NMR Measurement of Nonlocal Dispersion in Complex Flows

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The flow and diffusion driven separation of initially adjacent liquid molecules is known as dispersion. The primary physical quantity describing this process, the nonlocal dispersion tensor, provides insight regarding both the spatial and temporal correlations of molecular velocity fluctuations in complex flows. We here propose and demonstrate a nuclear magnetic resonance method for the measurement of this tensor, validating its implementation for the case of cylindrical Couette flow, and demonstrating its application to the study of fluid dispersion in a random bead pack.

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The migration apart of initially adjacent molecules, under flow and diffusion, underpins processes as diverse as cellular mitosis, blood perfusion in the brain, chromatography, filtration, secondary oil recovery, ground water remediation, catalysis, and the behavior of packed bed reactors. The fundamental physics of this stochastic process, known as dispersion, is governed by a subtle interplay of diffusion across streamlines, flow bifurcation, and holdup in stagnation flows or boundary layers. At high Reynolds number (Re), flow turbulence provides an additional mechanism for dispersion. The physics of dispersion resulting from diffusion across streamline flow was first examined theoretically by Taylor [1]. Given the significance of dispersion to so many physical processes of interest [2,3], the body of both theory and experimental work in fluid dispersion is considerable.

Because the physics of dispersion is governed by stochastic processes, the spatiotemporal correlations present in the velocity field provide crucial insight. In 1987 Koch and Brady [4] defined a primary function informing on these correlations, the nonlocal dispersion tensor, $\mathbf{D}^{\mathrm{NL}}$. This tensor describes the way in which the flow field is correlated at points separated in space and time. Since then, the tensor has been the subject of several theoretical studies [5] but has so far proven elusive in measurement. However, in 1996 Sternberg *et al.* [6] reported a one-dimensional tracer measurement in which the effects of nonlocal dispersion could be observed. The present Letter reports on the first full measurement of $\mathbf{D}^{\mathrm{NL}}$ using a noninvasive method in which all elements of the tensor are observable. Our method is based on nuclear magnetic resonance (NMR), in which special magnetic field gradient pulses provide the necessary signal encoding to track the velocities and spatial displacements of water molecules labeled by their proton spin states. We demonstrate this method experimentally for the particular spatiotemporal example of cylindrical Couette flow, a case where $\mathbf{D}^{\mathrm{NL}}$ may be exactly calculated. We then demonstrate the measurement of an element of $\mathbf{D}^{\mathrm{NL}}$ for dispersive low Re flow in a random bead pack.

We begin by defining a steady state Eulerian flow field $\mathbf{v}_E(\mathbf{r}, t) = \mathbf{v}_E(\mathbf{r})$ and stationary Lagrangian flow ensemble $\mathbf{v}_L(t)$ with mean flow $\langle \mathbf{v} \rangle$. The fluctuating (zero mean) parts of the velocities, $\mathbf{u}_E(\mathbf{r})$ and $\mathbf{u}_L(t)$, are thus defined by

$$\mathbf{v}_E(\mathbf{r}) = \mathbf{u}_E(\mathbf{r}) + \langle \mathbf{v} \rangle \tag{1}$$

and

$$\mathbf{v}_L(t) = \mathbf{u}_L(t) + \langle \mathbf{v} \rangle. \tag{2}$$

The asymptotic dispersion tensor, $\mathbf{D}^*$, is described in terms of the velocity autocorrelation function (VACF) of the Lagrangian velocities by [4,7]

$$\mathbf{D}^* = \lim_{t\to\infty} sym \int_0^t d\tau \langle \mathbf{u}_L(0)\mathbf{u}_\mathbf{L}(\tau) \rangle, \tag{3}$$

where $\langle \cdots \rangle$ represents the Lagrangian ensemble average. Note that $\mathbf{D}^*$ may also be defined in Einsteinian terms involving the dyadic of mean square displacements, $\sigma^2(t)$ by [7,8]

