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Double PGSE NMR with Stimulated Echoes: Phase Cycles for the Selection of Desired Encoding

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When two pairs of position-encoding pulses are used in a pulsed gradient spin echo (PGSE) NMR experiment, it is possible to examine velocity fluctuations. The one-dimensional version of double PGSE NMR uses identical pulse pairs whose amplitudes are stepped simultaneously. In the two-dimensional version (VEXSY) the pulse pairs are stepped independently, resulting in a velocity exchange spectrum. A key limitation in such experiments is transverse relaxation, so that stimulated echoes are often used as the method of choice. It is shown here that the use of stimulated echoes results in a superposition of signals arising from different magnetization pathways such that the spin phases may reflect both the sum and difference of displacements over the pulse pair encoding times, as well as the displacement over the exchange time between the pulse pairs. A phase cycle scheme that selects desired encodings as required is demonstrated.

INTRODUCTION

Pulsed gradient spin echo NMR (*1, 2*) is used to measure translational displacements of spin-bearing molecules over the duration between two gradient pulses. Each of these pulses produces a local phase shift in the transverse magnetization, which depends on the nuclear spin position. Because the two pulses are organized to produce opposite shifts, the cumulative effect of the spin pair is to produce a phase difference proportional to the change in position, i.e., displacement.

The basic PGSE NMR pulse sequence is shown in Fig. 1a. A gradient pulse of duration δ and amplitude $\mathbf{G}$ causes a local dephasing for a spin isochromat as position $\mathbf{r}$ by an angle $\phi = \gamma\delta\mathbf{G}.\mathbf{r}$, leading to a phase factor $\exp(i\phi)$. In the sequence shown in Fig. 1a, we will assume that the magnetic field gradient is applied along some particular axis of the sample (say the z axis) and that the amplitudes of the two gradient pulses are given by $G_{1,1}$ and $G_{1,2}$. Assuming the narrow gradient pulse approximation ($\delta \ll \Delta$), and labeling the position of a particular spin at the time of the two gradient pulses as z_1 and z_2 respectively, the net result of the spin echo sequence (neglecting relaxation effects) is to induce a phase shift, for that spin isochromat, of $\exp(i\gamma\delta[-G_{1,1}z_1, + G_{1,2}z_2])$, or in a simpler shorthand, $\exp(i[-\phi_{1,1} + \phi_{1,2}])$. The subtraction of phases is essential to the echo formation and leads to cancelation of precessions due to chemical shift effects and field inhomogeneities. In the standard PGSE NMR experiment $G_{1,1}$ and $G_{1,2}$ are set to be identical in value (G), so that there will also be a cancelation of phase shifts due to the mean spin position. Only the change in position, $Z = -z_1 + z_2$, over the duration Δ leads to a phase term and this may be written as $\exp(i\gamma\delta GZ)$.

It is conventional to regard the effect of the two pulses as defining a scattering wavevector (*2*), $q = (2\pi)^{-1}\gamma G\delta$. The normalized echo attenuation is related to the spin displacements Z_1 (parallel to the gradient direction) that take place over the duration Δ between the gradient pulses as

$$E(q) = \langle \exp(i2\pi qZ)\rangle. \qquad [1]$$

The ensemble average $\langle\cdots\rangle$ is precisely the integral of the phase factor $\exp(i2\pi qZ)$ weighted by the probability density for displacement over the time Δ, namely the average propagator $\bar{P_s}(Z, \Delta)$. Thus E is the Fourier transform of $\bar{P_s}(Z, \Delta)$ and this propagator can in principle be reconstructed by measuring E over a range of q values and performing an inverse FT.

In double PGSE NMR (*2, 3*), a second pair of PGSE gradient pulses is applied at a later time (along the same encoding axis) to the same transverse magnetization. The result is to add a second phase difference arising from the later displacement. Four separate phase encodings arise from the four different gradient pulses, $G_{1,1}$, $G_{1,2}$, $G_{2,1}$, and $G_{2,2}$. The choice of main subscripts 1 and 2 is based on a labeling that corresponds with the index of the RF pulse(s) around which the gradient pulse pairs are grouped, as apparent in Fig. 1 and where the RF pulse(s) associated with the mixing period have phase α_{m}.

We will distinguish these phases by $\phi_{1,1}$ to $\phi_{2,2}$ and the two phase differences of interest are $\phi_{1,2} - \phi_{1,1}$ and $\phi_{2,2} - \phi_{2,1}$. The corresponding q and Z values associated with these differences are q_1 and q_2 and Z_1 and Z_2. The basic double PGSE NMR pulse sequence is shown in Fig. 1b. The resultant echo has the normalized amplitude

$$E(q_1, q_2) = \langle \exp(i2\pi q_1Z_1 + i2\pi q_2Z_2)\rangle. \qquad [2]$$

In the case that the two pulse pairs have their q values varied entirely independently, a 2-dimensional data acquisition

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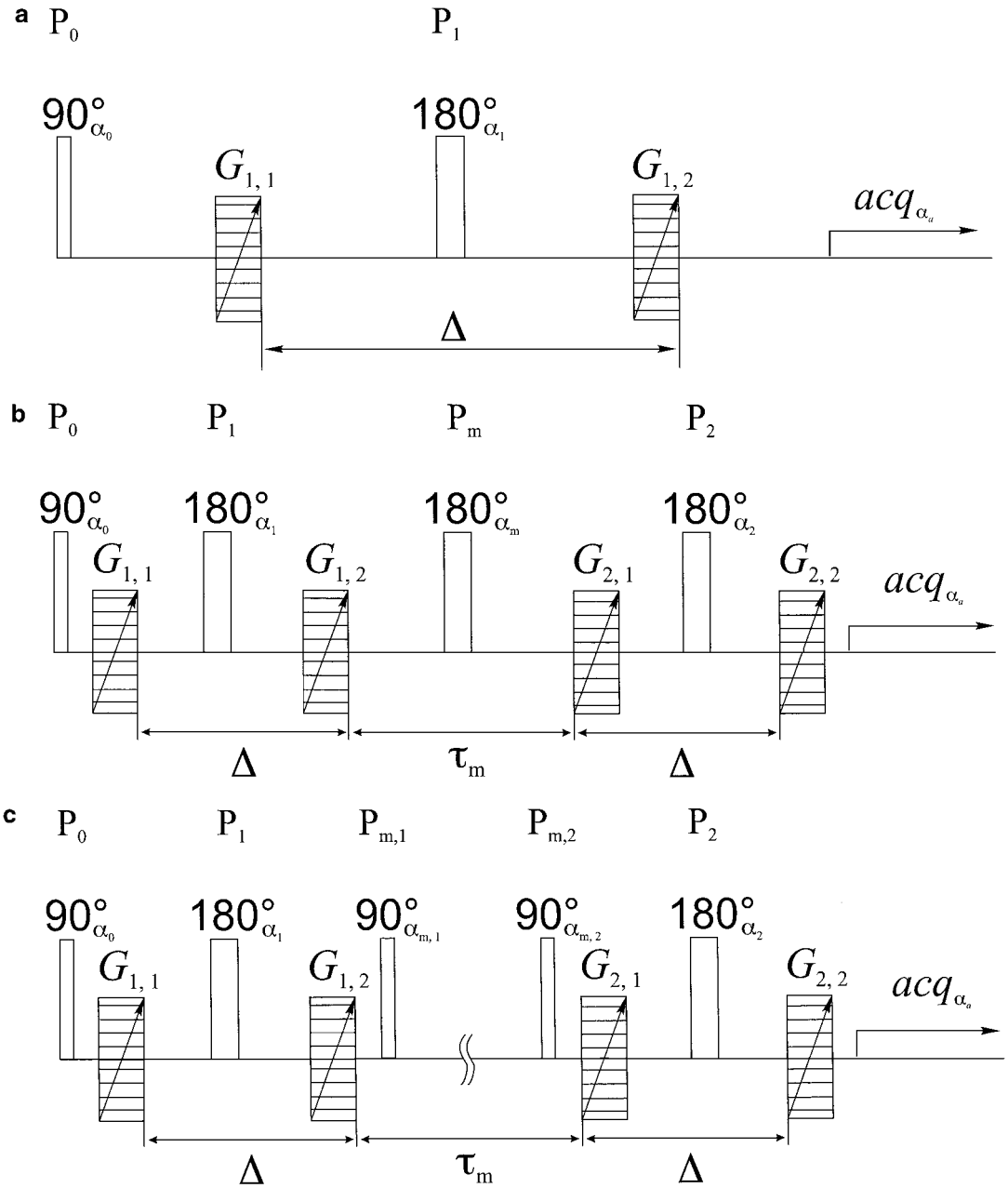

