Nuclear spin quenching
A new probe of exchange kinetics and droplet size in disperse systems

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A new experimental technique, nuclear spin quenching (NSQ), is introduced, which can be used to measure droplet size and inter-droplet exchange rates of various intrinsic molecular species in disperse systems. The physical basis of the method is the quenching of the fine structure in spin-coupled N.M.R. spectra by intermolecular proton exchange, the rate of which is controlled by droplet exchange. The theoretical framework needed to interpret NSQ experiments is presented as well as an experimental case study on a water-in-oil microemulsion system. Being non-perturbing and having a large dynamic range, the NSQ technique should become a valuable complement to existing techniques for the study of structure and dynamics in disperse fluids.

1. Introduction

Disperse systems containing distinct regions of supramolecular extent are frequently encountered in nature and constitute the basis of numerous technological applications. Of particular importance are surfactant-stabilized fluid dispersions, such as microemulsions, which have been extensively studied in recent years. Not only do these systems have great technological potential, but they also constitute prototype models for more complex naturally occurring fluid systems. As such they have contributed substantially to the current understanding of molecular organization and dynamics in complex fluids.

Water-in-oil microemulsions are thermodynamically stable systems which, in many cases, consist of discrete aqueous droplets dispersed in a continuous oil medium. The structure of such systems, in particular the droplet size, has been thoroughly examined by a variety of experimental techniques [1–3].

Being fluid, microemulsions are highly dynamic systems in which molecular processes on a wide range of time scales take place. Of particular interest are the processes whereby water-soluble species exchange between the droplets, as they may control the transport properties and reaction kinetics in such disperse media. Droplet exchange kinetics in microemulsions has been studied mainly by fast-flow techniques using various fast chemical processes as exchange indicators [2–5] and by photophysical techniques based on the exchange-limited quenching of an excited probe [6–14].

In this report we introduce a new experimental technique, which we call nuclear spin quenching (NSQ), that can be used to determine exchange rates and droplet sizes in disperse systems. The physical basis of the NSQ method is the electron-mediated coupling between nuclear spins residing in molecules that can engage in
proton exchange [15]. In common with chemical relaxation methods and photo-
physical methods, the NSQ method exploits the fact that the rate of the underlying
process becomes limited by droplet exchange if the reactants (probe and quencher)
initially reside in different droplets. In contrast to existing methods, the NSQ tech-
nique is non-perturbing since it utilizes chemical species intrinsic to the investigated
system. Furthermore, by suitable choice of resonant nucleus, the exchange of many
different molecular species can be studied. Finally, the NSQ method has a wide
dynamic range. For these reasons, we expect NSQ to become a valuable com-
plement to existing techniques for the study of exchange kinetics and structure in
disperse fluids.

The outline of this paper is as follows. After introducing the phenomenon of
exchange-modulated nuclear spin coupling in §2, we consider in §3 the spin state
kinetics in a disperse system. The kinetic treatment includes two types of mechanism
for droplet exchange: molecular migration of probes and/or quenchers and droplet
coalescence. The manifestation of these dynamic processes in the observed spectral
lineshape is considered in §4, where we present formal results of general validity as
well as closed-form analytical lineshape expressions for the important case of spin
coupling to two equivalent protons. To illustrate the potential of the NSQ tech-
nique, we present in §5 the results of an experimental study of the Aerosol-OT/iso-
octane/water microemulsion system, including a determination of the coalescence
rate constant and the radius of the aqueous droplets.

2. Spin coupling and exchange

A nuclear spin I scalarly coupled to one or more nonequivalent (with respect to
I) spins S gives rise to an N.M.R. spectrum consisting of several absorption lines,
their splitting being given by the spin–spin coupling constant J. If the spin coupling
is modulated at a rate comparable to J, the multiplet structure is perturbed and, if
the rate is much larger than J, it reduces to a single lorentzian absorption line. In
this so-called motional narrowing limit, the broadening of the lorentzian line due to
rapid modulation of the spin coupling, referred to as scalar relaxation, may be
broadened by second-order perturbation theory. The modulation of the I–S spin coup-
lung can arise either from transitions among the Zeeman levels of the S-spin or from
chemical exchange; usually transfer of a proton from one molecule to another.
These are well-known facts, discussed at length in N.M.R. textbooks [15]. Our
concern here is with the effect on the I-spin lineshape of S-spin chemical exchange
and we assume that the S-spin longitudinal relaxation rate is small compared to the
spin coupling or to the exchange rate, so that it does not affect the lineshape.

In a homogeneous system, the I-spin lineshape, \( I_{\text{mf}}(\omega) \), is determined by the
intrinsic transverse relaxation rate, \( R_0 \) (usually due to electric quadrupolar or direct
magnetic dipolar couplings), by the proton exchange rate, \( r \) (excluding processes
where the same proton is transferred back and forth [16]), by the spin coupling
constant, \( J \), and by the statistical spin state populations, \( p_i \), \( i = 1, 2, \ldots, \sigma \) (given by
the degeneracies of the Zeeman eigenstates of the S-spin system). For an I-spin
coupled to \( N_S \) mutually equivalent S-spins, there are \( \sigma = 2N_S + 1 \) spin states. As
an example, consider an S-system comprising two equivalent spin-1/2 nuclei (as for
H₂O with \( I = ^{17}\text{O} \) and \( S = ^{1}\text{H} \)). Then \( \sigma = 3 \) and \( p_1 = p_3 = 1/4 \), \( p_2 = 1/2 \), so that
the slow-exchange spectrum is a 1:2:1 triplet. In the presence of proton exchange,
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the (complex) lineshape is given by [17]

\[
L_\text{H}(\omega) = \frac{(2\Gamma + r)(\Gamma + r) + J^2}{(2\Gamma + r)[\Gamma(\Gamma + r) + J^2]},
\]

(2.1)

with

\[
\Gamma = R_0 + i\omega.
\]

(2.2)

It is easily checked that this lineshape reduces to an unbroadened triplet for \( r \ll J, R_0 \) and to an unbroadened lorentzian for \( r \gg J^2/R_0 \). In the motional narrowing limit, i.e. to leading order in \( R_0 \) and \( J \), one obtains a lorentzian line whose width corresponds to a transverse relaxation rate

\[
R = R_0 + \frac{J^2}{r},
\]

(2.3)

the last term being ascribed to scalar relaxation of the first kind [15].

3. Spin state kinetics in disperse systems

We consider an equilibrium fluid system consisting of a large number of well-defined (on some time scale) droplets dispersed in a continuous medium. Contained within the droplet pseudo-phase are molecules, referred to as probes, carrying the observed \( I \) spin scalarly coupled to \( N_S \) mutually equivalent \( S \) spins, with either \( I \) or \( S \) being an exchanging proton (or deuteron) spin. Also confined to the droplets are prototropic ions or molecules which can exchange protons with the probe, thus modulating the \( I-S \) spin coupling. Since they have the capacity to quench the fine structure in the N.M.R. spectrum, we refer to these species as quenchers.

