abundance, dipolar experiments should be combined with high-resolution conditions provided by MAS, and a wealth of homonuclear and heteronuclear dipolar recoupling experiments, providing precise values for the coupling constants, have been designed in the past decades.$^{37}$ However, most of these experiments are used to obtain structural information (distances), and only a few (in fact less sophisticated) approaches have gained importance in dynamic studies and deserve special attention: cross-polarization (CP) dynamics, separated-local field (SLF) and related recoupling techniques, and homonuclear double-quantum (DQ) experiments. The former two approaches rely on the heteronuclear dipolar coupling between abundant (like $^1$H) and rare spins (like $^{13}$C). In a CP experiment, the increase of rare-spin magnetization occurs with the buildup time $T_{CH}$ that is—similar to the relaxation time $T_1$—sensitive to dynamic processes in the kilohertz range$^{38}$ and correlates to important mechanical parameters like dynamic moduli.$^{39,40}$ The measurement of $T_{CH}$ became rather popular in dynamic investigations of organic solids; however, care must be taken in the interpretation of the data.$^{41}$ SLF experiments measure chemical shifts and dipolar coupling separately but in a way that they can be correlated.$^{36,42–44}$ Popular versions of SLF experiments are dipolar-rotational spin echoes (DRSE)$^{44–47}$ and wide-line separation (WISE) experiments.$^{48}$ An early example of DRSE is shown in Figure 5, where the dipolar spectra of a backbone and a ring carbon in polystyrene (PS) are compared: the latter exhibits a smaller dipolar coupling, due to the averaging by the flip motion. The WISE approach was first suggested as a dynamic filter$^{49}$ to separate mobile and rigid components in $^{13}$C spectra and has later found broad application in polymer science.$^{50}$ WISE data from a block-copolymer of PS and polydimethylsiloxane (PDMS) are shown in Figure 6: the different widths in the dipolar dimension reveal different mobilities of the glassy PS and the rubbery PDMS. Further developments of WISE include the suppression of the disturbing $^1$H-spin diffusion during the CP step that would transfer the $^1$H magnetization to different carbons and thus spoils the molecular resolution of the method.$^{51}$ The work of Frydman$^{52}$ deserves particular attention; it has shown that SLF experiments are possible even without homo-decoupling building blocks and for multispin systems: when sufficiently fast MAS rates are employed, quantitative dipolar sideband patterns from directly bonded spin pairs can be acquired in the absence of $^1$H–$^1$H multiple-pulse homonuclear decoupling even for 'real' organic solids. A special SLF version is the so-called PISEMA technique.$^{53}$ It works for static samples and is usually applied to oriented biological materials in which the X
nucleus is usually a $^{15}$N nucleus in a selectively isotopically enriched sample. The necessary spectral resolution is achieved by the isotopic labeling (reducing the number of resonances) and oriented samples (to avoid the broad anisotropic lines in the direct dimension). However, this experimental approach is restricted to specially labeled and prepared samples and hence to few laboratories around the world.

SLF variants that deserve attention are the efficient DIPSHIFT experiment\(^{54,55}\) (which is basically the DRSE experiment suggested by Schaefer et al.\(^{46}\) but running it in a more efficient mode) and the Lee-Goldberg CP (LG–CP) experiment.\(^{56}\) In these experiments, the homonuclear dipolar coupling is efficiently reduced by the irradiation of homonuclear $^1$H decoupling sequences like MREV or LG decoupling.