FIG. 1. (a) Schematic RF and gradient pulse sequence for a simple PGSE NMR experiment in which the gradient pulse area ($G\delta$) is stepped. (b) Schematic RF and gradient pulse sequence for a general double PGSE NMR experiment in which the gradient pulse areas ($G\delta$) are stepped either in unison/anti-unison or independently. Here, the 90°–$G_{1,1}$–180°–$G_{1,2}$–τ_m/2–180°–τ_m/2–$G_{2,1}$–180°–$G_{2,2}$–acq version is shown. In the 1-D version $G_{1,1} = \pm G_{1,2} = G$, depending on whether compensated or uncompensated phase addition is required. In the 2-D version (VEXSY), G_1 and G_2 are stepped independently. The corresponding phase cycle is given in Table 1. (c) The same as for (b), but for the 90°–$G_{1,1}$–180°–$G_{1,2}$–90°–τ_m–90°–$G_{2,1}$–180°–$G_{2,2}$–acq version in which z storage is used for the mixing period. The corresponding phase cycle is given in Table 2. (d) The same as for (b), but for the 90°–$G_{1,1}$–90°–90°–$G_{1,2}$–τ_m/2–180°–τ_m/2–$G_{2,1}$–90°–90°–$G_{2,2}$–acq version in which z storage is used for the encoding period. The corresponding phase cycle is given in Table 3. (e) The same as for (b), but for the 90°–$G_{1,1}$–90°–90°–$G_{1,2}$–90°–τ_m–90°–$G_{2,1}$–90°–90°–$G_{2,2}$–acq version in which z storage is used for the encoding and mixing periods. The corresponding phase cycles are given in Tables 4 and 5.

results. This method is known as velocity exchange spectroscopy (VEXSY) (*4*) and generates a 2-dimensional data set $E(q_1, q_2)$ as given by Eq. [2]. Double Fourier transformation with respect to q_1 and q_2 returns the two-dimensional Fourier spectrum $\bar{P}_s(Z_1, \Delta)P(Z_1, \tau_m|Z_2, \Delta)$, where $P(Z_1, \tau_m|Z_2, \Delta)$ gives the conditional probability that a molecule that moved by Z_1 over the time delay Δ will displace by Z_2 over Δ when this latter measurement is made after the delay τ_m. VEXSY may

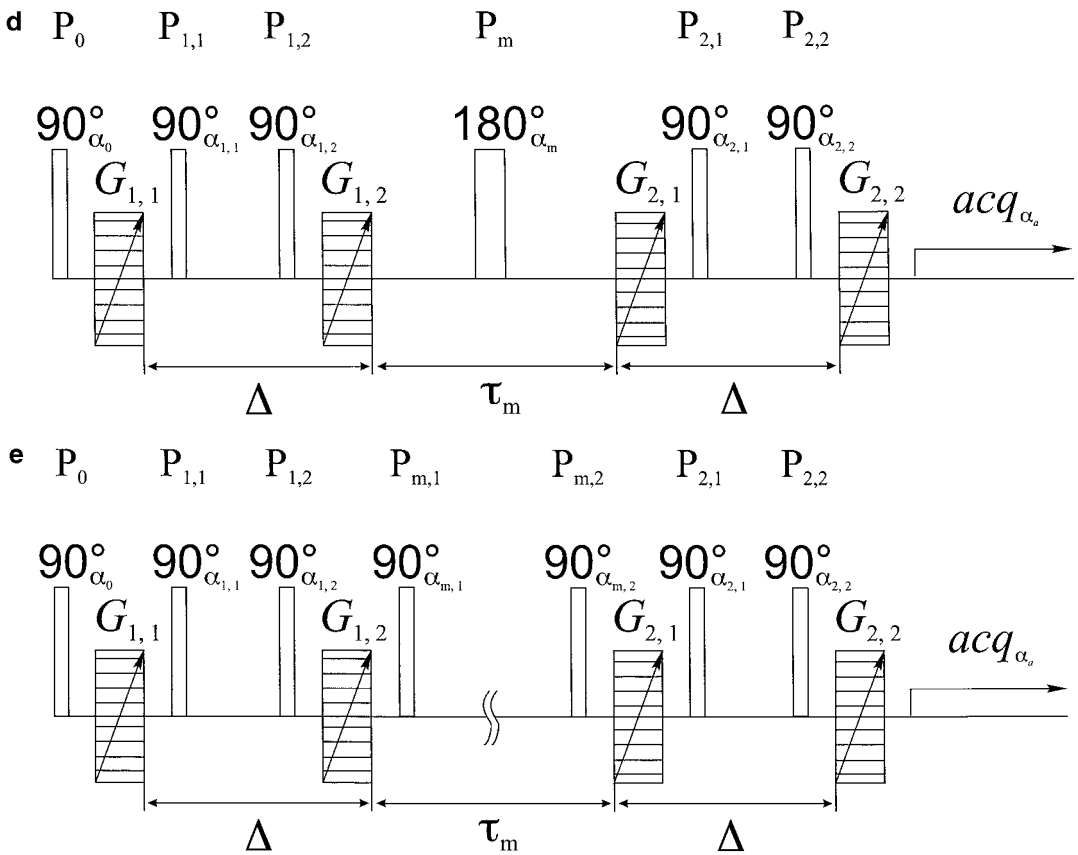

FIG. 1—*Continued*

be used to examine how the distribution of velocities during flow, changes over a well-defined timescale (*4*). In that sense τ_m plays the part of an exchange or mixing time, in the manner of a classical 2-dimensional NMR experiment (*5*).