$$\mathbf{D}^* = \lim_{t\to\infty} \frac{1}{2} \frac{d\sigma^2}{dt}. \tag{4}$$

The VACF link with the Eulerian field may be made via a propagator $P(\mathbf{r}|\mathbf{r}', \tau)$ which describes the conditional probability that a fluid element initially at $\mathbf{r}$ will migrate to $\mathbf{r}'$ at a later time τ. $P(\mathbf{r}|\mathbf{r}', \tau)$ is governed by the microscale advection-diffusion equation for the system. Given a starting probability $P(\mathbf{r})$, the velocity autocorrelation function becomes

$$\langle \mathbf{u}_L(0)\mathbf{u}_\mathbf{L}(\tau) \rangle = \int d\mathbf{r}' \int d\mathbf{r} u_E(\mathbf{r}) P(\mathbf{r}) P(\mathbf{r}|\mathbf{r}', \tau) u_E(\mathbf{r}'). \tag{5}$$

Clearly, just as the VACF contains details of the temporal correlations otherwise buried in the asymptotic dispersion tensor, so the expression $\int d\mathbf{r} u_E(\mathbf{r}) P(\mathbf{r}) \times P(\mathbf{r}|\mathbf{r}', \tau) u_E(\mathbf{r}')$ contains spatial correlation information buried in the VACF. This integral has been termed by Koch and Brady [4] the nonlocal dispersion tensor. It is a

primary quantity of interest in any detailed description of dispersive flow. Writing this quantity in terms of relative displacements in time and space we have

$$\mathbf{D}^{\mathrm{NL}}(\mathbf{R},\tau)=\int d\mathbf{r}u_E(\mathbf{r})P(\mathbf{r})P(\mathbf{r}|\mathbf{r}+\mathbf{R},\tau)u_E(\mathbf{r}+\mathbf{R}) \quad (6)$$

and

$$\langle \mathbf{u}_L(0)\mathbf{u}_\mathbf{L}(\tau)\rangle = \int d\mathbf{R}\mathbf{D}^{\mathrm{NL}}(\mathbf{R},\tau) \quad (7)$$

and

$$\mathbf{D}^* = \lim_{t\to\infty} sym \int_0^t d\tau \int d\mathbf{R}\mathbf{D}^{\mathrm{NL}}(\mathbf{R},\tau). \quad (8)$$

Nuclear magnetic resonance (NMR) provides a nearly ideal tracer method for the measurement of dispersion in that every single molecule is labeled noninvasively by its local precession frequency in a nonuniform magnetic field [9,10], the tracer being distributed uniformly within the pore space. Of course, in principle, magnetic resonance imaging (MRI) allows us to measure the complete Eulerian velocity field, to some specified resolution, limited by the intrinsic sensitivity of the NMR method. If, however, an ensemble-averaged signal from the entire sample is acquired, then resolution in time or with respect to molecular displacements may be optimized [9]. Foremost among such ensemble-averaged methods for the measurement of molecular displacements is pulsed gradient spin echo nuclear magnetic resonance (PGSE NMR) [9,11]. This class of experiment not only allows simple analysis of ensemble-averaged mean-squared displacements over a well-defined time interval [10], but has also been shown to be effective in measuring the VACF for porous media flow [12].

