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COMMUNICATIONS

Determination of Velocity Autocorrelation Functions by Multiple Data Acquisition in NMR Pulsed-Field Gradient Experiments

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An extension of NMR pulsed-field gradient experiments toward the generation, acquisition, and analysis of multiple echoes is presented. In contrast to currently used measurements where a single or double encoding of displacements by gradient pulses is followed by an acquisition of the echo signal at the end of the sequence, sampling and analyzing the intermediately occurring echoes allows a direct distinction between coherent and dispersive contributions to fluid motion without additional referencing measurements. It is shown that a series of gradient pulse pairs, leading to a train of echoes, can be employed to map the time-dependence of the velocity autocorrelation function between displacements within a single experiment for a system undergoing flow or motion. © 2001 Academic Press

Key Words: **velocity autocorrelation function; flow; diffusion; CPMG; PFG.**

INTRODUCTION

For many years, nuclear magnetic resonance pulsed-field gradient (PFG) techniques have been a powerful tool for the investigation of transport processes. The principle of encoding particle motion into a spin echo by applying a pair of short gradient pulses, separated by a time Δ (*1, 2*), has been employed to directly produce the probability density of displacements, or propagator (*3, 4*), exploiting the Fourier relationship between gradient strength and displacements. The shape of the propagator as a function of Δ contains important information about exchange processes in multicomponent systems, or restriction sizes and connectivities for diffusion of fluids in porous media. The same is true for pressure-driven fluid transport through materials of different geometries, a subject which has more recently attracted much interest in the NMR community and which has brought new impetus to the development of PFG techniques. Not only has the evolution of the flow propagator as a function of Δ been investigated and linked to structural features of the surrounding matrix (e.g., packings of spheres (*5, 6*) and natural rocks (*7, 8*)), but also strategies have been developed to determine the degree of correlation of the flow field between two separated time intervals (*9, 10*). The possibility to interrogate the propagator for a fluid in an opaque medium at different times within a single experiment, and to use this information to obtain a picture of how the propagator evolves between these times, is a feature unique to NMR. Callaghan and Manz (*10*) have presented a two-dimensional realization of this concept. Their experiment allowed the correlation of two distributions of velocities, separated by a mixing time, with each other in a two-dimensional representation and was dubbed Velocity EXchange SpectroscopY, or VEXSY. Mitra (*11*) has discussed a similar experiment but with arbitrary directions of the two independent wave vectors as a tool to probe diffusion in locally anisotropic pores.

With these two-dimensional experiments, it is possible to directly compare the behavior of particles with a given displacement in the first interval with their motion during a second interval. For the quantification of correlations, however, it is not necessary to obtain the full two-dimensional probability density of displacements, rather can such numbers be derived from averaged moments of displacements which are accessible by similar, but much less time-consuming one-dimensional NMR experiments where all PFGs are varied simultaneously. Such methods have, for instance, been applied to distinguish between coherent and fluctuating motions in Poiseuille flow (*12*), flow through hollow-fiber membranes (*13*), and rotating granular media (*14*).

For one-dimensional NMR experiments, the procedure of acquiring only the final signal after completion of the full pulse sequence possesses the disadvantage that the information obtained from this echo must be compared to a reference measurement to allow an investigation of correlations. Moreover, the temporal evolution of the correlation function has to be probed by repeated experiments for different mixing times. To the knowledge of the author, the feasibility of actually acquiring the intermediate echoes and of comparing them in a quantitative manner has not yet been discussed. In this paper, extensions of existing, one-dimensional PFG pulse schemes are presented along with the mathematical framework needed to compute the correlation functions of interest. The possibility of obtaining

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values of the correlation function at multiple times in a single shot by repeated refocussing of echoes is suggested. In analogy to related abbreviations in the literature, this new class of experiments is described by the acronym RODENT (Repeated Observation of Displacements Encoding N Time intervals).