In a homogeneous system, the quenching (proton exchange) rate \( r \) is proportional to the total quencher concentration. In a disperse system, each droplet is characterized by a quenching rate \( r_n \), determined by the number \( n \) of quenchers per droplet (the quencher occupancy) and the size of the droplet. If the exchange of probes and/or quenchers between the droplets is fast compared to the quenching rates in all droplets, then the disperse system behaves as if it were homogeneous with a lineshape

\[
L(\omega) = L_\text{H}(\omega | \langle n \rangle),
\]

(3.1)

i.e. with a quenching rate determined by the average quencher occupancy \( \langle n \rangle \). If, on the other hand, both probes and quenchers exchange slowly compared to the spin coupling \( J \) and to the quenching rates in all droplets, then the spectrum is a population-weighted superposition of homogeneous-system lineshapes associated with droplets of different quencher occupancy

\[
L(\omega) = \sum_{n=0}^{\infty} f_n L_\text{H}(\omega | n),
\]

(3.2)

where \( f_n \) is the fraction of droplets (assumed to be of equal size) containing precisely \( n \) quenchers. In neither of these limits does the N.M.R. lineshape depend on the rate of exchange of probes and quenchers between the droplets; hence, only a lower or an upper bound for the droplet exchange rate can be deduced.
If the phase containing probes and quenchers is dispersed into large droplets, as in a typical emulsion with droplet dimensions of several \( \mu \text{m} \), then the relative variation in quencher occupancy among the droplets is small. Since a probe then experiences essentially the same environment in all droplets, it follows that droplet exchange, whatever its rate, has no effect on the N.M.R. lineshape. [In this case, \( f_n \) is sharply peaked at \( n = \langle n \rangle \), whence (3.2) becomes identical to (3.1).]

The situation becomes more complex (and interesting) if the droplets are smaller and, hence, contain fewer quenchers. In particular, if some droplets are free of quenchers, then droplet exchange becomes the rate limiting process which governs the N.M.R. lineshape. Since the mean quencher occupancy \( \langle n \rangle \) is proportional to droplet volume, there is a rather well defined upper limit for the linear droplet dimension where exchange control prevails. As an example, consider spherical aqueous droplets at neutral pH with H_3O^+ and OH^- as the only quenchers. Then \( \langle n \rangle \approx 500 \) for a droplet radius of 1 \( \mu \text{m} \), while \( \langle n \rangle \approx 0.5 \) for a radius of 0.1 \( \mu \text{m} \). In thermodynamically stable water-in-oil microemulsions, droplet dimensions are of order 10 nm or less, so that exchange control can always be achieved.

In a general treatment of spin-state kinetics in disperse systems, one must consider not only transitions among the \( \sigma \) spin states of the probe in each type of droplet (characterized by its particular quenching rate \( r_n \)), but also transitions between different types of droplets through inter-droplet transfer of probes and/or quenchers. For a system with multiple quencher occupancy, the kinetic scheme thus involves a large number of states and transitions. However, for many systems of interest, the kinetic scheme may be simplified to the extent that closed-form analytical expressions can be obtained.

Proton transfer reactions are fast chemical processes that usually approach the diffusion-limited rate [18]. Given the availability of quenchers, the spin state of the probe will therefore be efficiently randomized. A peculiar feature of chemical kinetics in (mono)disperse media is that only certain discrete reactant concentrations are allowed. For aqueous droplets of 10 nm radius, these concentrations are \((4 \times 10^{-4})n \text{ mol dm}^{-3}\), where \( n \) is the quencher occupancy. With a typical second-order rate constant for proton transfer of \( 10^{10} \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \), the corresponding permissible quenching rates are \( r_n = (4 \times 10^6)n \text{ s}^{-1} \). Now, in many systems of interest, the droplet exchange rate \( \lambda \), is much smaller than \( 10^6 \text{ s}^{-1} \), as is the quantity \( J^2/R_o \), i.e.

\[
r_n(n \geq 1) \gg \lambda, J^2/R_o.
\]  

When these conditions, referred to in the following as the fast quenching limit, are satisfied, we need to distinguish neither between droplets with one or more quenchers, nor between the individual spin states of probes residing in such droplets. As a consequence, the kinetic scheme involves only transitions among the \( \sigma + 1 \) states \( F_1, F_2, \ldots, F_\sigma \) and \( Q \), where \( F_i \) denotes a quencher-free droplet with the probe in spin state \( i \) and \( Q \) denotes all other droplets, where the spin coupling is averaged out by rapid quenching. Figure 1 shows the effective kinetic scheme for the case of \( \sigma = 3 \).

† The precise meaning of \( \lambda \) depends on the mechanism of probe and/or quencher exchange between droplets, as discussed in the following. At this stage, we regard \( 1/\lambda \) as a typical probe lifetime in a state with a nonzero quenching rate.
Figure 1. The kinetic scheme in the fast quenching limit for the case of three spin states.

Under certain conditions (see below), the kinetic description amounts to a specification of the rates $\lambda_{ij}$, $\lambda_{iq}$ and $\lambda_{qi}$ of the three types of transitions

$$F_i \xrightarrow{\lambda_{ij}} F_j,$$  \hspace{1cm} (3.4a)

$$F_i \xrightarrow{\lambda_{iq}} Q,$$  \hspace{1cm} (3.4b)

$$Q \xrightarrow{\lambda_{qi}} F_i.$$  \hspace{1cm} (3.4c)

Depending on the mechanism of droplet exchange, these transformations may proceed via intermediate configurations, not explicitly accounted for in our kinetic scheme. The probe may, for instance, temporarily reside in the continuous phase or it may reside in a fused droplet dimer of transient existence (see below). We assume that the probe residence time (and equilibrium population) in such intermediate configurations is insignificant compared to that in the $\sigma + 1$ recognized states. Furthermore, we assume that droplet exchange may be treated as a stationary Markov process: the probe executes an uncorrelated random walk among the $\sigma + 1$ states with time-independent transition probabilities. The Markov approximation is valid if droplet exchange involves a substantial kinetic barrier; otherwise a more elaborate kinetic treatment, incorporating re-encounter effects, is required.

Since all rates in (3.4) are controlled by droplet exchange, the quenching rate plays no further role in the theory. In other words: as long as the fast quenching approximation (3.3) is valid, the droplet exchange rate can be determined without precise knowledge of the quenching rates $r_n$. On account of (3.3), each transition in (3.4) involves a large number of proton exchanges. The transition rates therefore depend on spin state only through the statistical populations $p_i$, rather than on the probabilities of switching from one particular spin state to another when a single
proton is exchanged. Furthermore, the dependence on \( p_i \) must be of the form

\[
\lambda_{ij} = p_j \lambda_F, \quad (3.5\ a)
\]
\[
\lambda_{iQ} = \lambda_Q^{-}, \quad (3.5\ b)
\]
\[
\lambda_{Qi} = p_i \lambda_Q^{+}, \quad (3.5\ c)
\]

where the rates \( \lambda_F, \lambda_Q^{+} \) and \( \lambda_Q^{-} \) are independent of spin state.

