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# Taylor dispersion and molecular displacements in Poiseuille flow

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We have used pulsed gradient spin echo (PGSE) NMR to measure longitudinal displacements of octane molecules undergoing Poiseuille flow in a 150 $\mu$m diameter pipe, accessing time scales which approach the Taylor dispersion limit. We monitor the change in displacement distribution which occurs as molecules undergoing Brownian motion sample an increasing proportion of the ensemble of streamlines, observing the effects of wall collisions and the gradual transition of the propagator from Poiseuille to Taylor-Aris behavior. The further use of a double PGSE sequence allows the direct measurement of the stochastic part of the motion alone. [S1063-651X(99)50310-3]

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Interactions between stochastic and deterministic motion play an elemental role in transport phenomena in natural and industrial systems. Research in this area has been of interest to engineers and physicists for many years [1,2] and significant current research is focused on modeling transport using dynamical systems which generate both types of motion [3–5]. One fundamental issue concerns the time dependent behavior of the fluid molecular displacements, one traditional measure being the variance, the second moment of the displacement probability density. Here we utilize pulsed gradient spin echo nuclear magnetic resonance (PGSE NMR) to directly measure the time dependence of the complete probability density for molecular displacements, using as our test example, the case of laminar capillary flow. Our results clearly elucidate the interactions between stochastic and deterministic molecular motions that result in the transition of the propagator from Poiseuille flow to Taylor-Aris dispersion.

In laminar pipe flow, the velocity gradients associated with shear result in the gradual separation of molecules which begin their history in close proximity on adjacent stream lines. Were the flow to be reversed however the separations would be canceled as all molecules returned to their initial displacements at a common time. This coherent spreading is to be contrasted with the spreading which arises from the stochastic sampling of velocities as self-diffusion causes molecules to cross the streamlines. For such incoherent spreading, flow reversal would not cancel the resulting separation. The molecular scale interaction between convection and diffusion controls transport in pipe flow and analysis of this simple physical model, has led to the development of generalized dispersion theory [1], which finds broad application in many disciplines [6], such as interpreting measurements of polymer diffusion under shear, understanding the physical chemistry of chromatographic separations, and enhancing engineering processes involving multiphase transport.

''Taylor dispersion'' specifically refers to the increase in effective diffusion that arises from molecules randomly sampling streamlines with different velocities [2] and has become a generic term for averaged transport phenomena theories [1]. If dispersion is observed on a timescale such that the molecules have sampled many streamlines then the process follows a diffusive model, i.e., the displacement variance varies linearly with time. In 1953 Taylor [2], in a study of laminar pipe flow, derived the asymptotic form of the stochastic dispersive behavior for the longitudinal direction of transport. In 1982, Van den Broeck [7] derived exact expressions for dispersion applicable at all time scales. Given a pipe of radius $a$, average fluid velocity $U$, and self-diffusion coefficient $D_0$, the characteristic diffusion time scale is $a^2/D_0$ while the Peclet number is $Ua/D_0$. The convective time scale corresponds to the time $t$ used to make measurements of the longitudinal displacements. The short time ($t \ll a^2/D_0$) character of the dispersion is represented by the power series expansion $D_0+\frac{1}{6}U^2t+\frac{4}{3}D_0U^2/a^2t^2+\cdots$. Note that the term $\frac{1}{6}U^2t$ represents the coherent spreading associated with the velocity shear. By contrast the asymptotic case ($t \gg a^2/D_0$) leads to a time-independent dispersion coefficient $D_0+U^2a^2/48D_0$, the term $U^2a^2/48D_0$ being known as the Taylor dispersion coefficient while the complete expression, involving the additional dispersion due to longitudinal molecular self-diffusion, is known as the Taylor-Aris limit [2]. At both short and long times the additional dispersion is quadratic in the velocity. However, in the short time limit, increased molecular self-diffusion enhances dispersion while in the long term limit, dispersion is diminished with increasing self-diffusion as more rapid sampling of the ensemble of streamlines results in more effective motional averaging.

