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A cumulant analysis for non-Gaussian displacement distributions in Newtonian and non-Newtonian flows through porous media

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Abstract

We use displacement encoding pulsed field gradient (PFG) nuclear magnetic resonance to measure Fourier components S_q of flow displacement distributions $P(\zeta)$ with mean displacement $\langle\zeta\rangle$ for Newtonian and non-Newtonian flows through rocks and bead packs. Displacement distributions are non-Gaussian; hence, there are finite terms above second order in the cumulant expansion of $\ln(S_q)$. We describe an algorithm for an optimal self-consistent cumulant analysis of data, which can be used to obtain the first three (central) moments of a non-Gaussian $P(\zeta)$, with error bars. The analysis is applied to Newtonian and non-Newtonian flows in rocks and beads. Flow with shear-thinning xanthan solution produces a $15.6\pm2.3\%$ enhancement of the variance σ^2 of displacement distributions when compared to flow experiments with water.

Keywords: NMR; Porous media; Cumulants; Non-Newtonian flow

Displacement encoding pulsed field gradient (PFG) nuclear magnetic resonance (NMR) experiments, such as classic diffusion experiments [1] or the 13-interval [2] alternating pulsed field gradient stimulated echo sequence (APGSTE) employed in this work, produces NMR signals equal to the ensemble average over all spins of their phase factors $S_q=\langle e^{iq\zeta}\rangle=\int e^{iq\zeta}P(\zeta)d\zeta$, where ζ is the displacement of a spin during the experimental evolution time Δ, q is set by PFGs and $P(\zeta)$ is the underlying distribution of molecular displacements. By implication, we consider unwanted coherence pathways to have been suppressed by phase cycling and spoiler gradients, and the definition Δ contains appropriate corrections for finite-length gradient pulses. The data are Hermitian ($S_q=S_{-q}*$) and can be analyzed by Fourier-transforming a set $\{S_q\}$ to obtain the volume-averaged propagator $P(\zeta)$ [3]. Fourier transform requires that data be sampled at adequate density [4] up to values of q such that S_q goes to 0. Alternatively, for small q, the data can also be analyzed using cumulant analysis [5]:

$$\ln\langle e^{iq\zeta}\rangle = \ln|\langle e^{iq\zeta}\rangle| + i\theta = \sum_{j=1}^{\infty}\frac{(iq)^j}{j!}X_j \qquad (1)$$

where θ is the phase of NMR signals and X_i are cumulants. Matching the real and imaginary parts shows that θ is expanded in odd powers of q and, therefore, has odd q-space inversion symmetry $\theta_q=-\theta_{-q}$. The logarithm of the magnitude $|S_q|$ of NMR signals is expanded in even powers of q and has even q-space inversion symmetry $\ln|S_q|=\ln|S_{-q}|$. The cumulant analysis of displacement encoding NMR data is useful for several practical reasons. Firstly, the first three cumulants take particularly simple forms $X_1=\langle\zeta\rangle$, $X_2=\langle(\zeta-\langle\zeta\rangle)^2\rangle=\sigma^2$ and $X_3=\langle(\zeta-\langle\zeta\rangle)^3\rangle=\gamma^3$, which are the mean, variance and third central moment, respectively. These scalar measures of displacement distributions are handy for comparisons between theory, simulation and experiment; furthermore, one can publish the data with error bars, adding quantitative meaning to such comparisons. Secondly, low-q cumulant data are accessible even when gradient strengths available in the laboratory are weak. Finally, measuring at

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low q permits the use of short PFG encoding times, which is particularly important for limiting magnetization losses in the presence of flow or diffusive displacements through internal fields, as they occur in rocks or samples containing gas bubbles. In this paper, we describe an algorithm for fitting in a self-consistent way [6] cumulants associated with non-Gaussian distributions, and we illustrate its use with one low-q data set obtained from a flow experiment through a sandstone. The algorithm requires Hermitian symmetrization of the data prior to their analysis in order to remove small deviations from hermiticity, which are typically caused by postpulse eddy currents. We discuss the benefits and limits of validity of the symmetrization step. Finally, we apply the cumulant analysis to Newtonian and non-Newtonian flows in bead packs.

For Gaussian displacement distributions, cumulant analyses are simple because all cumulants above the second vanish. PFG-derived diffusion data measuring Gaussian displacements are analyzed by plotting the logarithm of the magnitude of NMR signals against q^2 and by reading the slope of the straight line to determine the diffusion coefficient [1]. For non-Gaussian displacement distributions, higher-order terms do not vanish. Nevertheless, we want to fit the data to obtain the first three cumulants, using the truncated cumulant expansion, at small q:

$$\theta(q) = \langle\zeta\rangle q - \frac{1}{6}\gamma^3 q^3 \tag{2}$$

$$\ln|S(q)| = -\frac{1}{2}\sigma^2 q^2. \tag{3}$$

For a good fit to the data, the distribution of residuals must be free of systematics and Gaussian. We consider two effects as giving rise to systematic residuals. Firstly, they appear for fit ranges above some maximal fit range $|q_{\max}|$, where the truncated cumulant expansion is insufficient to