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**Figure 5**  $^{13}$C DRSE spectra of poly(styrene-co-sulfone). The homonuclear decoupling was achieved by the WAHUHA sequences, and the $^{13}$C spectra depending on the number of WAHUHA cycles are shown in (a). This number plays the role of the increment $t_1$ in the indirect dimension. (b) Dipolar sideband patterns for two CH pairs. (Reproduced from Ref. 46. © American Chemical Society, 1984)

**Figure 6** (a) Pulse sequence of the WISE experiment and (b) WISE spectrum of poly(styrene-co-dimethylsiloxane). In (a), the modulation of the carbon signals by the rigid and mobile protons is demonstrated. This appears in the indirect dimension as the dipolar linewidth (b). (Reproduced from Ref. 50. © American Chemical Society, 1992)
Figure 7  (a) Pulse sequence of the DIPSHIFT experiment. The homonuclear decoupling is efficiently achieved by frequency-switched LG decoupling (FSLG). The pulse at $T_R$ on the carbon channel serves to refocus the evolution due to the chemical shift. (b) DIPSHIFT dephasing curves. The data were calculated at a spinning rate of 4711 Hz, a $T_2$ of 2 ms, and for the dipolar couplings indicated in the figure.

Figure 8  (a) Pulse sequence of the LG–CP experiment. (b) Molecular structure and atom numbering of tyrosine·HCl. (c) 2-D LG-CP data. The dipolar couplings can be calculated from the dipolar oscillations. Note the longer period of the oscillations from the nonprotonated carbon 4'. (Reproduced from Ref. 56. © American Chemical Society, 2000)

In turn, only the heteronuclear dipolar coupling between the X nuclei (for example, $^{13}$C) and the $^1$H remains. In principle, every $^{13}$C still interacts with a number of $^1$H. However, owing to the strong distance dependence of the dipolar coupling, only the closest protons play a major role in the experiment. When applied to protonated carbons with a well-defined number of bonded $^1$H, these experimental schemes can be analyzed in terms of theoretical models that are well developed. All these experiments are 2-D experiments that provide the (normally) well-resolved $^{13}$C MAS spectrum in the direct and the $^{13}$C–$^1$H dipolar spectrum in the indirect dimension. The DIPSHIFT experiment is particularly efficient as it produces a $^{13}$C–$^1$H dipolar MAS spectrum that is periodic with the MAS period, $T_R$, and thus, it is only necessary to sample few data points during a single $T_R$. Furthermore, the second Fourier transform over the dipolar dimension is omitted, as it does not add additional information but might result in some artifacts like a zero-frequency peak. Thus, even samples with low signal intensity can be investigated in natural isotopic abundance.

For $\tau_c$ on the order of $10^{-5}$ s or less, all these experiments determine the dipolar coupling strength that is reduced by fast molecular dynamics. Information about the amplitude of the molecular process can be extracted from the reduction ratio.
with respect to the static value of the dipolar coupling in terms of an order parameter that contains the information about the anisotropy of the molecular reorientation, equation (5). Again, no information about the rate of motion can be made in this regime. Figure 7 displays calculated DIPSHIFT dephasing curves for different apparent dipolar couplings, which might be caused by fast but anisotropic molecular motions with different topologies (order parameters). The apparent $T_2$ relaxation of these curves is due to imperfections of the homonuclear decoupling sequences and residual couplings. LG-CP data are displayed in Figure 8 where the dipolar oscillations can be seen nicely. Please note the different apparent couplings, due to different amplitudes of motion, that are manifested in the different periods of these oscillations.