In the case that the two pulse pairs have their q values linked, a 1-dimensional data acquisition results. We shall call this approach 1-dimensional double PGSE NMR. Clearly q_1 and q_2 may be varied in either unison ($q_1 = q_2 = q$) or anti-unison ($q_1 = -q_2 = q$) with each other. The more interesting encoding is anti-unison, and the resulting experiment, known as compensated double PGSE NMR, results in a net phase shift due to fluctuations in the motion over the evolution (or "exchange") time τ_m between the pulse pairs, by virtue of its use of dual phase encoding in an opposite sense. Now the echo amplitude is given by

$$E(q) = \langle \exp(i2\pi q[Z_1 - Z_2]) \rangle. \qquad [3]$$

This compensated double PGSE NMR sequence gives information about the change in displacements, $Z_1 - Z_2$. This 1-D sequence has a number of important uses. First, it can be used to measure stochastic motion such as dispersion or self-diffusion, without the confounding effects of a superposed heterogeneous flow, such as may occur during shear flow (*6,7*) or convection (*8–10*). Second, it can be used to distinguish stationary random flow from pseudo diffusion (*2*). Third it may be used to probe fluctuations in the velocity field over the well-defined mixing time (*3, 7, 8, 11*). And finally it may be used to directly measure the velocity auto-correlation function in a fluctuating velocity field, such as may occur during flow in porous media (*12*).

It is not the purpose of this article to review these applications, which in fact are described in detail elsewhere (*2, 3, 6–13*). Rather it is to make clear some important practical details regarding the successful implementation of these methods. In particular, because the double encoding relies on recycling the same transverse magnetization, ideally over the widest range of possible exchange times τ_m, it is necessary to minimize the effects of T_2 relaxation. One effective means of achieving this is to use stimulated echoes rather than spin echoes, wherever possible. Both the encoding intervals Δ can be built around the stimulated echo and the exchange time, τ_m, can utilize "z-storage" in which the encoded magnetization is protected from transverse relaxation by storage along the longitudinal axis. The pulse sequence is shown in Fig. 1e. We have found that the use of such pulse schemes leads to a complex superposition of differently encoded magnetization and that great care is needed with phase cycling if the desired result is to be achieved. In what follows we detail the magnetization pathways and demonstrate the suggested phase cycles.

ENCODING SELECTION IN DOUBLE PGSE NMR

In order to follow the evolution of the magnetization during the various PGSE NMR pulse sequences considered here, we develop a simple formalism based on the complex number approach. Magnetization in the transverse plane of the rotating reference frame will be treated as a complex number in which the y axis is the real part and the negative x axis the imaginary. Executing a pulse sequence involves manipulation of the phase factors.

We need now to understand the role of the RF pulses and their phases, as well as the role of the gradient pulses. In the following description relaxation effects are ignored and the absolute amplitude of the initial magnetization is set to unity. We will take the initial excitation pulse to be a 90° pulse of x-phase, generating real magnetization along the y axis. Following the first 90° RF excitation pulse, a gradient pulse is applied. This gradient pulse causes a local dephasing for a given spin isochromat, corresponding to position $\mathbf{r}$ within the sample, which can be described by a phase factor $\exp(i\phi)$ where $\phi = \gamma\delta\ \mathbf{G}.\mathbf{r}$ as mentioned previously.

Next, we will be concerned with understanding the effect of subsequent 180° and 90° pulses on a particular spin isochromat whose transverse magnetization is given by a phase factor $\exp(i\phi)$. A 180°_x pulse results in the transformation $\exp(i\phi) \Rightarrow -\exp(-i\phi)$ while a 180°_y pulse yields $\exp(i\phi) \Rightarrow \exp(-i\phi)$. Stimulated echoes utilize 90°_x and 90°_y pulses and leave the desired magnetization along the (longitudinal) z axis for storage and subsequent recall. The component being transferred to the z axis depends on the phase of the 90° pulse. In all that follows we will assume that the residence time of the stored magnetization is sufficient that the transverse magnetization remaining during the storage interval is "homospoiled." That is, it will be dephased sufficiently that it will no longer contribute to the subsequent NMR signal.

Let us consider various 90° pulse pairs applied for storage and recall. In the following two examples, the pulse pairs are applied to a *preexisting* transverse magnetization given by $\exp(i\phi)$.

(a) $(90^\circ_x\text{–}\tau\text{–}90^\circ_x)$

The first 90°_x pulse stores the real part of $\exp(i\phi)$ as z magnetization. The second 90°_x pulse returns the stored magnetization to lie along the negative real axis.

Net result: $\exp(i\phi) \Rightarrow -\cos(\phi) = -0.5\{\exp(i\phi) + \exp(-i\phi)\}$.

(b) $(90^\circ_y\text{–}\tau\text{–}90^\circ_y)$

The first 90°_y pulse stores the imaginary part of $\exp(i\phi)$ as z magnetization. The second 90°_y pulse returns the stored magnetization to lie along the negative imaginary axis.

Net result: $\exp(i\phi) \Rightarrow -i\sin(\phi) = -0.5\{\exp(i\phi)+\exp(-i\phi)\}$.

Next we consider some simple pulse sequences.

(c) Single PGSE NMR with Spin Echo:
$90^\circ_{\alpha_0}\text{–}G_{1,1}\text{–}180^\circ_{\alpha_1}\text{–}G_{1,2}\text{–}acq_{\alpha_a}$

Implicit in this notation is a displacement-encoding period, Δ, encompassed by the time between the two gradient pulses, $G_{1,1}$ and $G_{1,2}$, as shown in Fig. 1a. The initial 90° pulse has phase, α_0, denoted X and generates real (in-phase) magnetization. The first gradient pulse induces a phase shift given by $\exp(i\phi_{1,1})$. The acquisition phase, α_a, is set to give a real signal for y magnetization. In other words, it is coincident with the phase of the first 90° pulse and denoted as X.

$$\text{For } \alpha_0 = X, \alpha_1 = Y, \alpha_a = X.$$
$$\text{Final phase factor:} -\exp(i[-\phi_{1,1} + \phi_{1,2}]).$$
$$\text{Ensemble average:} \langle\exp(i2\pi qZ)\rangle.$$

(d) Single PGSE NMR with Stimulated Echo:
$90^\circ_{\alpha_0}\text{–}G_{1,1}\text{–}(90^\circ_{\alpha_{1,2}}\text{–}90^\circ_{\alpha_{1,2}})\text{–}G_{1,2}\text{–}acq_{\alpha_a}$

Here the brackets indicate a period of z storage, where a 180° pulse of a spin echo has been split into two 90° pulses. Again, a displacement-encoding period, Δ, is encompassed by the time between the two gradient pulses, $G_{1,1}$ and $G_{1,2}$, as shown in Fig. 1b and the initial 90° pulse has phase, α_0, denoted X and generating real (in-phase) magnetization. The first gradient pulse again induces a phase shift given by $\exp(i\phi_{1,1})$ and the acquisition phase, α_a, is set to give a real signal for y magnetization and denoted X. It is assumed that sufficient duration exists between the z-storage pulses that homospoiling of residual transverse magnetization results.