Since the system is in equilibrium, the net flow must vanish for each step in the kinetic scheme (principle of detailed balance). Irrespective of the mechanism of droplet exchange, we must therefore have

\[
f \lambda_Q^{+} = (1 - f) \lambda_Q^{-}, \quad (3.6)
\]

where \( f \equiv f_0 \) is the fraction of quencher-free droplets.

To proceed further, we must specify the mechanism of droplet exchange. We shall discuss two kinds of mechanism: (i) molecular migration of probes or quenchers across the continuous phase, and (ii) droplet fusion–fission (coalescence–decoalescence). A detailed analysis of these two mechanisms in the context of fluorescence quenching has recently been given by Almgren et al. [12]. In systems with ionic or highly polar probes and quenchers dissolved in aqueous droplets dispersed in a nonpolar medium (as in water-in-oil microemulsions), the fusion mechanism is expected to be much more efficient than the migration mechanism [2–14, 19].

3.1. Molecular migration

In the migration mechanism, the spin state can be altered only when the probe resides in a Q-type droplet (since F-type droplets contain no quenchers). Transitions of the kind (3.4 a) are therefore forbidden, i.e. \( \lambda_F = 0 \). We consider first the case where only the probes are allowed to migrate. By assumption, the continuous phase contains a negligible fraction of the probes. Consequently, transfer from droplet to continuous phase (rather than the reverse) is rate-limiting, whence

\[
\lambda_Q^{+} = (1 - f) k_p^{-}, \quad (3.7\ a)
\]
\[
\lambda_Q^{-} = f k_p^{+}, \quad (3.7\ b)
\]

where \( 1/k_p^{-} \) is the mean residence time of a probe in a droplet (assumed independent of quencher occupancy).

For the case where only quenchers can migrate, we have the elementary processes

\[
(i\mid n) \xrightarrow{k_q^{\ast}} (i\mid n + 1), \quad (3.8\ a)
\]
\[
(i\mid n) \xrightarrow{nk_q^{-}} (i\mid n - 1), \quad (3.8\ b)
\]

where \( (i\mid n) \) denotes a droplet containing a probe in spin state \( i \) along with \( n \) quenchers. Equation (3.8 a) describes the entry of a quencher into a droplet; \( k_q^{+} \) is the associated second-order rate constant and \( c_q^{\ast} \) is the quencher concentration in the continuous phase. Equation (3.8 b) describes the escape of one out of \( n \) quenchers from a droplet. The associated rate constant is \( nk_q^{-} \), if we assume that the mean residence time, \( 1/k_q^{-} \), of a quencher in a droplet is independent of quencher occupancy. It follows from this assumption that the quenchers must be randomly distributed among the droplets. The fraction, \( f_n \), of droplets containing precisely \( n \)
quenchers is then given by the Poisson distribution

\[ f_n = \frac{\langle n \rangle^n}{n!} \exp \left( -\langle n \rangle \right), \]  

(3.9)

with a mean quencher occupancy

\[ \langle n \rangle = \frac{k_q^+ c_q}{k_q^-}. \]  

(3.10)

The desired transition rates can now be obtained from (3.6), (3.8) and (3.10) as

\[ \lambda_Q^+ = \langle n \rangle k_q^- \]  

(3.11a)

\[ \lambda_Q^- = \frac{\langle n \rangle f}{(1-f)} k_q^- \]  

(3.11b)

If multiple occupancy can be neglected (\( f \) close to 1), then (3.11) reduces to

\[ \lambda_Q^+ = (1-f)k_q^- \]  

(3.12a)

\[ \lambda_Q^- = k_q^- \]  

(3.12b)

This result is formally identical to (3.7) (with \( f \approx 1 \)), as expected from the symmetry between the two cases in the absence of multiple quencher occupancy. If both probes and quenchers are allowed to migrate, and if they do so independently of each other, then the total transition rates \( \lambda_Q^+ \) and \( \lambda_Q^- \) are obtained simply by adding (3.7) and (3.11).

### 3.2. Droplet coalescence

In the fusion–fission mechanism, inter-droplet transfer is achieved by coalescence of two droplets to form a fused dimer droplet. We assume that the mean dimer lifetime, \( 1/\lambda^* \), is short compared to the (monomeric) droplet lifetime, \( 1/\lambda \), but long compared to the diffusional mixing time, i.e.

\[ \lambda \ll \lambda^* \ll D_q/l^2, \]  

(3.13)

where \( l \) is the linear droplet dimension and \( D_q \) is the quencher diffusion coefficient. The fusion–fission mechanism presupposes a certain droplet size polydispersity, but, if \( \lambda^* \gg \lambda \), only a tiny fraction of the droplets need be fused at any time. The transitions among the \( \sigma + 1 \) states may then be regarded as instantaneous, i.e. fused droplets need not be explicitly incorporated into the kinetic scheme.

We make the reasonable assumption that the droplet lifetime \( 1/\lambda \) is independent of quencher occupancy. This implies that the quencher distribution is random and, if size polydispersity is neglected, given by (3.9). Provided also that diffusional mixing is complete \( (\lambda^* \ll D_q/l^2) \), the probability, \( \pi_{nm} \), of finding precisely \( m \) quenchers together with the probe in a droplet produced by fission of a dimer with \( n \) quenchers is given by the Bernoulli distribution

\[ \pi_{nm} = 2^{-n} \binom{n}{m}. \]  

(3.14)
The following elementary processes have to be considered in the fusion–fission mechanism

\[
(i | n) \xrightarrow{\lambda} (i | n + m)^*, \quad (3.15a)
\]
\[
(i | n) \xrightarrow{r_n} (j | n), \quad (3.15b)
\]
\[
(i | n)^* \xrightarrow{\lambda^*} (i | m), \quad (3.15c)
\]
\[
(i | n)^* \xrightarrow{r_{n^*}} (j | n)^*, \quad (3.15d)
\]

where the asterisk signifies a fused droplet. According to (3.15a, b), a droplet with \( n \) quenchers can either fuse with another droplet, with probability \( \lambda/(r_n + \lambda) \), or quench the probe, with probability \( r_n/(r_n + \lambda) \). Quencher-free droplets can, of course, only undergo fusion, whereas, according to (3.3), all other droplets (\( n > 1 \)) undergo quenching prior to fusion. According to (3.15 c, d), a dimer with \( n \) quenchers can either undergo fission, with probability \( \lambda^*/(r_{n^*} + \lambda^*) \), or quench the probe, with probability \( r_{n^*}/(r_{n^*} + \lambda^*) \). We shall consider only the limiting cases of fast (\( r_{n^*} \gg \lambda^* \)) or slow (\( r_{n^*} \ll \lambda^* \)) dimer quenching. In the latter case, quenching can occur only in state \( Q \); hence transitions of the type (3.4a) are forbidden (\( \lambda_F = 0 \)).