RESULTS AND DISCUSSION

A. Determination of the Displacement Correlation Coefficient from Double-Encoding Experiments

Following a PFG experiment with displacement encoding due to two gradient pulses of intensity g and duration δ being separated by an interval Δ, each spin experiences a phase shift proportional to its displacement $\boldsymbol{R}$ during Δ. Averaging over all spins in the sample leads to the attenuated signal intensity

$$\tilde{S}(\boldsymbol{q}, \Delta) = \frac{S(\boldsymbol{q}, \Delta)}{S(0, \Delta)} = \int \bar{P}(\boldsymbol{R}, \Delta) e^{i2\pi \boldsymbol{q} \boldsymbol{R}(\Delta)}\, d\boldsymbol{R}, \qquad [1]$$

where $\boldsymbol{q} = \frac{1}{2\pi}\gamma\delta\boldsymbol{g}$ and γ is the gyromagnetic ratio. The average propagator $\bar{P}(\boldsymbol{R}, \Delta)$ is available as the Fourier transform of the signal function $\tilde{S}(\boldsymbol{q}, \Delta)$ and is given by

$$\bar{P}(\boldsymbol{R}, \Delta) = \int \rho(\boldsymbol{r}_1) P(\boldsymbol{r}_1, 0; \boldsymbol{r}_1 + \boldsymbol{R}, \Delta)\, d\boldsymbol{r}_1 \qquad [2]$$

with the initial spin density $\rho(\boldsymbol{r}_1)$ and the conditional probability $P(\boldsymbol{r}_1, 0;\ \boldsymbol{r}_1 + \boldsymbol{R}, \Delta)$ of finding a displacement $\boldsymbol{R}$ during Δ for an initial position $\boldsymbol{r}_1$.

A double encoding by two identical gradient pairs, separated by a mixing time τ_m, can be described in a similar way by a product of a displacement density, $\bar{P}(\boldsymbol{R}_1)$, and a conditional probability between displacements, $P(\boldsymbol{R}_1; \boldsymbol{R}_2, \tau_m)$,

$$\begin{aligned}\tilde{S}(\boldsymbol{q}, \tau_m) &= \int \bar{P}(\boldsymbol{R}_1) P(\boldsymbol{R}_1; \boldsymbol{R}_2, \tau_m) e^{i2\pi \boldsymbol{q}(\boldsymbol{R}_1 \pm \boldsymbol{R}_2)}\, d\boldsymbol{R}_1\, d\boldsymbol{R}_2 \\ &= \int \bar{P}(\boldsymbol{R}_1 \pm \boldsymbol{R}_2, \tau_m) e^{i2\pi \boldsymbol{q}(\boldsymbol{R}_1 \pm \boldsymbol{R}_2)}\, d(\boldsymbol{R}_1 \pm \boldsymbol{R}_2), \qquad [3]\end{aligned}$$

where the encoding time Δ has been omitted, and the $\pm$ sign represents the two cases $\boldsymbol{q}_1 = \boldsymbol{q}_2$ and $\boldsymbol{q}_1 = -\boldsymbol{q}_2$, respectively (*14*). The propagator $\bar{P}(\boldsymbol{R}_1 + \boldsymbol{R}_2, \tau_m)$ then describes the probability density of the total displacements accumulated during both Δ intervals, while $\bar{P}(\boldsymbol{R}_1 - \boldsymbol{R}_2, \tau_m)$ measures the probability density of differences between displacements for the mixing time τ_m (*15, 16*). If the particle velocities in the two encoding intervals remain constant, one would observe $\bar{P}(\boldsymbol{R}_1 - \boldsymbol{R}_2, \tau_m) = \bar{P}(\boldsymbol{R}_1)\ \delta(\boldsymbol{R}_1 - \boldsymbol{R}_2)$, and the effective dispersion defined by the experiment with $\boldsymbol{q}_1 = -\boldsymbol{q}_2$ would be zero. The change of displacements, or velocities, as measured by this double-encoding pulse sequence has been shown to deliver important information about the loss of coherence between particles starting with the same velocity. To quantify this time-dependent correlation, a comparison of the single- and double-encoded propagators, $\bar{P}(\boldsymbol{R}_1)$ and $\bar{P}(\boldsymbol{R}_1 \pm \boldsymbol{R}_2, \tau_m)$, or the dispersion coefficients obtained from them is necessary (*12, 14, 17*).

The mathematical definition of the correlation coefficient of two quantities A, B is given by

$$\rho_{A,B} = \frac{\langle AB\rangle - \langle A\rangle\langle B\rangle}{\sqrt{\langle A^2\rangle - \langle A\rangle^2}\,\sqrt{\langle B^2\rangle - \langle B\rangle^2}}\ . \qquad [4]$$

A, B can be any power of displacements. In particular, if displacements in the same direction but at different times are compared to each other, $\rho_{A,B}$ becomes the velocity autocorrelation function (VACF, (*4, 5, 14*)) in the limit of vanishing encoding times Δ. This function is given by

$$R_v(\tau) = \langle v(t)\ v(t+\tau)\rangle, \qquad [5]$$

where $v(t)$ represents an instantaneous velocity. Each VEXSY experiment with a mixing time τ_m delivers one value of the VACF, $R_v(\tau = \tau_m)$, provided that velocity changes during Δ can be neglected.