$$\text{For } \alpha_0 = X, \alpha_{1,1} = Y, \alpha_{1,2} = Y, \alpha_a = X.$$
$$\text{Final phase factor: } 0.5\exp(i[-\phi_{1,1} + \phi_{1,2}]) - 0.5\exp(i[\phi_{1,1} + \phi_{1,2}]).$$
$$\text{Ensemble average: } 0.5\langle\exp(i2\pi qZ)\rangle.$$

In both the spin echo and simulated echo PGSE NMR examples, the final echo signal is an ensemble average of all phase factors, $\langle\exp(i\phi)\rangle$. Consequently terms such as $\exp(i[\phi_{1,1} + \phi_{1,2}])$, in which the phases due to local position add, lead to a wide phase spread and a zero contribution to the echo, whereas terms such as $\exp(i[-\phi_{1,1} + \phi_{1,2}])$, where phases due to local position subtract, lead to echo components whose phase spread depends on the displacements that occur over the duration between the gradient pulses $G_{1,1}$ and $G_{1,2}$. Where the amplitude of $G_{1,1}$ and $G_{1,2}$ are set to be equal, such terms lead to the standard result, $\langle\exp(i2\pi qZ)\rangle$.

(e) Double PGSE NMR with Spin Echo:
$90^\circ_{\alpha_0}\text{–}G_{1,1}\text{–}180^\circ_{\alpha_1}\text{–}G_{1,2}\text{–}\tau_m/2\text{–}180^\circ_{\alpha_m}\text{–}\tau_m/2\text{–}G_{2,1}\text{–}180^\circ_{\alpha_2}\text{–}G_{2,1}\text{–}acq_{\alpha_a}$

Again, a displacement-encoding period, Δ, is encompassed by the time between the two gradient pulses, $G_{1,1}$ and $G_{1,2,}$ as

shown in Fig. 1b and the initial 90° pulse has phase, α_0, denoted X and generating real (in-phase) magnetization. The purpose of the mixing time τ_m is to allow the system to evolve so that the subsequence displacement measurement using the $G_{2,1}$ and $G_{2,2}$ pulses can be compared with the first. This mixing time is divided into two periods of $\tau_m/2$ so that an interleaved 180° pulse can be used to refocus unwanted dephasing due to chemical shift or field inhomogeneities. Again, the acquisition phase is tied to the first RF pulse. Later we will consider the effect of altering this phase setting.

For $\alpha_0 = X, \alpha_1 = Y, \alpha_m = Y, \alpha_2 = Y, \alpha_a = X$.

Final phase factor: $\exp(i[-\phi_{1,1} + \phi_{1,2} - \phi_{2,1} + \phi_{2,2}])$.

Ensemble average: $\langle \exp(i2\pi[q_1 Z_1 + q_2 Z_2]) \rangle$.

Again, $G_{1,1}$ and $G_{1,2}$ are set to be equal so that $-\phi_{1,1} + \phi_{1,2}$ corresponds to $2\pi q_1 Z_1$ where Z_1 is the displacement over the first encoding period. Similarly where $G_{2,1}$ and $G_{2,2}$ are set to be equal, $-\phi_{2,1} + \phi_{2,2}$ corresponds to $2\pi q_2 Z_2$ where Z_2 is the displacement over the second encoding period.

(f) Double PGSE NMR with Stimulated Echoes:
$90^\circ_{\alpha_0}$–$G_{1,1}$–$90^\circ_{\alpha_{1,1}}$–$90^\circ_{\alpha_{1,2}}$–$G_{1,2}$–τ_m–$90^\circ_{\alpha_{m.1}}$–$90^\circ_{\alpha_{m.2}}$–$G_{2,1}$–$90^\circ_{\alpha_{2,1}}$–$90^\circ_{\alpha_{2,2}}$–$G_{2,1}$–acq_{α_a}

Here the 180° pulses of the pure spin echo version of example (e) have been split into 90° pulse pairs. Again, the brackets indicate a period of z storage. This pulse sequence, which consists of a combination of stimulated echo and z storage, is shown in Fig. 1e. It is especially useful as it minimizes exposure of the magnetization to transverse relaxation. Figures 1c and 1d show variants in which a combination of spin and stimulated echoes are used. In each case it is assumed that sufficient duration exists between these pulses that homospoiling of residual transverse magnetization results.

Here the behavior is much more complex. Retaining only those terms that survive ensemble averaging, i.e., those where the mean positions cancel, we have:

$$\text{For } \alpha_0 = X, \alpha_{1,1} = X, \alpha_{1,2} = X, \alpha_{m,1} = X, \alpha_{m,2} = X, \alpha_{2,1} = X, \alpha_{2,2} = X, \alpha_a = X.$$

Final ensemble-averaged phase factor:

$$\left(\frac{1}{8}\right)[-\langle \exp(i[-\phi_{1,1} + \phi_{1,2} - \phi_{2,1} + \phi_{2,2}]) \rangle - \langle \exp(i[\phi_{1,1} - \phi_{1,2} - \phi_{2,1} + \phi_{2,2}]) \rangle - \langle \exp(i[-\phi_{1,1} - \phi_{1,2} + \phi_{2,1} + \phi_{2,2}]) \rangle].$$

While different phases, α_n, for the 90° pulses produce different superpositions (see Tables 1–5) it is clear that the use of stimulated echoes results in three very different contributions:

First term (uncompensated, U): $\langle \exp(i\,[-\phi_{1,1} + \phi_{1,2} - \phi_{2,1} + \phi_{2,2}]) \rangle$. Let us consider the situation where $q_1 = q_2 = q$. This means that the two sets of gradient pairs, $G_{1,1} = G_{1,2}$ and $G_{2,1} = G_{2,2}$, are stepped in unison with the same corresponding values of gradient, i.e., $G_1 = G_2$. We denote this in the table by ↑↑. Then the term shown is encoded for the sum of displacements that occur over each encoding interval Δ, i.e.,

$$\langle \exp(i[-\phi_{1,1} + \phi_{1,2} - \phi_{2,1} + \phi_{2,2}]) \rangle = \langle \exp(i2\pi q[Z_1 + Z_2]) \rangle.$$

Second term (compensated, C): $\langle \exp(i\,[\phi_{1,1} - \phi_{1,2} - \phi_{2,1} + \phi_{2,2}]) \rangle$. When $q_1 = q_2 = q$, this term is encoded for the difference of displacements that occur over each encoding interval Δ, i.e.,

$$\langle \exp(i[\phi_{1,1} - \phi_{1,2} - \phi_{2,1} + \phi_{2,2}]) \rangle = \langle \exp(i2\pi q[-Z_1 + Z_2]) \rangle.$$

Third term (mixing, M): $\langle \exp(i[-\phi_{1,1} - \phi_{1,2} + \phi_{2,1} + \phi_{2,2}]) \rangle$. When $q_1 = q_3 = q$, this term is (approximately) encoded for the displacement that occurs over the mixing time, τ_m, i.e.,

$$\langle \exp(i[-\phi_{1,1} - \phi_{1,2} + \phi_{2,1} + \phi_{2,2}]) \rangle \approx \langle \exp(i2\pi 2q\, Z_m) \rangle.$$

We could consider each of these three examples again in the case of $q_1 = -q_2 = q$. This means that the two sets of gradient pairs, $G_{1,1} = G_{1,2}$ and $G_{2,1} = G_{2,2,}$ would be stepped in anti-unison with the same corresponding values of gradient, but oppositely signed, i.e., $G_1 = -G_2$. We denote this in the table by ↑↓. In this situation and in each of the three cases, the $\phi_{2,1}$ and $\phi_{2,2}$ phase factors have opposite sign. Tables 1–5 also illustrate this mode of gradient stepping.