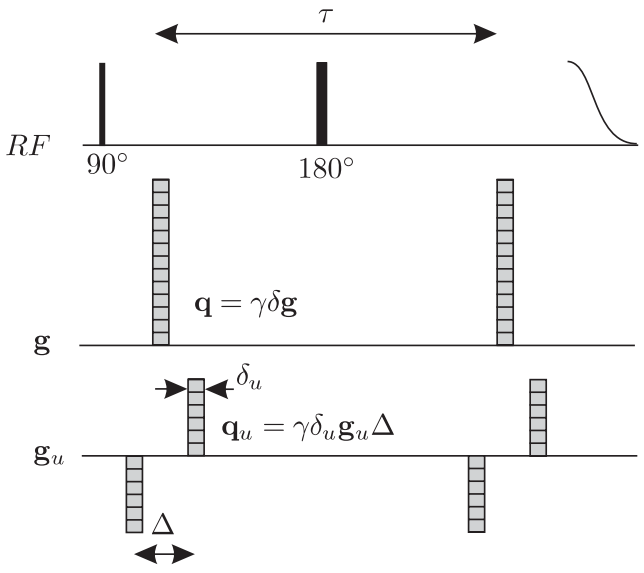

FIG. 1. Schematic NMR pulse sequence and effective gradients needed to measure $\mathbf{D}^{\mathrm{NL}}(\mathbf{R},\tau)$. $\mathbf{g}$ and $\mathbf{g_u}$ are stepped independently.

The tensor $\mathbf{D}^{\mathrm{NL}}(\mathbf{R},\tau)$ should also be amenable to direct measurement using PGSE NMR. One earlier such conjecture, by Ding and Candela [13], indicated the need to encode the NMR signal with information concerning the displacement propagator. However, the measurement of $\mathbf{D}^{\mathrm{NL}}$ requires that the experiment also be sensitive to velocities separated in space and time.

The essentials of our spin echo method are shown in Fig. 1 (technical details will be published separately). Phase encoding events occur in two clusters. In the first, an oppositely signed pair of weak gradient pulses, separated by duration Δ, provide a phase shift $\exp(i\mathbf{q}_u.[\mathbf{u}_E(\mathbf{r})+\langle\mathbf{v}\rangle])$ arising from the instantaneous velocity of the spin-bearing molecules, while another gradient pulse applies a position-dependent phase shift $\exp(i\mathbf{q}.\mathbf{r})$. This cluster is required to be applied over a time scale shorter than the correlation time for velocity fluctuations. After storing the magnetization for a period τ, a second encoding cluster is applied, such that the position-encoding pulse has fixed opposite sign, while the sign of the second $\mathbf{q}_u$ pair may be chosen. Note that $\mathbf{q}=\gamma\delta\mathbf{g}$ is the product of the gradient pulse amplitude $\mathbf{g}=\nabla B$, its duration, δ, and the magnetogyric ratio, γ, and is conjugate to the spin displacements $\mathbf{R}$ [9]. For convenience we include the pulse separation Δ as an additional factor in $\mathbf{q}_u$ so that this wave vector is conjugate to the velocity. $\mathbf{q}$ and $\mathbf{q}_u$ are independently varied as separate dimensions of the experiment.

The normalized signal acquired at the final spin echo may be written

$$\begin{aligned}E(\mathbf{q},\pm\mathbf{q}_u,\pm\mathbf{q}_u) = \int d\mathbf{R}\exp[i\mathbf{q}\cdot(\mathbf{R})]\int d\mathbf{r}\times\exp\{\pm i\mathbf{q}_u \\ \cdot[\mathbf{u}_E(\mathbf{r})+\langle\mathbf{v}\rangle]\times P(\mathbf{r})P(\mathbf{r}|\mathbf{r}+\mathbf{R},\tau) \\ \times\exp\mp i\mathbf{q}_u\cdot[\mathbf{u}_E(\mathbf{r}+\mathbf{R})+\langle\mathbf{v}\rangle]\}.\end{aligned} \quad (9)$$

Let $F_\mathbf{q}\{\ldots\}$ represent inverse Fourier transformation with respect to $\mathbf{q}$. Then

$$\begin{aligned}F_\mathbf{q}\{E(\mathbf{q},\mathbf{q}_u,-\mathbf{q}_u)\} = \int d\mathbf{r}\exp[i\mathbf{q}_u.\mathbf{u}_E(\mathbf{r})]P(\mathbf{r})P(\mathbf{r}|\mathbf{r}+\mathbf{R},\tau) \\ \times\exp[-i\mathbf{q}_u.\mathbf{u}_E(\mathbf{r}+\mathbf{R})].\end{aligned} \quad (10)$$