We now derive the transition rates in (3.5). According to (3.3) and (3.13), the dynamics is controlled by the coalescence rate \( \dot\lambda \). All transition rates are therefore proportional to \( \dot\lambda \). The proportionality factors, giving the fraction of all coalescence events that produce a given state, are obtained by summing over all pathways that connect the given states and ascribing to each pathway the proper statistical weight.

The transition \( F_i \rightarrow F_j \) involves the following sequence of elementary steps

\[
(i | 0) \xrightarrow{\lambda} (i | n)^* \xrightarrow{r_{n^*}} (j | n)^* \xrightarrow{\lambda^*} (j | 0). \quad (3.16)
\]

For the case of fast dimer quenching, we thus obtain

\[
\lambda_F = \lambda \sum_{n=1}^{\infty} f_n \pi_{n0} = f^{1/2}(1 - f^{1/2})\dot\lambda, \quad (3.17)
\]

where the last equality follows from (3.9) and (3.14). For intermediate dimer quenching rates (\( r_{n^*} \approx \lambda^* \)), the summand in (3.17) should be supplemented with the factor \( r_{n^*}/(r_{n^*} + \lambda^*) \).

The transitions \( F_i \rightarrow Q \) and \( Q \rightarrow F_i \) are independent of the quenching rate in the dimer. The former transition involves the sequence

\[
(i | 0) \xrightarrow{\lambda} (i | n)^* \xrightarrow{r_{n^*}} (j | n)^* \xrightarrow{\lambda^*} (j | m), \quad (3.18)
\]

whence

\[
\lambda_Q = \lambda \sum_{n=1}^{\infty} f_n \sum_{i=1}^{\sigma} p_i \sum_{m=1}^{\infty} \pi_{nm} = (1 - f^{1/2})\dot\lambda. \quad (3.19)
\]

The transition \( Q \rightarrow F_i \), finally, involves the sequence

\[
(j | m) \xrightarrow{\lambda} (j | n)^* \xrightarrow{r_{n^*}} (i | n)^* \xrightarrow{\lambda} (i | 0). \quad (3.20)
\]
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Summing over pathways as well as over initial 'microstates' \( (j|m) \), which occur in state \( Q \) with probability \( p_j f_m/(1 - f) \), we obtain

\[
\lambda_Q = \lambda \sum_{j=1}^{\sigma} p_j \sum_{m=1}^{\infty} \frac{f_m}{1 - f} \sum_{n=m}^{\infty} f_{n-m} \pi_{n0} = \frac{f}{1 + f^{1/2}} \lambda. \tag{3.21}
\]

As required, the rates in (3.19) and (3.21) satisfy the detailed balance condition (3.6).

### 3.3. Effect of droplet size

The transition rates \( \lambda_F, \lambda_Q^+ \) and \( \lambda_Q^- \) that govern the N.M.R. lineshape depend on an intrinsic exchange rate constant as well as on the overall concentration and distribution of quenchers. In the case of molecular migration, the intrinsic rate constant is \( k^+ \) or \( k^- \), whereas, for the fusion–fission mechanism, it is the second-order coalescence rate constant \( k_c \), usually defined through

\[
(3.22)
\]

where \( c_d \) is the droplet concentration. This relation may be regarded as a first-order expansion of \( \lambda \) in powers of \( c_d \); it is not expected to remain accurate when the volume fraction of droplets becomes large [12].

Since the lineshape depends on the concentration of quencher-bearing droplets, it contains information about droplet size as well as about exchange kinetics. As shown in §§3.1 and 3.2, the explicit dependence on droplet size enters through \( \langle n \rangle \), either directly as in (3.11) or via \( f = \exp (-\langle n \rangle) \), and, for the fusion–fission mechanism, also through \( c_d \). The explicit relation to the droplet volume \( v_d \) is revealed by expressing the mean quencher occupancy as

\[
\langle n \rangle = N_A c_q v_d, \tag{3.23}
\]

and the droplet concentration as

\[
c_d = \frac{\phi_d}{N_A v_d}. \tag{3.24}
\]

Here \( c_q \) is the quencher concentration in the dispersed pseudo-phase and \( \phi_d \) is the volume fraction of that phase, both being experimental variables. The intrinsic exchange rate constant can thus be determined from a single N.M.R. spectrum if \( c_d \) and \( v_d \) are known, while experiments at variable quencher concentration yield the exchange rate constant as well as the droplet size. (The intrinsic exchange rate constant may, of course, depend itself on droplet volume, as may \( R_0 \).)

For the fusion–fission mechanism, the lineshape contains information about droplet size only in the regime of multiple quencher occupancy. This follows from the fact that if \( f \) is very close to unity (i.e. if there is no multiple occupancy), then state \( Q \) does not contribute directly and the lineshape is governed by the transition rates \( \lambda_{ij} \) and \( \lambda_{iQ} \). From the preceding, it is seen that these rates are proportional to

\[
(1 - f) \lambda \approx \langle n \rangle \lambda = k_c c_q \phi_d, \tag{3.25}
\]

i.e. they are independent of droplet size.
4. N.M.R. lineshape

4.1. General case

Let $M(t)$ be the complex transverse magnetization in the rotating Larmor frame, normalized in such a way that

$$M(0) = 1.$$  \hspace{1cm} (4.1)

The N.M.R. lineshape is then given by [15]

$$L(\omega) = \int_0^{\infty} dt \exp(i \omega t) M(t),$$  \hspace{1cm} (4.2)

where $\omega$ is the frequency offset from the Larmor frequency, defined by the centre of the spectrum. Usually, the absorption-mode spectrum is recorded; this is given by the real part of $L(\omega)$. The normalization of the lineshape is

$$\int_{-\infty}^{\infty} d\omega L(\omega) = \pi.$$  \hspace{1cm} (4.3)

If the fast quenching approximation (3.3) is valid, the spin can reside in any of $\sigma + 1$ different states. The total transverse magnetization is then a sum over these states. In matrix notation

$$M(t) = \mathbf{1}^T \mathbf{M}(t),$$  \hspace{1cm} (4.4)

where $\mathbf{1}$ is a column vector with all elements equal to unity (superscript $T$ signifies transposition) and $\mathbf{M}$ is a column vector with elements $M_1, M_2, \ldots, M_\sigma, M_\varrho$.