The moments of displacements for a stationary process can be computed from the propagators obtained by the double-encoding sequences as

$$\langle(\boldsymbol{R}_1 \pm \boldsymbol{R}_2)^n\rangle = \int \bar{P}(\boldsymbol{R}_1 \pm \boldsymbol{R}_2)(\boldsymbol{R}_1 \pm \boldsymbol{R}_2)^n\, d(\boldsymbol{R}_1 \pm \boldsymbol{R}_2), \qquad [6]$$

where

$$\langle \boldsymbol{R}_1 + \boldsymbol{R}_2\rangle = 2\langle \boldsymbol{R}_1\rangle, \quad \langle \boldsymbol{R}_1 - \boldsymbol{R}_2\rangle = 0,$$

and

$$\langle(\boldsymbol{R}_1 \pm \boldsymbol{R}_2)^2\rangle = 2\langle \boldsymbol{R}_1^2\rangle \pm 2\langle \boldsymbol{R}_1 \boldsymbol{R}_2\rangle,$$

because $\langle \boldsymbol{R}_1^n\rangle = \langle \boldsymbol{R}_2^n\rangle$. The average displacement during two encoding intervals Δ is twice as large as the displacement during a single interval Δ, and the average change of displacements is zero as no net acceleration is allowed in stationary flow. The second moments, however, contain the mixed term which is necessary for quantifying the degree of correlation (see Eq. [4]).

One possibility to retrieve the mixed term $\langle \boldsymbol{R}_1 \boldsymbol{R}_2\rangle$ is to perform either of the two double-encoding experiments and determine $\langle \boldsymbol{R}_1^2\rangle$ independently employing a single-encoding sequence which has to be done only once and serves as a reference for all values of τ_m. Alternatively, one can perform two double-encoding experiments for identical mixing times but with the two wave vector settings $\boldsymbol{q}_1 = \boldsymbol{q}_2$ and $\boldsymbol{q}_1 = -\boldsymbol{q}_2$, respectively. Computing the sum and the difference of the second moments of displacements from these two probability density functions

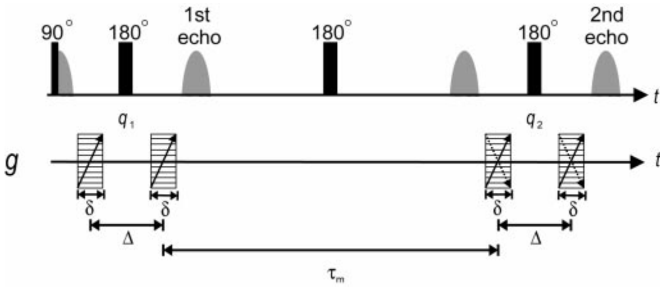

FIG. 1. PFG sequence for double encoding of displacements. All gradient pulses are stepped simultaneously as indicated by the arrows, where solid lines represent $\boldsymbol{q}_1 = \boldsymbol{q}_2$ and dashed lines $\boldsymbol{q}_1 = -\boldsymbol{q}_2$, respectively. Each 180° RF pulse changes the sign of all preceding effective gradient wave vectors.

then allows one to isolate the desired quantities:

$$\frac{1}{4}[\langle(\boldsymbol{R}_1 + \boldsymbol{R}_2)^2\rangle + \langle(\boldsymbol{R}_1 - \boldsymbol{R}_2)^2\rangle] = \langle \boldsymbol{R}_1^2 \rangle \quad [7]$$

$$\frac{1}{4}[\langle(\boldsymbol{R}_1 + \boldsymbol{R}_2)^2\rangle - \langle(\boldsymbol{R}_1 - \boldsymbol{R}_2)^2\rangle] = \langle \boldsymbol{R}_1 \boldsymbol{R}_2 \rangle\ . \quad [8]$$

It is intuitively clear that for long times when $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$ become independent, $\langle \boldsymbol{R}_1 \boldsymbol{R}_2\rangle \approx \langle \boldsymbol{R}_1\rangle\langle \boldsymbol{R}_2\rangle$ and the correlation disappears. This is always the case for purely random motion such as unrestricted self-diffusion (*17*).