In the 1-dimensional compensated double PGSE NMR method only the second (C) term is desired. In the 2-dimensional VEXSY method, both terms U and C are needed but only as appropriate to the relative gradient pulse signs. In neither experiment is the mixing term, M, desired. Thus, the challenge for both methods is to develop a suitable selective phase cycle.

Tables 1–5 show the respective contributions of the three terms in double PGSE NMR, for a variety of RF pulse combinations, where both the gradient signs and the RF pulse and acquisition phases are accounted for. These tables show the phases, α_n, of all pulses, P_n, subsequent to the excitation pulse, P_0, whose phase, α_0, is always set to X as a reference. In Table 1, the first and last 180° pulses belong to the PGSE pulse pairs while the middle 180° pulse divides the mixing time and provides refocusing of unwanted precession. In Table 2 the mixing time is bracketed by two 90° pulses, so that the magnetization is stored along the z axis. In Table 3, the first and last PGSE pulses pairs utilize a stimulated echo while mixing time periods is again refocused by a 180° pulse. In Tables 4 and 5, stimulated echoes are used, and the mixing time involves z storage and is bracketed by 90° pulses. In each case all phases are relative to

TABLE 1
Phase Cycle Table for Double PGSE NMR Experiment Based on Three 180° RF Refocusing Pulses

$90^\circ_{\alpha_0}$–$G_{1,1}$–$180^\circ_{\alpha_1}$–$G_{1,2}$–$180^\circ_{\alpha_m}$–$G_{2,1}$–$180^\circ\alpha_2$–$G_{2,2}$–acq_{α_a}

RF pulses				$G_{1,1}G_{1,2} \uparrow\uparrow G_{2,1}G_{2,2}$				$G_{1,1}G_{1,2} \uparrow\downarrow G_{2,1}G_{2,2}$			
α_0	α_1	α_m	α_2	***U***	***C***	***M***	α_a	***U***	***C***	***M***	α_a
X	*X*	*X*	*X*	−	0	0	*X*	0	−	0	*X*
X	*Y*	*Y*	*Y*	+	0	0	*X*	0	+	0	*X*
X	*X*	*Y*	*X*	+	0	0	*X*	0	+	0	*X*
X	*Y*	*X*	*Y*	−	0	0	*X*	0	−	0	*X*
X	*X*	*X*	*Y*	+	0	0	*X*	0	+	0	*X*
X	*Y*	*X*	*X*	+	0	0	*X*	0	+	0	*X*
X	*Y*	*Y*	*X*	−	0	0	*X*	0	−	0	*X*
X	*X*	*Y*	*Y*	−	0	0	*X*	0	−	0	*X*

Note. In each case $\alpha_0 = X$. For the 1-D experiment the gradient pulse pairs have equal magnitude while for the 2-D experiment the amplitudes of the first and second pairs are varied independently. In the 1-D case ↑↑ and ↑↓ refer to the unison and anti-unison gradient pulse pairs respectively.

TABLE 2
Phase Cycle Table for Double PGSE NMR Experiment Based on Two 180° RF Refocusing Pulses and One 90° RF Pulse Pair for *z*-Storage

$90^\circ_{\alpha_0}$–$G_{1,1}$–$180^\circ_{\alpha_1}$–$G_{1,2}$–$(90^\circ_{\alpha_{m,1}}$–$90^\circ_{\alpha_{m,2}})$–$G_{2,1}$–$180^\circ_{\alpha_2}$–$G_{2,2}$–acq_{α_a}

RF pulses				$G_{1,1}G_{1,2} \uparrow\uparrow G_{2,1}G_{2,2}$				$G_{1,1}G_{1,2} \uparrow\downarrow G_{2,1}G_{2,2}$			
α_0	α_1	$\alpha_{m,1}$ $\alpha_{m,2}$	α_2	***U***	***C***	***M***	α_a	***U***	***C***	***M***	α_a
X	*X*	(*X X*)	*X*	−	−	0	*X*	−	−	0	*X*
X	*Y*	(*Y Y*)	*Y*	−	−	0	*Y*	−	−	0	*Y*
X	*X*	(*Y Y*)	*X*	−	−	0	*Y*	−	−	0	*Y*
X	*Y*	(*X X*)	*Y*	−	−	0	*X*	−	−	0	*X*
X	*X*	(*X X*)	*Y*	+	+	0	*X*	+	+	0	*X*
X	*Y*	(*X X*)	*X*	+	+	0	*X*	+	+	0	*X*
X	*Y*	(*Y Y*)	*X*	+	+	0	*Y*	+	+	0	*Y*
X	*X*	(*Y Y*)	*Y*	+	+	0	*Y*	+	+	0	*Y*

Note. In each case $\alpha_0 = X$. For the 1-D experiment the gradient pulse pairs have equal magnitude while for the 2-D experiment the amplitudes of the first and second pairs are varied independently. In the 1-D case ↑↑ and ↑↓ refer to the unison and anti-unison gradient pulse pairs respectively.

TABLE 3
Phase Cycle Table for Double PGSE NMR Experiment Based on Two 90° RF Pulse Pairs to Generate Stimulated Echoes, and One 180° Pulse Pair Refocusing during the Mixing Time

$90^\circ_{\alpha_0}$–$G_{1,1}$–$(90^\circ_{\alpha_{1,1}}$–$90^\circ_{\alpha_{1,2}})$–$G_{1,2}$–$180^\circ_{\alpha_m}$–$G_{2,1}$–$(90^\circ_{\alpha_{2,1}}$–$90^\circ_{\alpha_{2,2}})$–$G_{2,2}$–acq_{α_a}

RF pulses				$G_{1,1}G_{1,2} \uparrow\uparrow G_{2,1}G_{2,2}$				$G_{1,1}G_{1,2} \uparrow\downarrow G_{2,1}G_{2,2}$			
α_0	$\alpha_{1,1}$ $\alpha_{1,2}$	α_m	$\alpha_{2,1}$ $\alpha_{2,2}$	***U***	***C***	***M***	α_a	***U***	***C***	***M***	α_a
X	(*X X*)	*X*	(*X X*)	−	−	0	*X*	0	−	0	*X*
X	(*Y Y*)	*Y*	(*Y Y*)	+	+	0	*X*	0	+	0	*Y*
X	(*X X*)	*Y*	(*X X*)	+	+	0	*X*	0	+	0	*Y*
X	(*Y Y*)	*X*	(*Y Y*)	−	−	0	*X*	0	−	0	*X*
X	(*X X*)	*X*	(*Y Y*)	−	−	0	*Y*	0	−	0	*X*
X	(*Y Y*)	*X*	(*X X*)	−	−	0	*Y*	0	−	0	*X*
X	(*Y Y*)	*Y*	(*X X*)	+	+	0	*Y*	0	+	0	*Y*
X	(*X X*)	*Y*	(*Y Y*)	+	+	0	*Y*	0	+	0	*Y*

Note. In each case $\alpha_0 = X$. For the 1-D experiment the gradient pulse pairs have equal magnitude while for the 2-D experiment the amplitudes of the first and second pairs are varied independently. In the 1-D case ↑↑ and ↑↓ refer to the unison and anti-unison gradient pulse pairs respectively.