A related class of experiments are heteronuclear dipolar recoupling techniques based on the famous rotational-echo double-resonance (REDOR) technique, which can be quantitatively applied to the $^1$H–X case if sufficiently fast MAS (usually $\sim 30$ kHz) is used. It is particularly robust and easy to set up (only the 90° pulse length must be calibrated carefully), and the common denominator is that the signal modulation over a single rotor period in an indirect dimension, or the Fourier transform of its extension yielding a sideband spectrum, can be used to extract (motionally averaged) dipolar couplings. There are in fact many variants in this class of techniques, including the combination with indirect $^1$H detection for signal enhancement, and a particularly efficient SLF-type variant termed REREDOR. Schematic pulse sequences and sideband
The technique is an earlier variant of REPT-HDOR (Figure 9f), with interchanged 90° pulses flanking $t_1$ and an additional 180° pulse on $^{13}$C in the middle of $t_1$—it has additional (here unnecessary) $^1$H chemical shift information in $t_1$. For the given purpose, REREDOR (Figure 9b) is nowadays more recommendable. (a) Molecular structure of the HBC. (b) Schematic display of molecular stacking of HBCs. Each gray disc is a molecule as shown in (a). (c) The patterns are the sum projections over the core CH signals in the 2-D spectra of HBC-$n$-C$_{12}$H$_{25}$ and HBC Ph-$n$-C$_{12}$H$_{25}$, respectively. Experimental temperatures were 35°C or room temperature and 120°C for the high-temperature LC phases. The MAS spectra on top were recorded at a MAS rate of 12 kHz while for the REPT-HMQC experiments, 25 kHz was used. The inserts are simulated spectra. (d) Visualization of motional modes of a single disc in the stacks. While the HBC with the Ph-$n$-C$_{12}$H$_{25}$ side chains performs a rotation around an axis perpendicular to the plane of the molecule only, the one with the $-n$-C$_{12}$H$_{25}$ side chains appears to do an additional wiggle in the plane of the molecule. This was concluded from the reduced $^1$H-$^{13}$C coupling, which can be qualitatively inferred from the reduced intensity of the outer dipolar sidebands.
patterns due to the rotor modulation in the indirect dimension are shown in Figure 9. An instructive early application of the recoupled polarization-transfer-heteronuclear multiple-quantum correlation (REPT-HMQC) variant to a liquid-crystal system is presented in Figure 10. In the meantime, these experiments have found many further applications on complex organic solids. However, a comparison of these indeed user-friendly experiments with LG-CP demonstrated that the latter is in fact superior, since LG-CP benefits from the better signal intensity from larger rotors (no fast MAS required, so rotors larger than 2.5 mm can be used). In this way, more accurate dipolar coupling information can be obtained, however, at the expense of a more elaborate setup of the NMR experiment.

If the motional rate approaches the value of the dipolar coupling constant, the dipolar spectrum is no longer periodic with $T_R$, for the incoherent dynamic process interferes with the coherent MAS rotation and leads to a substantial broadening of the dipolar spectrum or an exchange decay of the signal in the indirect dimension, as it does in 1-D NMR spectra in the intermediate-motional regime. To the best of our knowledge, there has been no investigation of this issue so far, and filling this gap was the concern of recent work of the authors. To calculate the spectra, the A–W approach or its refinements can be used. More elaborate approaches that include the effect of the MAS rotation and the molecular reorientation are nowadays available. Likewise, the application of the numerical approaches to LG-CP is straightforward. We like to note that though these approaches are computationally demanding, they work for any motional model. In particular, they do not rely on the assumptions made for the A–W theory. In Figure 11, we show simulations for DIPSHIFT experiments on the basal carbon of imidazole for jump rates ranging from the static to the fast-limit case. When the jump rate approaches the values of the C–H dipolar coupling, a kind of dynamic $T^*_2$ appears, i.e., the value of the dipolar signal at $t_1 = T_R$ does not reach that at $t_1 = 0$, indicating the loss of periodicity of the signal. At jump rates close to $10^4$ Hz, the apparent dipolar coupling that can be related to the value of the signal at $t_1 = T_R/2$ starts to decrease, in concert with an increase of the apparent $T^*_2$. For convenience, these effects are parameterized in Figure 11(c) as $T^*_2 = I(T_R)/I(0)$ and $(\Delta \omega) = I(T_R/2)/I(0)$. A comparison between the numerical approach and the A–W theory can be found where simple analytical procedures based on the A–W approximation are presented. In order to establish limits of validity of the A–W based formulas, a comparison with spin dynamics simulations based on the solution of the stochastic Liouville-von-Neumann equation is presented. It is shown that at short evolution times (less than 30% of the rotor period) the A–W based formulas are suitable for fitting the DIPSHIFT curves and extracting kinetic parameters even in the case of jump-like motions. However, full spin dynamics simulations provide a
more reliable treatment and extend the frequency range of the molecular motions accessible by SLF experiments. Also, the effect of molecular motion on LG-CP (as shown by numerical simulations in Figure 12a) as well as on the important issue of CP efficiencies was investigated in this article. In particular, if cross-polarization is used as the excitation method, the presence of a distribution of motional correlation times leads to a bias in the fitted distribution because of the signal decay during the contact time (CT). This holds in particular for segments deep in the intermediate-motional regime (with rates of $\sim 10^4$ to $10^5$ Hz), which are suppressed in the resulting carbon spectrum, while segments with little (or fast but anisotropic) mobility are overrepresented (see Figure 12b).