However, it is also possible to obtain the pure and the mixed second moments, $\langle \boldsymbol{R}_1^2\rangle$ and $\langle \boldsymbol{R}_1 \boldsymbol{R}_2\rangle$, from a single experiment in which the echo signals following the first and the second gradient pair, respectively, are both acquired. In Fig. 1, a simple representation of such an experiment is shown. The FID following the 90° RF pulse is refocussed into a first echo in which displacements during the first interval Δ are encoded by the wave vector $\boldsymbol{q}_1$. This encoding is carried forward to an intermediate echo which is generated preceding the second encoding interval. (In a real experiment and for transverse relaxation times T_2 short compared to τ_m, the 180° RF pulse in the center might be replaced by two 90° RF pulses in order to generate a stimulated echo (*18*)). The second interval Δ produces an additional encoding of displacements, depending on the choice of the wave vector ($\boldsymbol{q}_1 = -\boldsymbol{q}_2$ is indicated by dashed lines). Fourier transformation of the first and second marked echoes with respect to $\boldsymbol{q}_1$ then renders the propagators $\bar{P}(\boldsymbol{R}_1)$ and $\bar{P}(\boldsymbol{R}_1 \pm \boldsymbol{R}_2)$, respectively. Note that in order to generate a detectable first echo, the mixing time is restricted to $\tau_m > \Delta$.

B. Determination of the Full Displacement Autocorrelation Function from Multiple-Encoding Experiments

The interrogation of a complete VACF with the described method would still involve a series of individual experiments over a range of τ_m values, where $\bar{P}(\boldsymbol{R}_1)$ is identical for each measurement so that essentially no gain in experimental time is achieved. It is, however, entirely possible to repeat the encoding by a series of wave vectors $\boldsymbol{q}$ so that a train of echoes is generated each of which contains information about displacements accumulated during all preceding encoding intervals. Such multiple encoding has already been suggested (*11, 14*). A Carr–Purcell–Meiboom–Gill (CPMG) type sequence of 180° RF pulses (*19, 20*) interspersed with evenly spaced gradient pulses has been analyzed both theoretically (*21*) and experimentally (*22, 23*) in the context of frequency-dependent dispersion processes, but with only the final echo at the end of the sequence being analyzed. The simultaneous acquisition of each of the n echoes in such a pulse sequence, allows the determination of n propagators of combined displacements. The RODENT scheme is shown in Fig. 2, where all gradient pulses are assumed to be stepped with identical amplitudes $|\boldsymbol{q}|$. The resulting signal function for each echo i is Fourier transformed with respect to $\boldsymbol{q}$ and the second moments $m_{2,i}$ are given by the sum of the mixed terms weighted by the polynomial coefficients:

$$\begin{aligned}
\text{1st echo: } m_{2,1} &= \langle \boldsymbol{R}_1^2 \rangle, \\
\text{2nd echo: } m_{2,2} &= \langle(\boldsymbol{R}_1 \pm \boldsymbol{R}_2)^2\rangle = 2\langle \boldsymbol{R}_1^2\rangle \pm 2\langle \boldsymbol{R}_1\boldsymbol{R}_2\rangle, \\
\text{3rd echo: } m_{2,3} &= \langle(\boldsymbol{R}_1 \pm \boldsymbol{R}_2 + \boldsymbol{R}_3)^2\rangle \\
&= 3\langle \boldsymbol{R}_1^2\rangle \pm 4\langle \boldsymbol{R}_1\boldsymbol{R}_2\rangle + 2\langle \boldsymbol{R}_1\boldsymbol{R}_3\rangle, \\
n\text{th echo: } m_{2,n} &= \langle(\boldsymbol{R}_1 \pm \boldsymbol{R}_2 + \cdots (\pm 1)^{n+1}\boldsymbol{R}_n)^2\rangle \\
&= \sum_{k_1+\cdots+k_n=2} \frac{2}{k_1!k_2!\ldots k_n!} \\
&\quad \times \langle \boldsymbol{R}_1^{k_1}(\pm \boldsymbol{R}_2^{k_2})\cdots(\pm 1)^{n+1}\boldsymbol{R}_n^{k_n}\rangle. \quad [9]
\end{aligned}$$