We will be concerned with the low $\mathbf{q}_u$ limit of the experiment where both $\mathbf{q}_u$ pulses are applied collinearly, with amplitude q_u, but with independent sense. It is possible to find a suitable superposition of experiments in which the only second order terms surviving are $q_u^2\int d\mathbf{r}u_E(\mathbf{r})P(\mathbf{r})\times P(\mathbf{r}|\mathbf{r}+\mathbf{R},\tau)u_E(\mathbf{r}+\mathbf{R})$. In particular, in $\lim q_u^2\to 0$

$$4q_u^2\mathbf{D}^{\mathrm{NL}}(\mathbf{R},\tau) = F_{\mathbf{q}}\{E(\mathbf{q},q_u,-q_u)\} + F_{\mathbf{q}}\{E(\mathbf{q},-q_u,q_u)\} - F_{\mathbf{q}}\{E(\mathbf{q},q_u,q_u)\}\exp(-i2q_u\langle v\rangle) - F_{\mathbf{q}}\{E(-\mathbf{q},-q_u,-q_u)\}\exp(i2q_u\langle v\rangle). \quad (11)$$

At first sight, the phase correction factor, $\exp(i2q_u\langle v\rangle)$, appears to complicate the analysis. However, this factor is only present when there is a net velocity in the chosen direction and in any case can be easily obtained experimentally from the phase shift associated with signal $E(0, q_u, 0)$.

A simple Couette cell provides an excellent system for testing the NMR measurements of $\mathbf{D}^{\mathrm{NL}}(\mathbf{R},\tau)$. Neglecting diffusion, the velocity field is easy to calculate and is a function of radial position r only. While there is no Taylor dispersion, a Couette cell still shows interesting velocity correlations when sensitive to only one velocity component. The Couette cell is constructed from NMR tubes such that, in accordance with Fig. 2, $r_{\mathrm{out}} = 4.35$ mm and $r_{\mathrm{in}} = 3.25$ mm and the inner tube was rotated with a frequency of 4 Hz. To minimize diffusion effects the sample was 10 000 MW poly(dimethylsiloxane).

The velocity distribution in a Couette cell is given by

$$v(r) = \frac{V_{\max} r_{in}}{r_{\mathrm{out}}^2 - r_{\mathrm{in}}^2}\left(\frac{r_{\mathrm{out}}^2}{r} - r\right),$$

where $V_{\max}$ is the fluid velocity at r_{in}. The probability for the fluid element at a particular r to move a distance X in a time τ can be expressed as

$$P(X,r,t) = \frac{2r}{(r_{\mathrm{out}}^2 - r_{\mathrm{in}}^2)\pi X_{\max}}\left(1 - \frac{X^2}{X_{\max}^2}\right)^{-1/2},$$

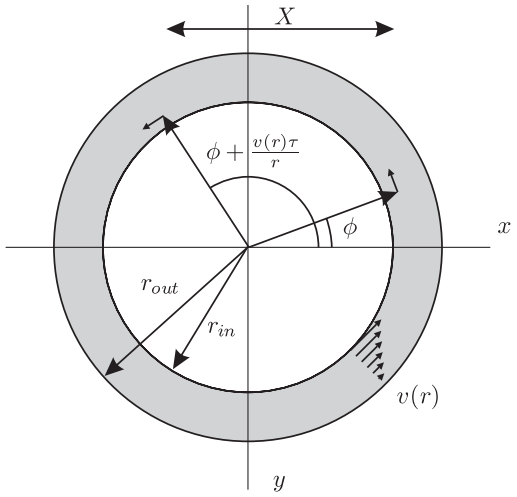

FIG. 2. Relevant coordinate system and velocities for flow in a Couette cell. The velocity is a function of r only. Measurement can be sensitive to either X or Y displacement and either x or y components of velocity.