Under certain conditions (see below), the magnetization vector $\mathbf{M}(t)$ obeys the equation of motion [15]

$$\frac{d}{dt} \mathbf{M}(t) = -[\mathbf{R} + i \mathbf{J} + \mathbf{K}] \mathbf{M}(t).$$  \hspace{1cm} (4.5)

The relaxation matrix is

$$\mathbf{R} = R_0 \mathbf{U},$$  \hspace{1cm} (4.6)

where $\mathbf{U}$ is the unit matrix of dimension $\sigma + 1$ and $R_0$ is the intrinsic transverse relaxation rate. It is assumed that $R_0$ is unaffected by the spin state dynamics, i.e. that the motions that are responsible for $R_0$ (usually rotational and translational diffusion of the probe molecule) are fast compared to droplet exchange and proton transfer. Furthermore, we assume that the intrinsic transverse relaxation is exponential, so that it can be described by a single relaxation rate. If this is not the case, (4.5) must be generalized so as to incorporate the coupled evolution of the $(\sigma + 1/2)$ odd-rank single-quantum coherences [15, 20]. The spin coupling matrix in (4.5) is given by

$$\mathbf{J} = J \text{diag} (\nu, \nu - 1, \ldots, -\nu, 0),$$  \hspace{1cm} (4.7)

where $J$ is the $I-S$ spin–spin coupling constant (rad s$^{-1}$) and $\nu = (\sigma - 1)/2 = N_s S$. It is assumed that $J$ is small compared to the difference between the Larmor frequencies of the $I$ and $S$ spins, so that the first-order perturbation treatment of the spin coupling, implicit in (4.5), is valid.
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The effect on the lineshape of droplet exchange is contained in the kinetic matrix \( K \) in (4.5). Its off-diagonal elements are given by the transition rates in (3.5) as

\[ K_{mn} = -\lambda_{nm}, \quad (4.8) \]

while the diagonal elements are obtained from the relation

\[ 1^T K = 0, \quad (4.9) \]

which simply states that the net flow out of any state vanishes at equilibrium.

The equation of motion (4.5) may be transformed to the frequency domain, where it reads

\[ \dot{M}(\omega) = [\Gamma U + iJ + K]M(\omega), \quad (4.10) \]

with \( \Gamma \) defined by (2.2) and

\[ \dot{M}(\omega) = \int_0^\infty dt \exp (i\omega t) \dot{M}(t). \quad (4.11) \]

The initial magnetization vector is

\[ M(0) = (p_1 f, p_2 f, \ldots, p_n f, 1 - f)^T, \quad (4.12) \]

where \( p_i \) is the statistical population of spin state \( i \) and \( f \) is the fraction of quencher-free droplets.

Combination of (4.2), (4.4), (4.10) and (4.11) now yields the lineshape

\[ L(\omega) = 1^T M(\omega) = 1^T [\Gamma U + iJ + K]^{-1} M(0). \quad (4.13) \]

The following limiting forms are obtained from (4.13)

\[ L(\omega | J = 0) = \frac{1}{R_0 + i\omega}, \quad (4.14a) \]

\[ L(\omega | f = 0) = \frac{1}{R_0 + i\omega}, \quad (4.14b) \]

\[ L(\omega | f = 1) = \sum_{n=1}^{\sigma} \frac{p_n}{R_0 + i(\omega + J_{nm})}, \quad (4.14c) \]

\[ L(\omega | K = 0) = fL(\omega | f = 1) + (1 - f)L(\omega | f = 0). \quad (4.14d) \]

In the motional narrowing limit, the lineshape (4.13) reduces to a lorentzian

\[ L(\omega) = \frac{1}{R + i\omega}, \quad (4.15) \]

where

\[ R = R_0 + R_{SC}. \quad (4.16) \]

The so-called scalar relaxation rate \( R_{SC} \) may be obtained by expanding (4.13) to leading order in \( \Gamma \) and \( J \) or, more directly, by using the conventional second-order perturbation theory of spin relaxation [15]. Using the latter approach, we derive in
the Appendix the following scalar relaxation rate (in the secular approximation)

\[ R_{SC} = \frac{1}{3} N_S S(S + 1)f \frac{J^2}{(\lambda_F + \lambda_Q^2)} . \]  

(4.17)

4.2. Two equivalent protons

We shall now derive the lineshape for an I-spin coupled to two equivalent protons. This is the case, for example, for the \(^{17}O\) resonance in \(H_2O\). The statistical populations of the \(\sigma = 3\) spin states are

\[ p_1 = \frac{1}{4}, \quad p_2 = \frac{1}{2}, \quad p_3 = \frac{1}{4}. \]  

(4.18)

The spin coupling matrix (4.7) is then

\[ J = J \begin{pmatrix} 1 & 0 & -1 & 0 \end{pmatrix} . \]  

(4.19)

The lineshape is obtained from (4.13) by solving the set of four coupled algebraic equations in (4.10), with the kinetic matrix constructed, according to (4.8) and (4.9), from the rates of the different transitions in the scheme shown in figure 1.

For the case of molecular migration of probes and/or quenchers, with transition rates according to § 3, we obtain the lineshape

\[ L(\omega) = \frac{f[\Gamma + (2 - f)k]A + (1 - f)B}{(\Gamma + f k)A - f(1 - f)k^2 A} , \]  

(4.20)

with

\[ A = 2[\Gamma + (1 - f)k]^2 + J^2 , \]  

(4.21 a)

\[ B = [\Gamma + (1 - f)k](A + J^2) , \]  

(4.21 b)

\[ k = k_p + \frac{\langle n \rangle}{(1 - f)} k_q . \]  

(4.22)

This result reduces correctly to the limiting forms (4.14). In the motional narrowing limit, (4.20) reduces to the lorentzian \((R_o + R_{SC} + i\omega)^{-1}\), with

\[ R_{SC} = \frac{f}{(1 - f) 2k} , \]  

(4.23)

in agreement with (4.17).

For the fusion–fission mechanism in the limit of fast dimer quenching, with transition rates as in § 3, we find

\[ L(\omega) = \frac{f[\hbar \Gamma + (2 - f)\hbar \lambda]A + (1 - f)\hbar B}{(\hbar \Gamma + f \hbar \lambda)A - f(1 - f)\hbar^{-1} \lambda^2 A} , \]  

(4.24)

with

\[ A = 2[\Gamma + (1 - f)\hbar \lambda]^2 + J^2 , \]  

(4.25 a)

\[ B = [\Gamma + (1 - f)\hbar^{-1} \lambda](A + J^2) + [\Gamma + (1 - f)\hbar \lambda]J^2 , \]  

(4.25 b)

\[ \hbar = 1 + f^{1/2} . \]  

(4.26)
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Equation (4.24) has the correct limiting behaviour, as in (4.14) and (4.15), with a scalar relaxation rate

\[ R_{SC} = \frac{f J^2}{(1 - f) 2\lambda}, \]

in agreement with (4.17).