Traditional measurements of Taylor dispersion have relied on observations of longitudinal spreading of tracer particles or molecules and have encompassed length scales from millimetres to metres [6]. In all these prior measurements the stochastic dispersion and coherent spreading effects were both present. Pulsed gradient spin echo (PGSE) NMR has long been established as a method capable of separating these effects [8], an example being the time dependence of the effective diffusion due to turbulence in pipe flow [9]. In this Rapid Communication we report on measurement of Taylor dispersion in a 150 $\mu$m diameter pipe using PGSE

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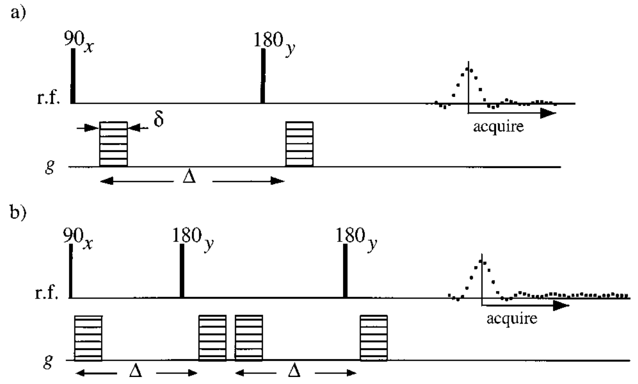

FIG. 1. (a) PGSE NMR experiment uses two narrow gradient pulses of amplitude $g$, duration $\delta$, and separation $\Delta$ to encode the spins for translational motion over the well-defined timescale, $\Delta$. The narrow pulse assumption requires $\delta \ll \Delta$. Note that the representation of the spin echo signal is schematic. Background gradients are insignificant in all the data reported here. (b) The double PGSE experiment encodes for fluctuations in the motion over the timescale $2\Delta$ as the phase shifts due to coherent flow during the first time interval $\Delta$ are canceled during the second time interval $\Delta$.

NMR methods. We are not only able to measure the dispersion coefficients but also to directly measure the longitudinal displacement distributions, and to do so over a wide range of reduced times that encompass the short and long time limits. The resulting distributions exhibit detailed structure associated with the impeded transverse diffusion as molecules at the pipe boundary collide with the walls. We compare these measurement distributions with those calculated by Monte Carlo simulations and find excellent agreement. Furthermore, we are able to separate the effect of coherent spreading and stochastic dispersion by means of a double spin echo technique which plays precisely the same role as flow reversal, all the while maintaining perfect steady state condition in the flow field. As a result we gain unique access to the stochastic motion over timescales (10 ms to 3 s) which, while much larger than the correlation time of molecular diffusion, are in a range where the effects of molecular sampling of streamlines provides the characteristic correlation time. These are the first measurements of the time dependence of the preasymptotic approach to Taylor dispersion separating the stochastic and deterministic portions and to our knowledge provide the first experimental verification of the preasymptotic dispersion theory [7].

Pulsed gradient spin echo NMR employs pairs of narrow magnetic field gradient pulses to label the positions of nuclear spins by the Larmor precession frequencies [8]. The basic experiment is shown in Fig. 1(a) in which the echo signal is given by

$$E=\int\int P(z_1)\exp(iqz_1)P_S(z_1,z_2|0,\Delta)\times\exp(-iqz_2)\,dz_1dz_2, \tag{1}$$

where $P_S(z_1,z_2|t_1,t_2)$ is a propagator that describes the conditional probability density for a molecule to displace from $z_1$ to $z_2$ in the time interval from $t_1$ to $t_2$ while $q$ is akin to a scattering wave vector and is given by the pulse area factor $\gamma g\delta$ where $\gamma$ is the nuclear magnetogyric ratio, $g$ the gradient amplitude, $\delta$ the pulse duration, and the usual narrow pulse conditions, $\delta \ll \Delta$ apply. Of course, we shall be concerned with the case where the magnetic field gradient is directed along the pipe axis, $z$.

Using the language of the average propagator [10], $\overline{P}_S(Z,t)$ where $Z=z_2-z_1$ and $t=t_2-t_1$, one may recast Eq. (1) as the Fourier relationship,

$$E(q)=\int \overline{P}_S(Z,\Delta)\exp(iqZ)\,dZ, \tag{2}$$

where $\overline{P}_S(Z,\Delta)$ describes the ensemble average probability that a spin will displace a distance $Z$ over the time duration $\Delta$ between the gradient pulses. Inverse Fourier transformation of $E(q)$ returns $\overline{P}_S(Z,t)$, the longitudinal displacement distribution. In the low $q$ limit

$$E\approx 1-\tfrac{1}{2}q^2\langle Z^2\rangle, \tag{3}$$

a relationship that can be used to define a dispersion coefficient [1,7] via $D^*=\langle Z(0,t)^2\rangle/2t$. Note, however, that this dispersion arises from the total molecular displacements $Z$ over the time interval $\Delta$ between the gradient pulses. We shall seek also to measure the dispersion which arises solely from stochastic displacements, $\delta Z$, namely, $D^*_{\text{stoch}}=\langle \delta Z(0,t)^2\rangle/2t$. Note that for the Taylor-Aris problem we expect $D^*=D^*_{\text{stoch}}$ at $t=0$ and in the asymptotic limit $t\rightarrow\infty$.