where $X_{\max} = 2\sin\frac{v(r)\tau}{2r}$. However, since the measured component, v_x or v_y, depends not only on r but also ϕ we need an expression that is a function of ϕ also. The final position of any fluid element is known from its initial position; thus, the propagator can be written as a delta function. For example, the component $D_{xx}^{\mathrm{NL}}(X,\tau)$ can be expressed as an integral over all starting position as

$$D_{xx}^{\mathrm{NL}}(X,\tau) = \int_0^{2\pi}\int_{r_{\mathrm{in}}}^{r_{\mathrm{out}}} v(r)\cos\phi\,\delta(r\cos\phi' - r\cos\phi - X) \times v(r)\cos\phi' dr d\phi, \quad (12)$$

where $\phi' = \phi + \frac{v(r)\tau}{r}$. Other components of the tensor can be found similarly.

The experiments were performed using a Bruker Avance 400 MHz instrument equipped with three axis microimaging gradients, the NMR signal being obtained from the protons of poly(dimethylsiloxane) molecules. The method is based on a bipolar [14] PGSE NMR sequence incorporating a stimulated echo "z-storage" interval [12].

Figure 2 shows the relevant velocities and axis system for laminar flow in a Couette cell defined by r_{in} and r_{out}; in the transverse plane we have 8 components of $\mathbf{D}^{\mathrm{NL}}(\mathbf{R},\tau)$ to measure but due to symmetry only three independent components remain $D_{xx}^{\mathrm{NL}}(X,\tau)$, $D_{xx}^{\mathrm{NL}}(Y,\tau)$, and $D_{xy}^{\mathrm{NL}}(X,\tau)$. Examples of two of these components are shown for various times in Fig. 3. The agreement between measurement and calculation is excellent. Of particular note is how the structure in the graphs change dramatically over relatively short times (<1 revolution). As shown in Fig. 4 the

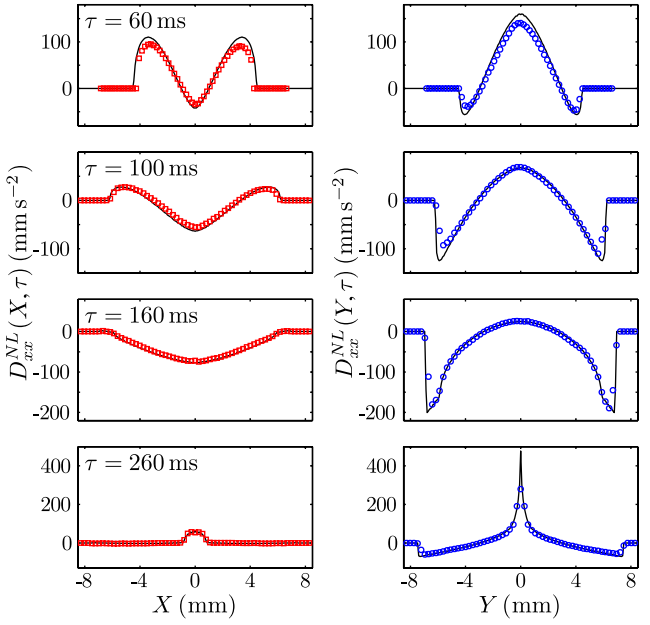

FIG. 3 (color online). $D_{xx}^{\mathrm{NL}}(X,\tau)$ (□) and $D_{xx}^{\mathrm{NL}}(Y,\tau)$ (○) measured in a Couette cell with $r_{\mathrm{out}} = 4.35$ mm and $r_{\mathrm{in}} = 3.25$ mm; the inner tube was rotated with a frequency of 4 Hz. The solid line shows the calculated results.

