Correlation spectroscopy is an analytical technique that can identify the residence time of reflective or fluorescent particles in a measurement spot, allowing particle velocity or diffusion to be inferred. We show that the technique can be applied to data measured with a time-domain terahertz sensor. The speed of reflectors such as silica ballotini or bubbles can thus be measured in fluid samples. Time-domain terahertz sensors can therefore be used, for the first time, to measure rheological properties of optically opaque fluids that contain entrained reflectors, such as polyethylene beads.

The transparency of many optically opaque solids and fluids to terahertz radiation allows terahertz time-domain sensors to noninvasively measure chemical spectra and image three-dimensional structures inside previously inaccessible systems [1]. Changes over time of the internal structure of specimens, such as the ingress of a hydration front into a polymer sample, have been observed using such methods [2]. We show in this Letter that the method of correlation spectroscopy [3], developed for confocal fluorescence microscopy, can be applied to data from a time-domain terahertz sensor to measure particle velocity as a spot measurement, and also to measure a one-dimensional velocity profile of a fluid.

In terahertz pulsed imaging, a subpicosecond pulse of terahertz radiation is focused into a beam that is mechanically scanned over a sample in lateral x- and y-directions, and time-of-flight measurements of the reflected radiation are used to obtain z-positions of reflective features. Although the narrowest focus of such a beam is diffraction-limited to about 200 μm in diameter, and the axial position is determined from the time-of-flight data with a resolution limited by the pulse duration, this spot-scanning system can support many of the same measurements made by an optical confocal microscope—except on a coarser scale, and often in optically opaque media such as polymers and ceramics.

An important confocal imaging technique that we believe has not previously been adapted to terahertz instruments is fluorescence correlation spectroscopy (FCS). In FCS, the fluorescence intensity from a static observation volume within a fluid specimen is recorded for a period of typically milliseconds or seconds. When the fluid contains dilute fluorescent species that move, by diffusion or advection (flow), the varying number and positions of fluorophores in the observation volume cause the emitted light intensity to fluctuate. The durations of the "bumps" in the fluorescence signal depend on the speeds of the fluorophores and the size of the observation volume. The correlation time of the fluorescence signal can be evaluated using established mathematics, and this can be related to the speed of a fluid containing entrained fluorophores. FCS can also be used to identify the numerical density of fluorophores, their diffusion coefficient, and fluid viscosity [3]. It is also established that reflective particles may be used instead of fluorescent probe molecules [4], and it is this approach that we adapt for terahertz imaging.

In correlation spectroscopy, it is typically assumed that the response function of the measurement instrument, usually a confocal microscope, is described by a prolate ellipsoidal Gaussian observation volume [5]. The signal $I(x, y, z)$ that is detected from a point source at position $(x, y, z)$ therefore has the following form:

$$I(x, y, z) = I_0 \exp \left( \frac{-2(x^2 + y^2 + (\xi)^2)}{w^2} \right), \quad (1)$$

where $w$ defines the lateral spot width, and $\xi w$ its axial width. A calibration measurement is needed to establish that Eq. (1) describes the detection of particles by the terahertz sensor, and to determine $w$. Provided that this is established, the autocorrelation of the terahertz reflection signal from a fluid containing randomly distributed reflectors should be identical to the behavior that has been established for FCS. If the fluctuation of a signal is defined as $\delta I = (I - \bar{I})$ where $\bar{I}$ is the mean intensity, the normalized autocorrelation $G$ is given as follows:

$$G(r) = \frac{\int \delta I(t)\delta I(t+r) \, dt}{\int \delta I(t)\delta I(t) \, dt}. \quad (2)$$

In the case of particles moving at uniform velocity with negligible diffusion, the expected autocorrelation curve was
established as Eq. (3), where $\tau_{\text{flow}} = w/V$ for uniform particle flow of speed $V$ in the $x$-direction, and $N$ is the average number of particles within the observation volume [3]:

$$G(r) = \frac{1}{N} \exp\left(-\frac{\tau}{\tau_{\text{flow}}}^2\right).$$

(3)

This enables the particle velocity to be inferred from experimentally measured terahertz reflection signals, by fitting the value of $\tau_{\text{flow}}$ to the normalized autocorrelation of the detected signal.