Figure 1(b) shows a variant (double PGSE) in which the effective phase shifts due to displacements are reversed in the two cycles. Now the resulting phase shift arises from fluctuations in the motion while all phase shifts due to coherent flow over the time interval $\Delta$ are canceled. The resulting signal is akin to that which would arise if the flow were reversed at the midpoint of the pulse sequence shown in Fig. 1(a). Let us define a streamline velocity $v$ such that for particles originating on that streamline the total displacement in the flow direction over time $t$ is given by $Z=vt+\delta Z(0,t)$. Equation (1) may therefore be recast as

$$\begin{aligned}E_D(q)=&\int\int\int P(v)P(v|\delta Z,\Delta)\\&\times\exp(iq\delta Z)P(v|\delta Z',2\Delta)\\&\times\exp(iq(\delta Z-\delta Z'))\,d\delta Z\,d\delta Z'\,\delta v,\end{aligned} \tag{4}$$

where $\delta Z=\delta Z(0,\Delta)$, $\delta Z'=\delta Z(0,2\Delta)$, and $P(v|\delta Z,t)$ is a conditional probability for a displacement to be $\delta Z'$ over the time $t$ for a particle originating on the streamline labeled by $v$. Thus it may be shown [11] that in the low $q$ limit

$$E_D(q)\approx 1-\tfrac{1}{2}q^2\{\langle \delta Z(0,2\Delta)^2\rangle-4\langle \delta Z(0,\Delta)\,\delta Z(\Delta,2\Delta)\rangle\} \tag{5}$$

so that the effective dispersion coefficient measured by the double PGSE NMR experiment over the total period $2\Delta$ is [11]

$$D^*_{\text{eff}}=D^*_{\text{stoch}}(2\Delta)-(1/\Delta)\langle \delta Z(0,\Delta)\,\delta Z(\Delta,2\Delta)\rangle. \tag{6}$$

Hence the double PGSE experiment of Fig. 1(b) returns the true stochastic dispersion coefficient in the asymptotic limits

$\Delta \gg \tau_c$, and $\Delta \rightarrow 0$ when the velocity field stochastic fluctuations are uncorrelated, while at finite values of $\Delta$ the difference between $D^*_{\mathrm{eff}}$ and the true stochastic dispersion coefficient, gives us a measure of the displacement correlation function $\langle \delta Z(0,\Delta)\,\delta Z(\Delta,2\Delta)\rangle$.

For the case of Taylor-Aris dispersion in a pipe, Van den Broeck used propagator eigenmode expansions to evaluate the mean-squared total displacement as a function of time. His result is equivalent to the quantity $\langle Z^2\rangle$ defined in Eq. (3), and which is measured using a single pulse pair PGSE experiment. We have used Van den Broeck's propagator eigenmode method to evaluate Eq. (6), for the case of the double pulse pair PGSE experiment [11]. We find that $D^*_{\mathrm{eff}}$ is identical to the apparent total dispersion calculated by Van den Broeck, evaluated at time $t=2\Delta$, minus a term $4a^4/D^2\Sigma_n(b_n^2/\mu_n^4)[1-\exp(-D\mu_n^2 2\Delta/a^2)]$ where the $b_n$ and $\mu_n$ are, respectively, Fourier-Bessel coefficients and Bessel function roots [7]. In the short time limit one finds that the double PGSE NMR apparent mean squared displacement is identically the full Van den Broeck dispersion at $2\Delta$, minus the coherent term due to the velocity shear.

In carrying out PGSE NMR measurements of longitudinal displacements we used octane ($D_0=2.35\times10^{-9}\,\mathrm{m}^2\,\mathrm{s}^{-1}$) flow in a 150 $\mu$m diameter capillary for which the characteristic time, $a^2/D_0$ is 2000 ms. A range of mean flow velocities on the order of a few $\mathrm{mm\,s}^{-1}$, corresponding to Reynolds numbers less than 1, were employed while the dispersion observation times accessed ranged from 50 to 3000 ms, this upper limit being determined by nuclear spin lattice relaxation. The apparatus comprised a commercial fused silica capillary (Polymicro Technologies, Inc.) of 120 mm length, cemented into a glass support tube to which inlet and outlet couplings to the 2 mm ID feed tubes had been attached. This capillary unit was centered in the 5 mm diameter RF coil within the vertical bore of a 7 T superconducting magnet and 300 MHz NMR signals were obtained from the protons resident in the octane molecules. Flow rates were controlled by adjusting the pressure head. Gradient pulse amplitudes were typically in the range 0.1 to 1 $\mathrm{T\,m}^{-1}$ with durations on the order of 500 $\mu$s. The background gradients were below 1 $\mathrm{mT\,m}^{-1}$ and, due to the use of stimulated echo techniques for long observation times, were insignificant in all measurements reported here.