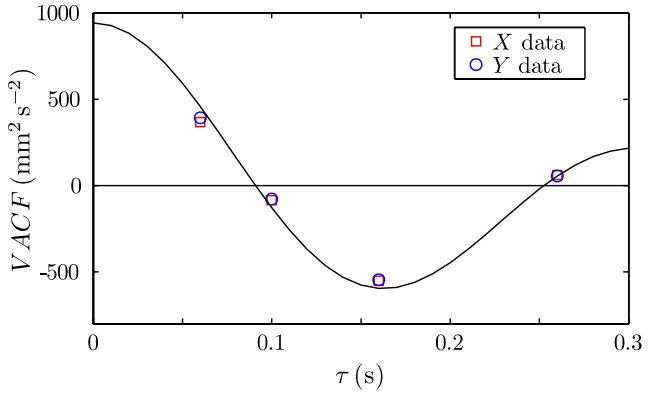

FIG. 4 (color online). The calculated VACF in a Couette cell. Overlaid is the measured VACF from the nonlocal dispersion measurements.

integral over displacement for $D_{xx}^{\mathrm{NL}}(Y,\tau)$ and $D_{xx}^{\mathrm{NL}}(X,\tau)$ give the same result, namely, the velocity autocorrelation function at time τ. However, the structure remains at long time in $D_{xx}^{\mathrm{NL}}(Y,\tau)$ whereas $D_{xx}^{\mathrm{NL}}(X,\tau)$ tends to zero for all X as τ gets large.

Having shown that the nonlocal dispersion tensor may be measured in simple Couette flow, we note that the method is equally applicable to more complex flows. One example, shown in Fig. 5, being flow through a porous medium, in this case a randomly packed bed of 0.5 mm spheres. We find that the oscillatory character seen in Fig. 5 agrees very well with calculations of this tensor element in random bead backflow, using Lattice-Boltzmann modeling along with Monte Carlo simulation of superposed Brownian motion, an approach which has previously produced good agreement with measured velocity distributions [15]. Our D^{NL} comparisons, over a range of times and displacements, will be published elsewhere.

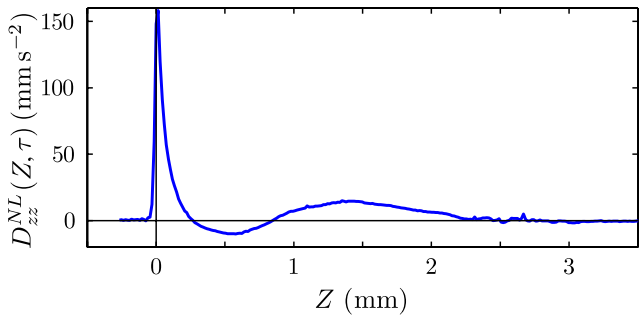

FIG. 5 (color online). The measured $D_{zz}^{\mathrm{NL}}(Z,\tau)$ for flow in a beadpack of monosized spheres, $d_{\mathrm{bead}} = 0.5$ mm, $Pe = 2000$, and a tube velocity of 8.1 mm s^{-1}. A decorrelation lobe is clearly visible for particles that have moved one bead diameter.

It is worth noting that all elements of $\mathbf{D}^{\mathrm{NL}}(\mathbf{R},\tau)$ are accessible by NMR, simply by appropriate choice of the $\mathbf{q}$ and $\mathbf{q}_u$ gradients. Furthermore, NMR signal chemical shifts may be used to distinguish different molecular species in two-phase or multiphase flow. Nonlocal dispersion tensor elements can be measured over a continuous range of delay time, τ, lower limited by the pulse cluster duration, and upper limited by the longitudinal spin relaxation time. For liquids 1 ms $\gtrsim \tau \gtrsim$ 1 s with other limits for NMR of gases. Measurement of $\mathbf{D}^{\mathrm{NL}}(\mathbf{R},\tau)$ may help resolve the complex relationship between spatial and temporal decay in velocity correlations, anomalous dispersion, and the trend to asymptotic limits [16].

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