TABLE 4
Phase Cycle Table for Double PGSE NMR Experiment Based on Two 90° RF Pulse Pairs to Generate Stimulated Echoes, and One 90° RF Pulse Pair for *z* Storage during the Mixing Time

$90^\circ_{\alpha_0}$–$G_{1,1}$–($90^\circ_{\alpha_{1,1}}$–$90^\circ_{\alpha_{1,2}}$)–$G_{1,2}$–($90^\circ\alpha_{m,1}$–$90^\circ\alpha_{m,2}$)–$G_{2,1}$–($90^\circ_{\alpha_{2,1}}$–$90^\circ_{\alpha_{2,2}}$)–$G_{2,2}$–acq_{α_a}

RF pulses				$G_{1,1}G_{1,2} \uparrow\uparrow G_{2,1}G_{2,2}$				$G_{1,1}G_{1,2} \uparrow\downarrow G_{2,1}G_{2,2}$			
α_0	$(\alpha_{1,1}\,\alpha_{1,2})$	$(\alpha_{m,1}\,\alpha_{m,2})$	$(\alpha_{2,1}\,\alpha_{2,2})$	***U***	***C***	***M***	α_a	***U***	***C***	***M***	α_a
X	$(X\,X)$	$(X\,X)$	$(X\,X)$	−	−	−	X	−	−	−	X
X	$(Y\,Y)$	$(Y\,Y)$	$(Y\,Y)$	+	−	+	Y	−	+	−	Y
X	$(X\,X)$	$(Y\,Y)$	$(X\,X)$	+	−	+	Y	−	+	−	Y
X	$(Y\,Y)$	$(X\,X)$	$(Y\,Y)$	−	−	−	X	−	−	−	X
X	$(X\,X)$	$(X\,X)$	$(Y\,Y)$	+	+	−	Y	+	+	−	Y
X	$(Y\,Y)$	$(X\,X)$	$(X\,X)$	+	+	−	Y	+	+	−	Y
X	$(Y\,Y)$	$(Y\,Y)$	$(X\,X)$	−	+	+	X	+	−	−	X
X	$(X\,X)$	$(Y\,Y)$	$(Y\,Y)$	−	+	+	X	+	−	−	X

Note. In each case $\alpha_0 = X$. For the 1-D experiment the gradient pulse pairs have equal magnitude while for the 2-D experiment the amplitudes of the first and second pairs are varied independently. In the 1-D case $\uparrow\uparrow$ and $\uparrow\downarrow$ refer to the unison and anti-unison gradient pulse pairs respectively.

the excitation pulse (X). In addition, the acquisition phase is shown, along with the relative signs of the PGSE gradient pulse pairs.

RECOMMENDED PHASE CYCLES USING STIMULATED ECHO SEQUENCES

(a) One-dimensional Compensated Double PGSE NMR

We will focus our attention on the case of stimulated echoes with z storage since this represents the best practical case for protection against T_2 decay. Note, again, that in each case, the initial excitation pulse, P_0, is of phase $\alpha_0 = X$ and not shown. Inspection of Table 4 shows how individual components may be selected. The phases of all subsequent pulses, $P_{\mathrm{n},}$ are labeled $(\alpha_{1,1}\alpha_{1,2})(\alpha_{\mathrm{m}}\alpha_{\mathrm{m}})(\alpha_{2,1}\alpha_{2,2}) - \alpha_a$. The echo condition requires $G_{1,1} = G_{1,2}$ and $G_{2,1} = G_{2,2}$. For the 1-D sequence we also require $|G_1| = |G_2|$ or in other words either $q_1 = q_2 = q$ or $q_1 = -q_2 = q$. These unison and in anti-unison cases are denoted ($\uparrow\uparrow$) and ($\uparrow\downarrow$) in the tables.

For example when anti-unison gradients ($\uparrow\downarrow$) are used for the pulse pairs, the combination **add** $(YY)(YY)(YY) - Y$ and **subtract** $(XX)(XX)(XX) - X$ gives pure C, as does **add** $(XX)(YY)(XX) - Y$ and **subtract** $(YY)(XX)(YY) - X$. Inspection of Table 4 shows that these combinations remove the U and M components and retain the desired C component. It is a trivial matter to design cycles that return pure U or pure M should these be desired.

(b) Two-dimensional VEXSY

In the VEXSY experiment the PGSE gradient pulse pairs are varied in amplitude independently so as to acquire the signal in the two-dimensional q-space (q_1, q_2). Again we use $G_{1,1} = G_{1,2}$ and $G_{2,1} = G_{2,2}$ for the echo condition but G_1 and G_2 are independent. In the quadrants where gradients have the same sign, the U case is desired since we expect that the phase

TABLE 5
As with Table 4 but Using Alternate Phases in Successive 90° Pulses

$90^\circ_{\alpha_0}$–$G_{1,1}$–($90^\circ_{\alpha_{1,1}}$–$90^\circ_{\alpha_{1,2}}$)–$G_{1,2}$–($90^\circ\alpha_{m,1}$–$90^\circ\alpha_{m,2}$)–$G_{2,1}$–($90^\circ_{\alpha_{2,1}}$–$90^\circ_{\alpha_{2,2}}$)–$G_{2,2}$–acq_{α_a}

RF pulses				$G_{1,1}G_{1,2} \uparrow\uparrow G_{2,1}G_{2,2}$				$G_{1,1}G_{1,2} \uparrow\downarrow G_{2,1}G_{2,2}$			
α_0	$(\alpha_{1,1}\,\alpha_{1,2})$	$(\alpha_{m,1}\,\alpha_{m,2})$	$(\alpha_{2,1}\,\alpha_{2,2})$	***U***	***C***	***M***	α_a	***U***	***C***	***M***	α_a
X	$(X\,Y)$	$(X\,Y)$	$(X\,Y)$	+	−	+	X	−	+	−	X
X	$(Y\,X)$	$(Y\,X)$	$(Y\,X)$	+	+	+	Y	+	+	+	Y
X	$(X\,Y)$	$(Y\,X)$	$(X\,Y)$	+	+	+	Y	+	+	+	Y
X	$(Y\,X)$	$(X\,Y)$	$(Y\,X)$	+	−	+	X	−	+	−	X
X	$(X\,Y)$	$(X\,Y)$	$(Y\,X)$	+	−	−	Y	−	+	+	Y
X	$(Y\,X)$	$(X\,Y)$	$(X\,Y)$	+	−	−	Y	−	+	+	Y
X	$(Y\,X)$	$(Y\,X)$	$(X\,Y)$	+	+	−	X	+	+	−	X
X	$(X\,Y)$	$(Y\,X)$	$(Y\,X)$	+	+	−	X	+	+	−	X

Note. In each case $\alpha_0 = X$. For the 1-D experiment the gradient pulse pairs have equal magnitude while for the 2-D experiment the amplitudes of the first and second pairs are varied independently. In the 1-D case $\uparrow\uparrow$ and $\uparrow\downarrow$ refer to the unison and anti-unison gradient pluse pairs respectively.