We like to place a short comment here: although the DIPSHIFT experiment is more efficient in terms of experimental time, it seems to have difficulties when there is overlap of signals resulting from different molecular dynamics leading to different dipolar dephasings. In these cases, it appears difficult to separate the different contributions in the DIPSHIFT dephasing curves, since—at least in the fast limit when the signal is periodic with $T_R$—two components with differently averaged coupling can hardly be distinguished from a single component with an in-between coupling. In contrast, in LG-CP experiments, these components would appear in the dipolar dimension (in time domain) with different initial slopes and dipolar oscillations (or alternatively with different widths of the well-structured line shapes when a Fourier transform in $t_1$ is performed) and can easily be told apart.

6 DOUBLE-QUANTUM EXPERIMENTS

One alternative way of dealing with the complex coupling topology in abundant dipolar-coupled spin systems is the excitation of higher-quantum coherences (see Multiple Quantum Coherence in Spin-1/2 Dipolar Coupled Solids; Multiple Quantum Coherences in Extended Dipolar Coupled Spin Networks; Multiple Quantum NMR in Solids). Many applications in solid-state NMR were pioneered by Pines in the 1980s. The buildup of $DQ$ coherences in particular serves to extract information on the dipolar coupling between the two spins in question. Effects due to the time-dependent modulations of pair couplings were first reported for DQ experiments on $^{19}$F. Advances in NMR hardware recently paved the way for ultrafast MAS experiments with commercially available MAS rates of 35 kHz, and recently even up to 70 kHz. Such spinning rates, in combination with high fields, enable solid-state $^1$H experiments with considerably improved (as compared to wide-line experiments) but still limited spectral resolution. These MAS rates efficiently suppress the homonuclear dipolar interaction between more remote nuclei but affect those between next-neighbour nuclei much less. DQ–DQ exchange experiments select only those nuclei with nearby like spins and reveal spatial correlations between such spins. The precise value of the dipolar coupling that carries information on structure and, importantly, the geometry of fast motions, can reliably be extracted from DQ sideband intensities. DQ–MAS techniques proved particularly useful in characterizing the anisotropy of mesogenic molecules in liquid crystals, or fast-moving polymer chains in elastomers, polymer melts, and block copolymers. A number of applications of such experiments to different complex macro- and supramolecular systems has recently been reviewed. However, the limited resolution still leaves them far from being generally applicable methods—they are restricted to cases in which the molecular moiety in question is well resolved in the $^1$H MAS spectrum. Moreover, apart from a pioneering scaling analysis of the relationship between polymer chain dynamics and DQ intensities, DQ-MAS techniques have to date not been used to elucidate the actual timescale of fast-to-intermediate motions.

In relatively simple systems such as single-component polymer melts or elastomers, chemical selectivity is often not an important issue. Then, static DQ methods have in fact proven to be more quantitative with respect to the precise absolute determination of weak motionally reduced (residual) $^1$H–$^1$H dipolar couplings. The absence of complications due to the additional MAS timescale then even allows for a much simpler quantitative treatment of intermediate-motional effects in DQ experiments (in terms of Anderson–Weiss theory), and an application to chain dynamics in elastomers is described in Ref. 34.