Experimental measurements of terahertz reflection were made with a commercial time-domain terahertz sensor (TPI imaga 2000, Teraview Ltd., Cambridge, UK) with a focal length of 7 mm, and an established optical setup [6] in which we simply replaced the solid sample with a fluid sample. The instrument emits subpicosecond pulses generated from a Ti:sapphire laser [7], and the reflected terahertz radiation is captured by the same lens system used for illumination. The axial resolution is about 50 $\mu$m. First, calibration images were captured of silica ballotini (Q.A. Equipment Ltd., UK, density 2640 kg/m$^3$, diameter 425 $\mu$m) that were fixed to a mirror (Thorlabs, flatness 100 nm) with double-sided tape and immersed in paraffin oil (Sigma Aldrich UK, density 880 kg/m$^3$, and kinematic viscosity 101 ± 5 mPa·s measured on a Brookfield viscometer at 20°C). The sample was rastered through the beam to capture a reflection intensity image [6], which confirmed that the assumption of a Gaussian point spread function with $w = 350$ $\mu$m was approximately valid for this setup when the sample was in focus. Interestingly, the backreflected images had a similar value of $w$ for all the sizes of ballotini in this study, perhaps because the signal was dominated by reflection from a single point of perpendicular surface on the glass spheres. Therefore the terahertz reflection signal from the ballotini can be used to infer particle velocity via Eq. (3) without much difficulty.

To perform terahertz correlation velocimetry as a spot measurement, silica ballotini of diameters 212, 425, 600, and 850 $\mu$m were separately dispersed into 1 ml volumes of the paraffin oil so that the particles comprised 1% vol. of the fluid. Drop-time observations were used to establish the actual sedimentation velocity of individual ballotini. Small volumes of dispersed ballotini were added to the top of 30 ml of static paraffin oil in a polyethylene drop-tube. The terahertz reflection intensity of ballotini falling through the static focal spot of the sensor was measured side-on through the polyethylene, as shown in Fig. 1. The refractive index contrast of silica ($n = 1.98$) and paraffin oil ($n = 1.5$) at 1 THz [8] provided ample reflected signal for analysis. Time-resolved signals are shown in Fig. 2. The autocorrelation of these measured signals can be obtained by a standard MATLAB function, and the average residence time of the reflective particles within the observation volume (and hence their velocities) can be inferred by fitting Eq. (3) to this processed data. The velocities that are found by correlation spectroscopy are consistent with Stokes drag and drop-time observations. Sample data and MATLAB code for data analysis are given in Dataset 1, (Ref. [9]).

The upper limit on accurate velocity measurement by terahertz correlation velocimetry arises from the Nyquist criterion. Our sensor sampled the reflection from the system at 30 Hz, and so given a measurement spot diameter of 350 $\mu$m, it follows that ballotini moving faster than about 5 mm/s may yield unreliable velocities. In practice the Gaussian observation volume extends weakly beyond 350 $\mu$m, and speeds up to 8 mm/s were measured with less than 10% error. The dynamic range of velocity measurement could be extended by a faster sampling rate; a wider instrument response function; or cross-correlative measurement of terahertz reflection signals at multiple localizations along the direction of fluid flow. A lower limit of accurate velocity measurement comes about if very few particles are observed (say, in a region of very slow flow), in which case variations of the background noise level may lead to incorrect velocity estimates.