Figure 2 shows a set of longitudinal displacement distributions, $\overline{P}_S(Z,\Delta)$, obtained over a range of observation times using the pulse sequence shown in Fig. 1(a), the average fluid velocity in all these measurements being 2.6 $\mathrm{mm\,s}^{-1}$. 64 $q$ steps were employed covering both positive and negative values up to a magnitude sufficient to avoid truncation artifacts in the subsequent Fourier transform. Superposed on the data are curves calculated by Monte Carlo simulations in which the identical experimental parameters were used, along with the known diffusion coefficient of octane. The agreement is remarkably good. These data exhibit a gradual transition from the near rectangular distribution expected for Poiseuille flow (convoluted with the Gaussian distribution for molecular diffusion), to the Gaussian distribution resulting from dispersion found in the asymptotic limit. Between these limits a distinct peaking in the distribution is found at low displacements, an effect caused by collision of the particles with the walls and a consequent inhibition of transverse diffusion and hence longitudinal dispersion. To our knowledge this is the first time that the temporal progression from Poiseuille to Taylor-Aris displacement distributions has been directly measured.

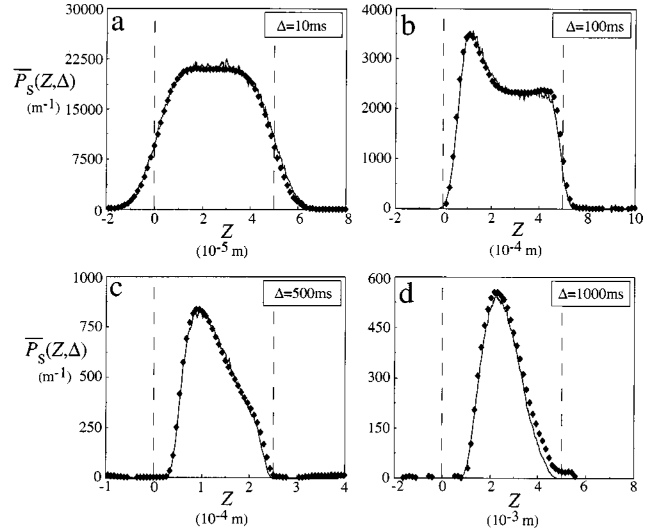

FIG. 2. Longitudinal displacement distributions, $\overline{P}_S(Z,\Delta)$, obtained over a range of observation times for octane flowing in a 150 $\mu$m capillary with $U=2.6\,\mathrm{mm\,s}^{-1}$. The results are obtained by a Fourier transform of the data acquired using the pulse sequence shown in Fig. 1(a). The solid lines were calculated using Monte Carlo simulations in which identical experimental parameters were used, along with the known diffusion coefficient of octane. The dashed lines demonstrate the limits to axial displacement that would occur in the absence of diffusion.

Figure 3 shows the echo attenuations observed in both the single and double PGSE experiments for the cases $\Delta$

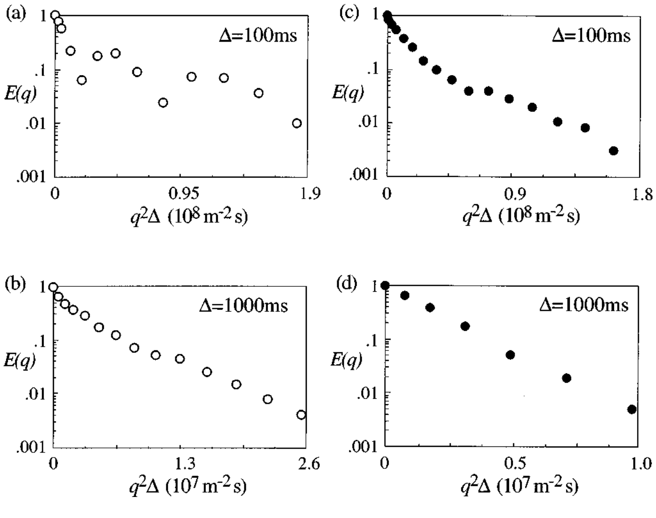

FIG. 3. Echo attenuations observed using the single PGSE sequence (closed circles) for octane flowing ($U=2.6\,\mathrm{mm\,s}^{-1}$) and (a) $\Delta=100$ ms and (b) $\Delta=1500$ ms. The closed circles in (c) and (d) result from the application of the double PGSE NMR sequence. Note in (a) the ''sinc modulation'' which arises because $E(q)$ is the Fourier spectrum of a nearly square displacement distribution [see Fig. 2(a)], and in (b) the almost linear decay indicates the displacement distribution is approaching a Gaussian [see Fig. 2(d)].