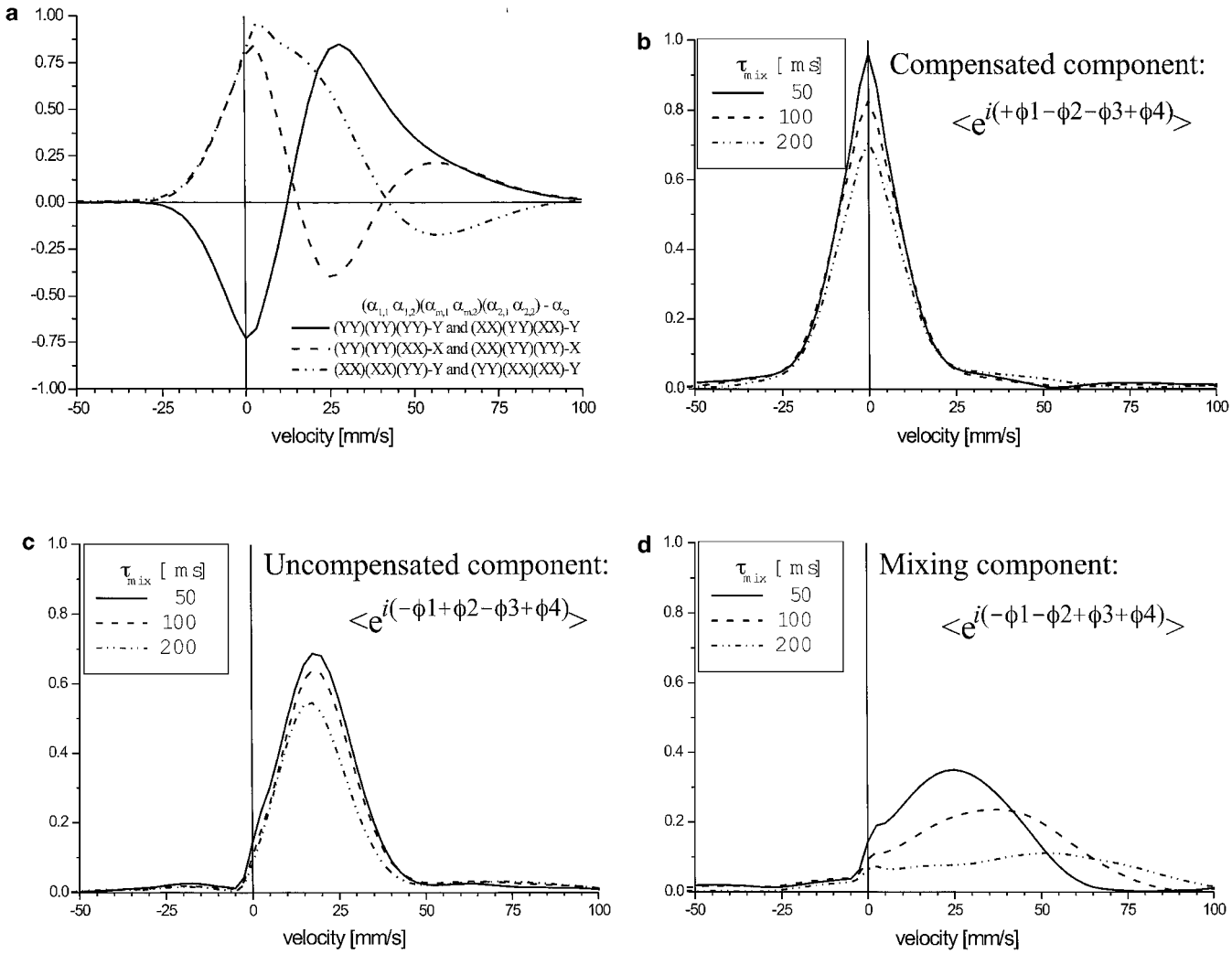

FIG. 2 One-dimensional displacement distributions calculated by Fourier transforming the double PGSE echo amplitude E, with respect to the stepped wavevector, q. In each case the stimulated echo sequence of Fig. 1c was used. (a) Distributions arising from the sequences $(YY)\,(YY)\,(YY)-Y$ and $(XX)\,(YY)\,(XX)-Y$ for which the U, C, and M components have respective signs $(+-+)$, the distribution $(-++)$ from the sequences $(YY)\,(YY)\,(XX)-X$ and $(XX)\,(YY)\,(YY)-X$, and the distribution $(++-)$ from the sequences $(XX)\,(XX)\,(YY)-Y$ and $(YY)\,(XX)\,(XX)-Y$. (b) The case of a pure C component, obtained using the phase cycle [**add** $(YY)\,(XX)\,(XX)-Y$ and **add** $(YY)\,(YY)\,(XX)-X$] for different mixing times as shown. Note that the distribution is centered on zero displacement and represents changes in molecular displacements over the mixing time. The slight reduction in amplitude is due to T_1 effects. (c) The case of a pure U component, obtained using the phase cycle [**add** $(XX)\,(XX)\,(YY)-Y$ and **add** $(XX)\,(YY)\,(XX)-Y$] for different mixing times as shown. Note that the distribution reflects the net displacement of the spins over both encoding times, Δ. (d) The case of a pure M component, obtained using the phase cycle [**add** $(YY)\,(YY)\,(YY)-Y$ and **add** $(YY)\,(YY)\,(XX)-X$] for different mixing times as shown. Note that the distribution reflects the net displacement of the spins over (approximately) the mixing time τ_m, so that in calculating the velocity based on an assumed encoding time, Δ, an apparent velocity that depends on mixing time results.

exponents $q_1 Z_1$ and $q_2 Z_2$ will add constructively. In the quadrants where gradients have opposite sign, the C case is desired since we expect that the phase exponents $q_1 Z_1$ and $q_2 Z_2$ will add destructively. Furthermore the M component is entirely unwanted and must be removed. Table 5 shows a phase cycle that achieves this result. All eight steps are needed to achieve the desired result. The sum of all eight experiments provides perfect M cancelation and generates U and C contributions in the appropriate quadrants.