For the case of slow dimer quenching, (4.24) remains valid, but (4.25) is replaced by

\[ A = 2[\Gamma + (1 - f)h^{-1}\lambda]^2 + J^2, \]  
\[ B = [\Gamma + (1 - f)h^{-1}\lambda](A + J^2). \]

The scalar relaxation rate becomes

\[ R_{SC} = \frac{fh J^2}{(1 - f) 2\lambda}. \]

In the absence of multiple quencher occupancy \((1 - f \ll 1)\), the lineshape (4.24) reduces to \(L(\omega) = A/B\). According to (3.25), (4.25) and (4.28), \(A\) and \(B\) then depend only on the overall quencher concentration in the dispersed pseudo-phase; hence, the lineshape is independent of droplet size.

5. An experimental case study

As an illustration of the NSQ technique, we present in this section the results of an experimental study of droplet exchange in a water-in-oil microemulsion. For this study, we chose the well-characterized microemulsion (L2) phase of the AOT/iso-octane/water system, which is known to consist of essentially spherical aqueous droplets coated by the surfactant AOT and dispersed in the continuous oil phase [1-3]. The probe was H2O, the 17O resonance of which was observed. The quenchers were H3O+ and a carboxylic acid formed by self-hydrolysis of a very small fraction of the AOT surfactant.

5.1. Methodology

AOT [Aerosol-OT, sodium bis(2-ethyl-hexyl)sulphosuccinate] from Sigma and iso-octane (2,2,4-trimethyl pentane, 99.9 per cent) from Aldrich were used without further purification. As a result of self-hydrolysis, the AOT contained a small amount (about 50ppm) of carboxylic acid and alcohol [21, 22]. The water was millipore filtered and enriched to 6 per cent in 17O. Microemulsion samples were prepared by weighing the three components into N.M.R. tubes (10mm diameter), which were then shaken to obtain clear homogeneous solutions.

The quencher concentration in the aqueous pseudo-phase was calculated from

\[ c_q = 10^{-\text{pH}^*} + 55.5 \frac{x_a}{x_w}. \]

The first term represents the concentration of added H3O+ in the aqueous pseudo-phase, with \(\text{pH}^*\) defined as \(-\log [(\text{mol added H}_3\text{O}^+ - \text{mol added OH}^-)/(\text{dm}^3 \text{H}_2\text{O in sample after addition})].\) (The contribution to \(c_q\) from self-dissociation of H2O is completely negligible in the investigated pH* range.) The second term in (5.1) is the concentration of carboxylic acid impurity in the aqueous pseudo-phase, with \(x_a = \text{mol acid/mol AOT}\) and \(x_w = \text{mol H}_2\text{O/mol AOT}\). The acid may be partly
dissociated, but this does not affect \( c_d \). We assume that the AOT molecule is incapable of exchanging protons with \( \text{H}_2\text{O} \) on the time scale \( 1/J \).

The quencher concentration was varied by adding (by weight) small amounts of HCl and NaOH solutions (made from Merck titrisol ampoules) of carefully determined pH. As a result of these additions, \( x_w \) varied by 10 per cent in the experiment. The consequent small variations in \( f \) and \( \lambda \) were accounted for in the data analysis by assuming spherical monodisperse droplets with a radius given by

\[
r_d = \alpha + \beta x_w. \tag{5.2}
\]

This linear relationship, suggested by simple geometrical considerations, is well established experimentally \([1-3]\). Since the variation of \( x_w \) is small, the parameters \( \alpha \) and \( \beta \) cannot be individually determined with precision from our data. In the following we therefore quote only \( r_d \) values (for \( x_w = 30 \)).

The droplet concentration was calculated from (3.24), with the volume fraction aqueous pseudo-phase based on the weighed sample composition, molar masses (444.6, 114.2 and 18.02 \( \text{g mol}^{-1} \) for AOT, iso-octane and \( \text{H}_2\text{O} \), respectively) and bulk densities (1.138, 0.692 and 0.998 \( \text{g cm}^{-3} \)). The investigated samples contained 4.81 \( \text{mol iso-octane/mol AOT} \) and had \( x_w \) values in the range 29.5-32.6. (This corresponds to an overall AOT concentration of 0.56-0.58 \( \text{mol dm}^{-3} \).) The coalescence rate \( \lambda \) and the mean quencher occupancy \( \langle n \rangle \) were calculated from (3.22)-(3.24), (5.1) and (5.2).

Oxygen-17 N.M.R. spectra were recorded on a Bruker MSL-100 spectrometer at a resonance frequency of 13.57 MHz. The probe temperature was maintained at \( 25.9 \pm 0.5^\circ \text{C} \). All measurements were performed within 10 hours of sample preparation; no time dependence (indicative of further AOT hydrolysis) could be detected on this time scale.

The \( \text{^{17}O} \) quadrupolar relaxation rate, \( R_0 \), was deduced from the linewidth of the (lorentzian) spectrum obtained from a double-resonance experiment, wherein the water protons were decoupled by continuous rf irradiation. The broadband decoupler power raised the sample temperature by less than 0-4\(^\circ \text{C} \). Since \( R_0 \) depends on droplet size [23], i.e. on \( x_w \), decoupled spectra were recorded at each pH* value. This was accomplished by alternately accumulating blocks of free induction transients with and without decoupling, thus ensuring that the sample temperature was the same in both cases. The \( R_0 \) values so obtained were in the range 311-327 s\(^{-1} \), which includes a small contribution from magnetic field inhomogeneity. Since the inhomogeneity broadening is present also in the undecoupled spectra, it is essentially cancelled out. By varying the decoupler power, we found that 0.7 W power was sufficient to achieve complete proton decoupling.

For the \( ^1\text{H}--^{17}\text{O} \) spin–spin coupling constant in \( \text{H}_2\text{O} \) we used the value \( J = 510 \text{ rad s}^{-1} \), which is known with a precision of 1–2 per cent [17].

### 5.2. Results and discussion

In analysing the experimental data, we assume that exchange of probes (\( \text{H}_2\text{O} \)) and quenchers (\( \text{H}_3\text{O}^+ \) and carboxylic acid) via droplet coalescence is much faster than via molecular migration through the oil phase. The validity of this assumption, which rests on the low solubility of probes and quenchers in the oil phase, has been confirmed for a variety of predominantly polar or ionic probes and quenchers [2–14, 18]. Furthermore, we assume that the fast quenching condition (3.3) is satis-
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Figure 2. Comparison of the experimental oxygen-17 lineshape at pH* 4.67 (solid) with (a) the best-fitting lorentzian and (b) with the theoretical lineshape according to (4.24)–(4.26).

fied (see below), so that the theoretical results of §4.2 are applicable. The lineshape is then determined by the four quantities $J$, $R_0$, $\lambda$ and $f$ (or $\langle n \rangle$). The experiment yields the lineshape $L(\omega)$ as a function of pH*. Using the theoretical lineshape expressions in §4.2 and the known values of $J$ and $R_0$, we can thus determine the coalescence rate constant $k_c$, the droplet radius $r_d$, and the fraction $x_a$ of hydrolysed AOT.