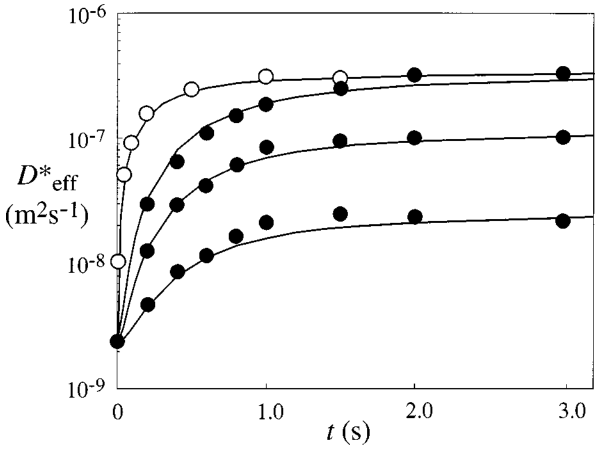

FIG. 4. The open circles show the effective total dispersion as measured from the initial attenuation of the single PGSE experiment for octane flowing with $U = 2.6\,\mathrm{mm\,s^{-1}}$. The solid circles show the stochastic dispersion results obtained using the double PGSE variant, the three values of $U$ being 2.6 $\mathrm{mm\,s^{-1}}$, 1.6 $\mathrm{mm\,s^{-1}}$ and 0.7 $\mathrm{mm\,s^{-1}}$. Superposed on the experimental data are the theoretical curves generated using a propagator eigenmode expansion approach [7,11]. The time axis corresponds to $\Delta$ for the single (open) PGSE data and $2\Delta$ for the double (solid) PGSE data.

$= 100$ ms and $\Delta = 1500$ ms and $U = 2.6\,\mathrm{mm\,s^{-1}}$. In both sets of experiments the initial decay was used to obtain the respective dispersion coefficient. We note however that in the shorter time double PGSE NMR experiments, the distribution of displacements suggested by the scattering pattern is far from Gaussian, again indicative of the fact that the asymptotic limit has not yet been achieved. Clearly such measurements have the potential to provide quite detailed information concerning the stochastic part of the longitudinal displacements and their temporal correlations.

The open dots in Fig. 4 show the effective total dispersion as measured from the initial attenuation of the single PGSE experiment while the open circles show the dispersion results of the double PGSE variant. Superposed on the four sets of data are solid curves generated using Van den Broeck's analytic expression for the total dispersion [7] and our expression [11] for the double PGSE evaluation of the stochastic dispersion, $D^*_{\mathrm{eff}}$. For average velocity $U = 2.6\,\mathrm{mm\,s^{-1}}$ a comparison between single (open circles) and double (closed circles) PGSE attenuations can be made. In addition the double PGSE experiment results are shown for $U = 1.6\,\mathrm{mm\,s^{-1}}$ and $U = 0.7\,\mathrm{mm\,s^{-1}}$. The agreement of all the curves with the respective data sets is excellent for all velocities over all times. Note that in the asymptotic limit, $t \gg a^2/D_0$, both the single and double PGSE experiments return the absolute Taylor-Aris value for the system parameters used. At an observation time of 3000 ms we are approaching this asymptotic limit.

Recently there has been significant application of the PGSE technique to study the time evolution of molecular displacements in porous media flow [12–15]. Such studies are complicated by the irregular geometries, the wide range of Reynolds and Peclet numbers which may prevail, and the fact that mechanical, holdup and Taylor dispersion all play a role. We suggest that our results for the simple laminar pipe flow case may provide a useful template. In particular we have shown that the detailed and useful structure present in the molecular displacement distributions is clearly and accurately revealed by the PGSE NMR method. Furthermore, we find utility in the flow compensation effects of the double PGSE NMR approach, which elucidates the stochastic portion of the motion, albeit in the face of some subtle influences which arise from correlations in the flow field. It is our hope that data from such NMR measurements will be of value in the current debate concerning the existence of asymptotic dispersion coefficients in solid-liquid systems of fixed and mobile beds [16,17] and in the exploration of transport phenomena in nonlinear fluid flows [3,4].

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