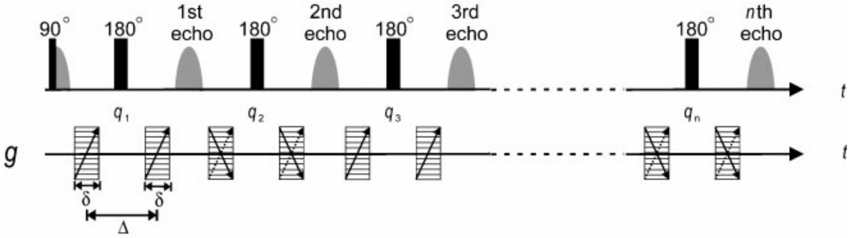

FIG. 2. Generation of n echoes during a RODENT experiment. Each pair of gradient pulses is placed symmetrically around the 180° RF pulses of a CPMG sequence. All gradient pulses are stepped simultaneously as indicated by the arrows, where solid lines represent $\boldsymbol{q}_1 = \boldsymbol{q}_i$ and dashed lines $\boldsymbol{q}_1 = -\boldsymbol{q}_i$, respectively.

Here, $\langle \boldsymbol{R}_l \boldsymbol{R}_{l+m} \rangle$ represent the mixed moments of displacements encoded into the echoes l and m, respectively. Due to the stationarity condition, they are identical for any l, and equal to $\langle \boldsymbol{R}_1 \boldsymbol{R}_{1+m} \rangle$ in particular; they only depend on the time *difference* τ_m which is equal to m times the echo separation. (The option of a succession of gradient pairs with equal or sign-inverted wave vectors, i.e., $\boldsymbol{q}_i = \boldsymbol{q}_{i+1}$ and $\boldsymbol{q}_i = -\boldsymbol{q}_{i+1}$, has been considered and is indicated symbolically by the $\pm$ sign.) This condition allows the straightforward simplification of Eq. [9] to

$$m_{2,n} = n\left\langle \boldsymbol{R}_1^2 \right\rangle + \sum_{m=1}^{n-1} (\pm 1)^{m+1} 2(n-m) \langle \boldsymbol{R}_1 \boldsymbol{R}_{1+m} \rangle. \qquad [10]$$

The relevant mixed moments of displacements for increasing echo separations can then be isolated from the echoes' second moments,

$$\begin{aligned} \left\langle \boldsymbol{R}_1^2 \right\rangle &= m_{2,1}, \\ \langle \boldsymbol{R}_1 \boldsymbol{R}_2 \rangle &= \pm \frac{1}{2}[m_{2,2} - 2m_{2,1}], \\ \langle \boldsymbol{R}_1 \boldsymbol{R}_3 \rangle &= \frac{1}{2}[m_{2,3} - 2m_{2,2} + m_{2,1}], \end{aligned}$$

and

$$\langle \boldsymbol{R}_1 \boldsymbol{R}_n \rangle = (\pm 1)^{n+1} \frac{1}{2}[m_{2,n} - 2m_{2,n-1} + m_{2,n-2}] \qquad [11]$$

for $n \geq 3$.

Each of the mixed moments of displacements is obtained from three successive echoes only. For the computation of the correlation coefficient, the first and second moments of the first echo also need to be known:

$$\begin{aligned} \rho_{\boldsymbol{R}_1, \boldsymbol{R}_n} &= \frac{\langle \boldsymbol{R}_1 \boldsymbol{R}_n \rangle - \langle \boldsymbol{R}_1 \rangle^2}{\left\langle \boldsymbol{R}_1^2 \right\rangle - \langle \boldsymbol{R}_1 \rangle^2} \\ &= (\pm 1)^{n+1} \frac{(m_{2,n} - 2m_{2,n-1} + m_{2,n-2}) - m_{1,1}^2}{2\left(m_{2,1} - m_{1,1}^2\right)}. \qquad [12] \end{aligned}$$

Equation [12] is exact for stationary flow conditions if background gradients remain negligible and if perfect 180°-pulses are assumed. In order to account for pulse imperfections, a suitable compensated CPMG-sequence such as those discussed in (*24*) has to be used in order to preserve both orthogonal components of the magnetization. In such cases, it can become necessary to gradient-encode and acquire not every echo but only one echo per repetition cycle of the compensated sequence.