EXPERIMENTAL IMPLEMENTATION

In order to demonstrate the effectiveness of the phase cycles we have carried proton NMR experiments at 300 MHz using water flowing in a 500-μm bead pack at ambient temperature (24°C). A Bruker AMX300 spectrometer was used along with the three-axis microimaging gradient set. Flow in a bead pack may be described by a correlation time, τ_c, corresponding to the duration of flow around the characteristic length scale, the bead

diameter, d, i.e.,

$$\tau_c = d/\langle v \rangle, \quad [4]$$

where $\langle v \rangle$ is the average interstitial pore velocity, given by $\langle v_{tube} \rangle / \phi$, ϕ being the porosity. For a flow rate Q, in a tube of radius r, the "tube velocity," $\langle v_{tube} \rangle$, is given by $Q/\pi r^2$. The dimensionless parameter characterizing the flow is the Peclet number (*12*)

$$\mathrm{Pe} = \frac{\langle v \rangle l}{D_0}, \quad [5]$$

where l is a characteristic length scale, which can be taken to be the bead diameter. First we look at the 1-dimensional double PGSE NMR experiment. The encoding time Δ is 50 ms and the mixing time τ_m is 50 ms. The flow rate is 2.0 $\mathrm{l\,h^{-1}}$, giving an average interstitial pore velocity of 20 mm $\mathrm{s^{-1}}$. The correlation time is 25 ms while the Peclet number for these conditions is 4800.

Figure 2 presents the results of measurements in which the echo amplitude E is Fourier transformed with respect to q so as to reveal the probability distribution of displacements. In Fig. 2a we see the distribution arising from the sequences $(YY)(YY)(YY) - Y$ and $(XX)(YY)(XX) - Y$. This particular combination of phases gives a superposition of U, C, and M with respective signs $(+-+)$. Also shown in Fig. 2a is the distribution $(-++)$ arising from the sequences $(YY)(YY)(XX) - X$ and $(XX)(YY)(YY) - X$, as well as the distribution $(++-)$ from the sequences $(XX)(XX)(YY) - Y$ and $(YY)(XX)(XX) - Y$. The shapes of these three distributions are quite different because of the different relative signs of the U, C, and M contributions to the echo.

Figure 2b shows the result of the phase cycling experiments [**add** $(YY)(YY)(YY) - Y$ and **subtract** $(XX)(XX)(XX) - X$] where pure C is selected while Figs. 2c and 2d show selection of pure U and pure M respectively. In each case the results of data obtained using three different mixing times (50, 100, and 200 ms) are shown. It is clear in the case of the U experiment that the asymmetric propagator reflects the mean flow, and in fact results from a constructive sum of phase shifts for each encoding interval, Δ. By contrast the propagator for C is centered at zero displacement since only the change in displacement over the mixing time is apparent. The M propagator reflects displacements occurring over the mixing time itself, and thus leading to different displacements being recorded, and an apparent velocity that depends on mixing time.

Next we present data obtained in a VEXSY experiment carried using an encoding time $\Delta = 50$ ms and a mixing time $\tau_m = 50$ ms. Figure 3a shows the result of an experiment in which no phase cycling is used ($(XX)(XX)(XX) - X$) while Fig. 3b shows the result of the 8-step cycle of Table 5. The latter spectrum contains only the desired components.

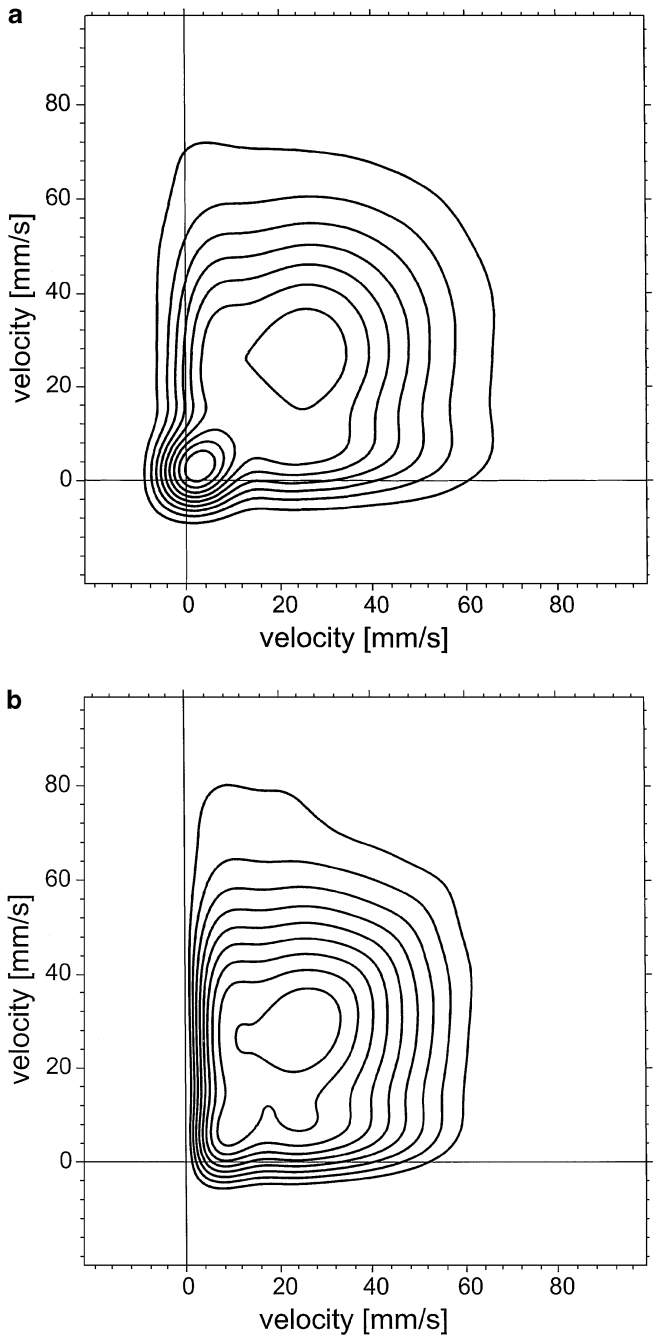

FIG. 3 Two-dimensional displacement distributions obtained from water flowing at 20 mm $\mathrm{s^{-1}}$ in a 500 μm bead pack, using a VEXSY sequence, with mixing time 50 ms, in which the stimulated echo sequence of Fig. 1c is used. In (a) a simple $(X\,X)\,(X\,X)\,(X\,X) - X$ phase setting was used while in (b) the full 8-step phase cycle of Table 5 was used.

CONCLUSION

Double PGSE NMR methods have the potential to provide important new information regarding velocity fluctuations in complex flows. In all such experiments, T_2 effects limit the range of velocities as well as the fluctuation times, which can

be accessed. Minimization of T_2 relaxation is possible by using stimulated echoes for the displacement encoding and z storage for the mixing time. We have shown here that these sequences, which employ 90° RF pulses, cause complex superpositions of wanted and unwanted magnetization. Use of appropriate phase cycling techniques, as outlined here, makes it possible to select the desired magnetization. In the case of velocity exchange spectroscopy, an 8-step phase cycle has been demonstrated to provide excellent results in which nearly all artifacts are eliminated. We suggest that such phase cycling is essential if the VEXSY method is to be effectively applied to study problems such as transport in porous media, where velocity fluctuations are of considerable interest.

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