The terahertz sensor can also be used to observe one-dimensional fluid velocity profiles. A wide-gap Taylor–Couette concentric cylinder viscometer was set up, with a polyethylene outer cylinder that permitted the fluid gap to be observed using the TPI imaga 2000 instrument. A brass bob of radius 4.0 mm was fabricated in-house, and the fluid gap was 3.5 mm. The bob was driven at known rotation rates up to 24 rpm using a motor controlled via an Arduino Uno with a motor shield (Arduino Ltd.). Polyethylene spheres of 200 $\mu$m diameter (1 g, Stamylan UH, DSM Engineering Plastics) were coated with a colloidal silver paint (0.5 ml, N36BA paint, Maplin) and dispersed into paraffin oil. The suspension was loaded into the viscometer. The coated particles were almost neutrally buoyant, with sedimentation velocities less than 20 mm/h. The silver coating ensured a strong terahertz reflection was observable, and was necessary because the weak refractive index contrast between bare polyethylene spheres ($n = 1.52$) and paraffin oil ($n \sim 1.5$) resulted in negligible signal otherwise. The time- and depth-resolved terahertz reflections of the coated spheres suspended in the viscometer are shown in Fig. 3, together with inferred velocity profiles. In this analysis, the terahertz reflection signals were first binned into 70 $\mu$m slices before analysis as before, and some velocity estimates in regions of
very low signal within 0.3 mm of the static wall are excluded. Plotted alongside the Taylor–Couette velocity profile of a Newtonian fluid at the same rotation rate, the terahertz correlation spectroscopy measurements of the entrained polyethylene spheres are close to the expected velocity of the surrounding fluid. The axial resolution of the TPI imaga 2000 is specified as 50 μm; however, in this experiment the resolution of the velocity measurement is limited by the particle diameter of 200 μm.

Gas bubbles can also be studied using terahertz correlation spectroscopy. As well as determining the velocity of a bubble based on its residence time in the observation volume, it is possible to simultaneously measure the bubble diameter from the separation in the double-reflection of terahertz radiation from opposite bubble surfaces. To show this experimentally, a polyethylene tube containing 48 ml of paraffin oil and 2 ml of air was shaken by hand to disperse small bubbles. The rising bubbles were observed using the same geometry established for imaging ballotini in Fig. 1. In Fig. 4, time- and depth-resolved terahertz reflections are shown for a region of fluid between 3 and 4.2 mm from the tube wall, so that wall effects are not very significant. These data were recorded after large bubbles had already risen to the top of the fluid, and the separation between paired terahertz echoes, \( d \), indicates a bubble diameter of 0.1 mm. To analyze the velocity of individual bubbles, the total time-resolved reflection intensity of a bubble was manually cropped from the data and its duration fitted to Eq. (1) using \( \frac{y}{D} = \frac{r}{R} \) and \( x = V(t - t_0) \). Autocorrelation as per Eq. (2) was not necessary because strong, sparse signals were obtained. Here, the bubble diameters were observed to be much smaller than the observation volume determined for ballotini, and the diffraction-limited value of \( w \) (350 μm) was used to interpret the bubble velocity. The estimated bubble velocity of 0.2 mm/s is plausible for spherical bubbles of this size rising in creeping flow, although faster than the predicted Stokes velocity for a single bubble [10].

Terahertz imaging offers several unique advantages for the measurement of solid structures, and some of these features may be valuable in rheometry. Most essentially, the ability to noninvasively measure flow in optically opaque fluids is...
individual echoes allow time-domain terahertz sensors to be used for particle velocimetry within some fluids. The measurement is found to be consistent with other velocity measurements and creeping flow equations. Because many optically opaque fluids can be studied by terahertz imaging, this technique may allow flow profiles to be determined that were previously inaccessible for measurement. Furthermore, because an entire one-dimensional flow profile can be measured at once, it seems possible to characterize non-Newtonian flow via a terahertz correlation velocity profile obtained in a Taylor–Couette viscometer at a single rotation speed. Terahertz correlation spectroscopy could be used for flow-metering inside hydrocarbon oils, for studying the rheology of gel formation in waxy crude oils, or lubricants clouded by carbon black or magnetic particles. In confocal microscopy the technique of FCS has long been established as a method for measuring dynamic properties such as diffusion and particle density, as well as velocity, and so this terahertz version of the technique should be adaptable to quantify such phenomena as well, and we hope that many fluid dynamics questions could be studied by this type of terahertz rheology. Commercial time-domain terahertz cameras could readily be equipped with software methods to perform correlation spectroscopy measurements. Data and software are provided in Dataset 1, (Ref. [9]).

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