Due to the trace amounts of carboxylic acid present in the AOT, the quencher concentration in the aqueous pseudo-phase is about $10^{-4}$ mol dm$^{-3}$ in the pH range 5–9. If it were not for this impurity, the $^{17}$O spectrum would have been in the slow exchange limit (4.14d) in this pH range. Now, however, the fine structure has collapsed into a single line. In the most informative range of pH* < 5 (where $c_q$ can be varied), the lineshape is nearly lorentzian and, hence, may be characterized by a single parameter, conventionally chosen as the linewidth, $\Delta v_{1/2}$ (the full width at half amplitude). This is illustrated in figure 2(a), which shows the most non-lorentzian lineshape in the experimental series and the best-fitting lorentzian. As shown in figure 2(b), the theoretical expression (4.24) describes the lineshape quite well.

The observed $^{17}$O linewidths are shown in figure 3 as a function of pH*. At pH* < 2.5, there are virtually no quencher-free droplets, so that the lineshape is given by (4.14b) with a width $\Delta v_{1/2} = R_0/\pi$. As the quencher concentration is reduced, the linewidth increases nearly twofold and then levels off at pH* 5, where $c_q$ is dominated by carboxylic acid quenchers. The linewidth is most sensitive to droplet size in the range pH* < 3.5, where multiple quencher occupancy is important ($\langle n \rangle \gtrsim 0.5$), cf. §3.3, whereas it is most sensitive to the fraction $x_a$ of hydrolyzed AOT in the range pH* > 3.5, where carboxylic acid quenchers contribute substantially.

The solid curve in figure 3 was obtained from a fit according to the theoretical expressions (4.24)–(4.26), corresponding to the limit of fast dimer quenching, while the dashed curve was calculated from the motional narrowing approximation (4.27). Even though the deviation from lorentzian lineshape is small (cf. figure 2), the motional narrowing approximation is clearly inadequate so that the linewidth must be calculated from the full lineshape expression.
Figure 3. Oxygen-17 linewidth versus pH*. The solid curve is the result of a fit according to the theoretical expressions (4.24)-(4.26), while the dashed curve was obtained from (4.27) with the same parameter values.

The experimental data points were obtained from samples to which variable amounts of HCl and NaOH solutions had been added. As a consequence, we have two independent variables: pH* and x_w. It is therefore not meaningful to calculate linewidths at intermediate pH* values (where x_w is undefined). Hence the irregular appearance of the theoretical curves. The slight complication of the data analysis due to x_w variation (cf. § 5.1) could have been avoided by preparing samples with different c_q but with identical x_w.

The parameter values resulting from the fit shown in figure 3 are given in the first row of the table. An equally good fit was obtained for the case of slow dimer quenching, i.e. by using (4.28) instead of (4.25), but with slightly different parameter values (second row of the table). Our coalescence rate constants may be compared with the value $k_c = 8.1 \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$ obtained for the same microemulsion system by a fast-flow technique based on an electron transfer reaction [5]. It should be noted, however, that this value refers to somewhat different temperature (20°C rather than 26°C) and AOT concentration (0.1 rather than 0.57 mol dm$^{-3}$). Our

<table>
<thead>
<tr>
<th>Dimer quenching</th>
<th>pH* range</th>
<th>$k_c$ (10$^6$ dm$^3$ mol$^{-1}$ s$^{-1}$)</th>
<th>$r_d(x_w = 30)$ (nm)</th>
<th>$x_w$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast</td>
<td>2-5-4.7</td>
<td>6.4</td>
<td>7.4</td>
<td>45</td>
</tr>
<tr>
<td>Slow</td>
<td>2-5-4.7</td>
<td>8.7</td>
<td>8.2</td>
<td>54</td>
</tr>
<tr>
<td>Fast‡</td>
<td>2-5-3.4</td>
<td>9.9</td>
<td>7.6</td>
<td>—</td>
</tr>
</tbody>
</table>

† The experimental uncertainty in the deduced parameter values is estimated to ca. 10 per cent.
‡ Analysis restricted to samples with the hydronium ion as the dominant quencher species.
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droplet radii are significantly larger than the values of around 5 nm obtained previously (by other methods) for similar AOT-based microemulsions with \( x_w = 30 \) [24, 25].

We now return to the theory to check if the deduced parameter values are consistent with the approximations introduced to simplify the treatment. We consider first the fast quenching approximation (3.3). Since \( \lambda \approx 2000 \text{s}^{-1} \) and \( J^2/R_0 \approx 800 \text{s}^{-1} \), we require that \( r_n \gg 2000 \text{s}^{-1} \) for \( n \geq 1 \). For the investigated system, the quenching rate is given by

\[
r_n = k_h \hat{c}(n_h) + k_a \hat{c}(n_a),
\]

where \( k_h \) and \( k_a \) are the second-order rate constants for proton exchange between water and hydronium ion (h) or carboxylic acid (a). For a droplet radius of 7.4 nm, the quencher concentration within a droplet is \( \hat{c}(n) \approx n \times 10^{-3} \text{mol dm}^{-3} \).

The rate constants for proton exchange in the microemulsion droplets are not precisely known, but for an estimate we can use the values pertaining to bulk solutions. For proton exchange with \( \text{H}_3\text{O}^+ \) at 28°C, \( k_h = 7 \times 10^9 \text{dm}^3\text{mol}^{-1}\text{s}^{-1} \) [17], whence the first term in (5.3) becomes \( (7 \times 10^6)n_a \text{s}^{-1} \). The fast quenching approximation is thus valid with wide margin for droplets containing one or more hydronium ions.

Proton exchange between water and carboxylic acids takes place via a cyclic mechanism involving two water molecules with \( k_a \approx 10^6 \text{dm}^3\text{mol}^{-1}\text{s}^{-1} \) [26]. In a droplet containing \( n_a \) carboxylic quenchers (and no hydronium ions), the quenching rate is therefore \( n_a \times 10^3 \text{s}^{-1} \), indicating that the fast quenching approximation may not be valid for such droplets. If this is the case (as is also suggested by the linewidth behaviour in the neutral pH range), a more elaborate (but straightforward) theoretical treatment is required, in which the merged Q state is replaced by distinct states \( Q_i \) corresponding to the different spin states of the probe. With this extension of the theory, the NSQ technique may be used to determine the proton exchange rate in the droplets.

Since our aim here is merely to illustrate the potential of the NSQ method, we defer a more complete analysis of the data. An indication of the result of such an analysis can, however, be obtained simply by restricting the present analysis to data at \( \text{pH}^* < 3.4 \), where the quencher population is dominated by hydronium ions. In this manner we obtained the parameter values in the last row of the table, which are in close agreement (taking the temperature difference into account) with the aforementioned electron transfer results [5].