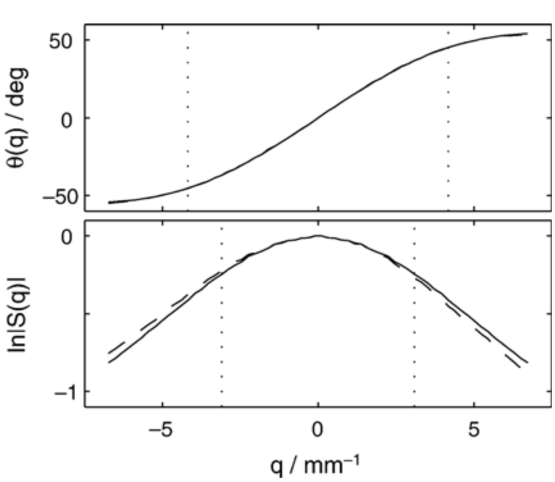

Fig. 1. Low-q data from displacement encoding an NMR experiment on water flow through a sandstone: $\langle\zeta\rangle$=233 μm, Δ=200 ms, plotted against q. Solid lines represent symmetrized data; dashed lines represent raw data. Dotted lines indicate maximal fit ranges determined automatically, as described in the text.

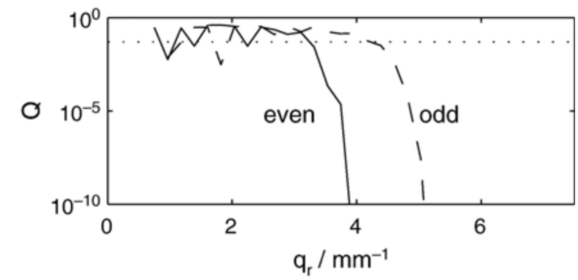

Fig. 2. Quality Q of odd and even cumulant fits to the symmetrized data shown in Fig. 1 as a function of fit range q_r. The horizontal dotted line indicates the threshold Q_c=0.05. Large fit ranges for which $Q<Q_c$ corresponds to non-negligible contributions of the fourth and fifth cumulants to the signal, for the even and odd fits, respectively.

describe the data. We will use this consistency requirement to define $|q_{\max}|$ later on. Secondly, the data may not be strictly Hermitian due to experimental artifacts breaking the odd and even q-space inversion symmetries of Eqs. (2) and (3). The non-Hermitian component is a small fraction of the signal—if it were large there would be something seriously wrong with the experiment—but it may not be small when compared to the noise on the data.

For quantitative illustration, we now consider two APGSTE echoes with broken Hermitian symmetry E_q=$A\mathrm{e}^{i\theta}$ and E_{-q}=$(A+\epsilon)\mathrm{e}^{-i(\theta+\alpha)}$, where ϵ and α parameterizes a small deviation from hermiticity. Suppose we want to fit these signals, using standard least squares methods, to find our best estimate of the true Hermitian signal by F_q=F^*_{-q}=$B\mathrm{e}^{i\phi}$. In this simple case, we can manually perform the least squares fit by writing down the two terms of the respective sums of squared residuals χ^2_{M}=$(A-B)^2$+$(A+\epsilon-B)^2$ for magnitudes and χ^2_v=$(\theta-\phi)^2$+$(-\theta-\alpha+\phi)^2$ for phases. Minimizing the expressions of χ^2 with respect to B and ϕ, we obtain B=A+ϵ/2 and ϕ=θ+α/2; thus, the fitted result is $F_q = (A+\frac{1}{2}\varepsilon)e^{i(\theta+\alpha/2)}$. Now we construct hermitically symmetrized data $H_q = \frac{1}{2}\left(E_q + E_{-q}\right)$ for comparison with the fitted F_q. Using the definition of our example, $H_q = \left(A\cos(\alpha/2) + \frac{1}{2}\varepsilon e^{i\alpha/2}\right)e^{i(\theta+\alpha/2)}$. We observe that by keeping terms to first order in (α,ϵ), the symmetrized H_q reduces to the least squares result F_q. Consequently, for small α and ϵ/A, we can fit Eqs. (2) and (3) to either the unsymmetrized E_q or to the symmetrized H_q; the fit results will be the same. We will fit to symmetrized data because the χ^2 and noise v^2 evaluated from these fits do not include contributions from symmetry breaking experimental artifacts.

We now maximize the range over which symmetrized data can be fitted well. The consistency of the distribution of residuals with a Gaussian distribution, for a given fit range q_r, is a function of χ^2 and v^2, the number of degrees of freedom m of the fitting function and the number of data points N. It is measured by the incomplete Γ function:

$$Q \equiv \frac{1}{\Gamma(a)} \int_x^\infty e^{-t} t^{a-1} dt \tag{4}$$