The choice of either identical or alternating signs of the $\boldsymbol{q}$ wave vectors during the experiment has no effect on the weighting of the moments. The behavior of the echoes, on the other hand, will be different if the contribution of coherent motion to the total displacements is strong. For $\boldsymbol{q}$ vectors of identical sign, each propagator samples a displacement averaged over all preceding intervals. For alternating $\boldsymbol{q}$ vectors, on the other hand, even echoes are only sensitive to the accumulated differences between displacements and thus decay slower than the odd echoes as the magnitude of $\boldsymbol{q}$ is increased. This is the case for a time-invariant gradient and the different behaviour of odd and even echoes was already pointed out by Carr and Purcell in their original paper (*19*). In the RODENT pulse sequence of Fig. 2, alternating $\boldsymbol{q}$ encoding vectors are generated if each pulsed gradient possesses the same sign. By using only the propagators of the even echoes, one can thus follow the evolution of displacement *differences*,

$$\langle (\boldsymbol{R}_2 - \boldsymbol{R}_1)(\boldsymbol{R}_4 - \boldsymbol{R}_3) \rangle = \frac{1}{2}[m_{2,4} - 2m_{2,2}],$$

and

$$\langle (\boldsymbol{R}_2 - \boldsymbol{R}_1)(\boldsymbol{R}_n - \boldsymbol{R}_{n-1}) \rangle = \frac{1}{2}[m_{2,n} - 2m_{2,n-2} + m_{2,n-4}],$$

for $n \geq 6$ and n even.

In the finite-time approximation, this corresponds to the correlation function of accelerations, defined as the velocity change during the echo separation (*15, 25*).

C. Determination of the Full Displacement Autocorrelation Function from the Low-q Behavior in Multiple-Encoding Experiments

The second moment of displacements is closely linked to the dispersion coefficient D^*, which can be defined as a time-dependent quantity via $2D^*(\Delta)\Delta = \langle (R - \langle R \rangle)^2 \rangle$ (only one spatial direction shall be considered here, for simplicity). Previous works have discussed the different responses of flowing systems to single or double encoding sequences in terms of effective dispersion coefficients and it was suggested that these values can be obtained from the low-q data of the signal intensities rather than from the full propagators themselves (*5, 14, 17*), using the relation

$$D^*_{\mathit{eff}}(\Delta) = \lim_{q \to 0} \frac{-1}{4\pi^2 \Delta} \partial \ln(|\tilde{S}(q)|)/\partial q^2. \qquad [13]$$

For small q, $\tilde{S}(q)$ can be approximated as

$$|\tilde{S}(q)| = e^{-2\pi^2 q^2 \langle (R - \langle R \rangle)^2 \rangle}, \qquad [14]$$

so that the normalized intensity of the nth echo can be written with the abbreviations of Eq. [9]:

$$|\tilde{S}_n(q)| = e^{-2\pi^2 q^2 \left(m_{2,n} - n^2 m_{1,1}^2\right)}. \qquad [15]$$

(Under experimental conditions, care has to be taken that the low-q condition must remain valid for echoes of higher order which involve larger total displacements.) The mixed terms of displacements are now obtained from ratios of the echo intensities (see Eq. [11]):

$$\langle R_1 R_2\rangle - \langle R_1\rangle^2 = \pm \lim_{q\to 0} \frac{-1}{4\pi^2} \partial \ln\left(\left|\frac{\tilde{S}_2(q)}{\tilde{S}_1^2(q)}\right|\right) \Big/ \partial q^2, \quad [16]$$

$$\langle R_1 R_n\rangle - \langle R_1\rangle^2 = (\pm 1)^{n+1} \lim_{q\to 0} \frac{-1}{4\pi^2} \partial \ln\left(\left|\frac{S_n(q) S_{n-2}(q)}{S_{n-1}^2(q)}\right|\right) \Big/ \partial q^2, \quad [17]$$

and the correlation coefficient from dividing this expression by $\langle R_1^2\rangle - \langle R_1\rangle^2 = \lim_{q\to 0} \frac{-1}{2\pi^2} \partial \ln(|\tilde{S_1}(q)|)/\partial q^2$ (see Eq. [12]). Note that the additional attenuation due to relaxation is cancelled in the quotient of the echo intensities.

CONCLUSIONS

Multiple encoding of spin displacements by means of NMR pulsed-field gradient sequences and repeated signal acquisition within one sequence (RODENT) offers the possibility of considerably speeding up the determination of correlation functions between displacements. The method can be employed for flow processes but also for self-diffusion in restricted geometries, provided that the decay time constants for correlations are within the experimentally accessible range which is primarily given by gradient switching times and the relaxation time of the sample. The scheme can be generalized toward arbitrary directions of wave vectors for probing locally anisotropic dispersion behavior. A fast determination of correlation functions of displacements provides a suitable tool for the estimation of structural sizes which are relevant for the dispersion process of fluids in porous media.

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