The assumptions (3.13) of negligible dimer population and of fast diffusional mixing imply that

\[
10^3 \ll \lambda^* \ll 10^7 \text{ s}^{-1},
\]

if the quencher diffusion coefficient is of the order \( 10^{-9} \text{m}^2\text{s}^{-1} \). The dimer fission rate \( \lambda^* \) is not precisely known, but a value of the order \( 10^5 \text{s}^{-1} \) seems likely [5], in which case (5.4) would be satisfied. It follows then that quenching occurs in dimers containing \( \text{H}_3\text{O}^+ \) but not in those containing carboxylic acid as the only quencher.

6. Conclusions

In the foregoing, we have presented and applied a new method, nuclear spin quenching (NSQ), for determining exchange rates and droplet sizes in disperse
systems. Most disperse systems of interest contain one or more molecular species that can act as probe or quencher in an NSQ experiment. In the case of aqueous droplets, the prototropic ions H$_3$O$^+$ and OH$^-$ are always present as quenchers and H$_2$O (or D$_2$O) as a potential probe. It is also possible to use surfactant molecules with prototropic headgroups as probes, in which case molecular migration may be of importance. Although the freedom to choose probe, quencher and resonant nucleus provides a variety of possibilities, it should be borne in mind that the NSQ method is limited to systems that contain some droplets in which the spin state lifetime of the probe is long compared to the inverse spin coupling. A less fundamental limitation is the sensitivity of the method to trace amounts of prototropic impurities.

In contrast to chemical relaxation methods, the NSQ experiment monitors fluctuations in an equilibrium system. If droplet exchange is diffusion-controlled, this difference can be of importance. Since the NSQ method does not rely on a high quencher occupancy, it can be used to study droplet exchange processes on a wide time scale; the only requirements being that $(1-f)^2\lambda$ (where $1/\lambda$ is the droplet lifetime, or the residence time of probe or quencher in the droplet) is of the same order of magnitude as the spin coupling $J$ (typically in the range 10–1000 rad s$^{-1}$) and that $\lambda$ is smaller than, or of the same order of magnitude as, the intra-droplet quenching rates $r_q$ (otherwise homogeneous solution kinetics obtains, cf. equation (3.1)). The possibility of measuring high exchange rates makes NSQ a valuable complement to stopped-flow techniques, which are limited to rates of the order $10^3$ s$^{-1}$ or less [5].

In contrast to photophysical techniques, the NSQ method exploits chemical processes that are intrinsic to the investigated system. Photophysical studies typically require bulky multivalent luminescent probes, which may significantly perturb the system [11, 13]. This complication is avoided in NSQ. The range of exchange rates $\lambda$ accessible with the luminescence quenching technique is determined by the intrinsic excited state decay rate $k_0$ and the intra-droplet quenching rate $k_q$. The NSQ analogues of these rates are the spin coupling $J$ and the proton exchange rate $r_p$, respectively. In fluorescence quenching studies, $k_0$ is typically of the order $10^6$ s$^{-1}$ or larger so that only relatively fast exchange processes can be studied. Since the spin coupling $J$ is always much smaller, NSQ does not suffer from this limitation.

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Appendix

Scalar relaxation of the first kind in the motional narrowing regime

If the rates of the spin state transitions are large compared to the spin–spin coupling which they modulate (motional narrowing limit), the lineshape is lorentzian, $(R + i\omega)^{-1}$, and the linewidth is given by $R = R_0 + R_{sc}$. The transverse scalar relaxation rate $R_{sc}$ may be obtained from the conventional second-order perturbation theory of spin relaxation starting from Liouville's equation of motion for the
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Evolution of the density operator under the semiclassical Hamiltonian

\[ H(t) = \hbar J \sum \psi(t) I_z S_z, \quad (A.1) \]

where \( \psi(t) \) is a random function which takes the values 1 or 0 depending on whether the reference \( I \)-spin is, or is not, spin-coupled to (resides in the same molecule as) the \( i \)-th \( S \)-spin. The sum extends over all \( S \)-spins in the system. Equation (A.1) is valid provided that the spin state transition rates are small compared to the difference between the Larmor frequencies of the \( I \)- and \( S \)-spins, so that only the secular part of the spin–spin coupling has to be retained. (This is usually the case if \( I \) and \( S \) correspond to different nuclear species.)

According to standard spin relaxation theory, the Hamiltonian (A.1) leads to the scalar relaxation rate [15]

\[ R_{SC} = \frac{1}{3} S(S + 1) J^2 \int_0^\infty dt \sum \langle \psi_i(0) \psi_i(t) \rangle. \quad (A.2) \]

The correlation function in (A.2) may be expressed as

\[ \langle \psi_i(0) \psi_i(t) \rangle = \langle \psi_i \rangle p(t), \quad (A.3) \]

where \( p(t) \) is the conditional probability that a given \( S \)-spin is coupled to the reference \( I \)-spin at time \( t \), if it is known to be so initially. Furthermore, it is clear that

\[ \sum_i \langle \psi_i \rangle = N_s, \quad (A.4) \]

where \( N_s \) is the number of \( S \)-spins coupled to an \( I \)-spin at any time (neglecting the duration of the actual exchange event). If only a fraction of the exchanging nuclei are magnetic (as in a mixture of oxygen isotopes with \( S = { }^{17}O \)), the the right-hand side of (A.4) should be multiplied by that fraction.

On combining (A.2)–(A.4), we obtain

\[ R_{SC} = \frac{1}{3} N_s S(S + 1) J^2 \tau, \quad (A.5) \]

where

\[ \tau = \int_0^\infty dt p(t) \quad (A.6) \]

is the mean time between events whereby a given \( S \)-spin is exchanged for a different one.

Consider first a homogeneous solution with proton exchange rate \( r \). Since \( 1/r \) is the mean time between events whereby any one of the \( N_s \) \( S \)-spins in the molecule is exchanged for a different one, we have

\[ \tau = \frac{N_s}{r} \quad (A.7) \]

and, with (A.5),

\[ R_{SC} = \frac{1}{3} N_s^2 S(S + 1) \frac{J^2}{r}. \quad (A.8) \]

The special case of (A.8) with \( N_s = 1 \) is given in Abragam’s book [15]. For the case \( N_s = 2 \) and \( S = 1/2 \), (A.8) yields \( R_{SC} = J^2/r \), in agreement with (2.3).
In a disperse system, there are environments with different proton exchange rates. In the fast quenching limit (3.3), we need distinguish only two environments: a fraction $f$ of $I$-spins reside in droplets with no proton exchange, and a fraction $1 - f$ in droplets with fast (compared to $\tau$) proton exchange. Consequently,

$$\tau = \frac{f}{(\lambda_F + \lambda_Q)^{-1}},$$

(A 9)

where $(\lambda_F + \lambda_Q)^{-1}$ is the mean residence time of an $I$-spin in a quencher-free droplet. (Note that an exchange event now involves all $N_S S$-spins.) Combination of (A 5) and (A 9) yields the desired result, equation (4.17).

References