7 DIPOLAR EXCHANGE NMR—SLOW MOTIONS

The slow motion regime (A) is commonly called the static case, i.e., although there might be an appreciable amount of molecular mobility, it is too slow to be observed in NMR spectra (‘it is slow on the NMR timescale’). Such dynamic processes can, however, be observed in so-called exchange experiments or specific NMR relaxation experiments. The application of the dipolar interaction in the framework of exchange experiments, i.e., the observation of the reorientation of a dipolar vector connecting two nuclei during time periods much longer than the lifetime of the FID and quantitative interpretation is in principle possible; however, it requires the existence of spin pairs, as otherwise, magnetization exchange processes (spin diffusion, etc.) dominate and severely restrict the dynamic range. This can be facilitated by isotopic labeling, inserting the desired spins into the molecules, or by experimental conditions that suppress multispin interactions. Such situations can be found—for example—in $^1$H-depleted substances where only few $^1$H spins are around, and the interaction between remote nuclei is further suppressed by very fast MAS. Experiments of the latter kind are in progress and will certainly be reported soon. The methodology of DQ experiments has been extended to DQ–DQ exchange experiments permitting the investigation of slow motion. Generally, applications of exchange-type experiments utilizing the dipolar coupling are rare and are thus not discussed here at length.

8 SUMMARY

Homo- and heteronuclear dipolar couplings belonged to the tool box of dynamic solid-state NMR from the early days of NMR. Owing to the progress in NMR hardware, the development progressed from low-resolution wide-line spectra via separated-local field experiments, employing
Fluxional Motion; Relaxation Effects of Chemical Exchange. Solids; Multiple Quantum Coherences in Extended Dipolar Dynamics and Order from Multidimensional Solid State NMR; Solid Organic Compounds: Intramolecular Motions; Polymer Dipolar and Indirect Coupling Tensors in Solids; Dynamics in 9 RELATED ARTICLES

2H NMR experiments, organic solids at natural isotopic abundance is still the exploration of the quadrupolar coupling in fast MAS. Although the most accurate NMR tool for dynamic studies is still the exploration of the quadrupolar coupling in 2H NMR experiments, organic solids at natural isotopic abundance are clearly most preferably studied by use of dipolar couplings.

9 RELATED ARTICLES

Dipolar and Indirect Coupling Tensors in Solids; Dynamics in Solid Organic Compounds: Intramolecular Motions; Polymer Dynamics and Order from Multidimensional Solid State NMR; Multiple Quantum Coherence in Spin-1/2 Dipolar Coupled Solids; Multiple Quantum Coherences in Extended Dipolar Coupled Spin Networks; Multiple Quantum NMR in Solids; Fluxional Motion; Relaxation Effects of Chemical Exchange.

10 REFERENCES

DIPOLAR COUPLING: MOLECULAR-LEVEL MOBILITY

Biographical Sketches

Detlef Reichert, b. 1960, Dipl. 1985 (Merseburg, East Germany), Ph.D. 1990 (Merseburg). Habilit. 2000 (Halle, Germany). The author was first involved with NMR when studying physics and polymers. After Ph.D. on 1H-NMR and polymers and post-doctoral studies with Z. Luz (Rehovot, Israel), he joined the solid-state NMR group in Halle and later the biophysics lab as a research fellow. He has published approximately 60 papers. His research interests include dynamic studies in organic solids.

Kay Saalwächter, b. 1970, Dipl. 1997 (Freiburg, Germany), Ph.D. 2000 (Mainz, Germany). Habilit. 2004 (Freiburg, Germany), Professor of Experimental Physics (Halle, Germany) since 2005. Since his first contact with solid-state NMR on an exchange visit to the University of Massachusetts (Amherst, USA) working with K. Schmidt-Rohr (now at Ames, Iowa), his continuing research interest is the development and application of NMR techniques to the study of structure and dynamics in polymeric, liquid-crystalline, and other 'soft' materials, which have been published in about 50 papers.