

Unveiling The Origin of Spurious Features in THz-TDS of Powder Compacts

Jon Gorecki, Keir N. Murphy, Daniel Markl, Andrew D. Burnett, Mira Naftaly

Abstract—Terahertz time-domain spectroscopy (THz-TDS) is a vital tool for scientific and industrial analysis, however, many commonly analysed products, such as those found in pharmaceutical, agriculture, and mining sectors, are produced as powders or granular materials, and these sample morphologies have been reported to produce anomalous spectral features which can often obscure known material resonances. The cause of these anomalous features has been poorly understood, making it difficult to predict their presence and limiting the applicability of THz-TDS for such materials. Here we systematically study how the sample morphology of granular compacts produces anomalous spectral features by performing extensive experimental measurements on two-part powder compacts with varying microsphere size and concentration. Further, we employ ray-tracing simulations to identify the physical mechanism whereby these spectral features arise owing to variations in optical path length within the heterogeneous sample. We believe this is the first time that the physical cause of spurious spectral features within powder samples has been adequately explained and that a robust method has been presented for modeling this effect. By understanding these features, we propose that instead of being seen as a parasitic effect, their presence can be utilised to extract morphological properties of the samples, thereby enhancing the utility of THz-TDS for granular materials.

Index Terms—THz-TDS, time-domain-spectroscopy, scattering, pharmaceuticals, spectra.

I. INTRODUCTION

TERAHERTZ time-domain spectroscopy (THz-TDS) is a powerful spectroscopic technique that has found applications in a range of scientific [1] and industrial [2] areas. Among its various applications, one of the most prominent is the analysis of granular materials, compacts, and porous samples, which are of particular interest across multiple industrial sectors including pharmaceutical [3], food and agriculture [4], [5] and mining [6]. To perform THz-TDS, granular compacts

typically consist of a composite blend containing the analyte as a powder suspended in a THz-transparent matrix such as Polytetrafluoroethylene (PTFE). The compaction of the blend aims to yield samples whose vibrational spectra can be examined across a wide frequency range, which is of particular importance for materials with multiple absorption features. However, reports over the past several decades indicate the emergence of anomalous spectral features in such samples. These features vary with sample morphology, often obscuring the spectral characteristics of the constituent components.

The presence of anomalous spectral features has been observed when performing THz-TDS on granular samples [7], [8], [9], [10], [11] and samples with rough surfaces [12], [13], [14], [15]. For compacted granular samples, these features have been observed in polyethylene [7], ammonium nitrate powder, flour, and salt [8], Prussian Blue dye [9], Dinitrotoluene [11], and common sugars [11], [13]. Importantly, it has been shown that the size of microspheres (or pores) plays a crucial role in the presence of anomalous spectral features [9], [11]. Theberge et al [13] observed that compacted samples of both α -lactose monohydrate and cyclotrimethylene trinitramine (a nitramine explosive) powders presented anomalous spectral features when the powder grains were ground to 200 - 300 μm in diameter, however when the diameter was reduced to 5 μm these spectral features disappeared.

Authors have tried to model the effects of heterogeneous samples using a range of analytical techniques such as effective medium theories [16], [7], Mie scattering theory [8], [11], finite difference time domain modelling [14], and by the summation of multiple waves travelling through samples of slightly different thickness and refractive indices [12], [13]. However, analytical models such as Mie theory and effective medium theories often break down when the particles size and wavelength are of a similar dimension [16], and have produced predictions which match experiments with varying degrees of accuracy. Further, these models do not account for the large degree of intra-batch variation in spectra which have been observed when performing measurements on samples prepared with the same morphological properties [14]. To investigate the spatial distribution of THz waves scattered by spherical microspheres, Born et al. [10] used a quantum cascade laser and a Golay cell detector mounted on a translation stage to measure the emitted power as a function of scattering angle, which found that while Mie theory was able to describe some samples accurately, it was not suitable in all cases in reproducing the power as a function of scattering angle. Research by Murphy et al. [17], [18], [19], [20] has documented the presence of anomalous spectral features

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Jon Gorecki is with Imperial College London, Exhibition Road, London, UK (email: j.gorecki@imperial.ac.uk)

Keir N. Murphy is with The University of Manchester, Oxford Road, Manchester, UK (email: keir.murphy@manchester.ac.uk)

Daniel Markl is with The University of Strathclyde, Richmond Street, Glasgow, UK (email: daniel.markl@strath.ac.uk)

Andrew D. Burnett is with The University of Leeds, Woodhouse, Leeds, UK (email: a.d.burnett@leeds.ac.uk)

Mira Naftaly is with the National Physical Laboratory, Hampton Road, Teddington, UK (email: mira.naftaly@npl.co.uk)

within two-part granular compacts, which were observed to fluctuate depending on microsphere size and concentration. This observation raises concerns surrounding the accuracy and reproducibility of analysis conducted on granular compacts.

As seen above, spurious spectral loss features in THz-TDS measurements of granular materials have been observed in multiple studies encompassing various materials. These features have never been adequately explained or modelled, and have often been dismissed. In our recent work, we proposed an explanation based on varying optical path lengths experienced by photons travelling through granular material and undergoing scattering [17], [18].

In this paper, we demonstrate a ray-tracing model which shows how scattering in a granular material can produce spurious features in a THz time-domain spectrum, and explains the relationship between the size and concentration of scattering centres with the resulting spectral features. Moreover, the model is validated by extensive experimental measurements. Our combination of experimental measurements alongside ray-tracing simulations provides a theoretical framework to explain and interrogate the nature of spurious spectral features produced by granular samples. By explaining the underlying cause of this effect, and providing a robust simulation method, we are able to predict the presence of these features and understand the morphological conditions necessary to avoid them. This work will allow researchers to have increased confidence in the applicability of THz-TDS for granular powder or heterogeneous samples, thereby enhancing its application for spectroscopy and metrology.

II. EXPERIMENTAL OBSERVATION OF SPURIOUS FEATURES

A. Materials & Methods

Borofloat glass microspheres of various size distributions (Cospheric LLC, 2.2 g/cm^{-3} , 38 - 45, 90 - 106, 125 - 150, 150 - 180 & 180 - 212 μm diameter) were blended with PTFE powder (Sigma Aldrich, free flowing, mean particle size $1 \mu\text{m}$, 2.2 g/cm^{-3}) as a matrix. The microspheres were chosen owing to their well-controlled particle size distributions, spherical shape, and their large difference in complex refractive index relative to PTFE. All compacts were fabricated from PTFE & Borofloat microsphere blends of varying concentrations and sizes of microspheres. The blends were compacted (400 MPa) using a force and displacement-controlled compaction simulator (HB50, Huxley-Bertram Engineering, Cambridge, UK; London, UK) and were allowed one week to undergo elastic relaxation to ensure reproducible measurements. Fabricated samples were plane parallel disk-shaped compacts with diameter 9 mm and thickness 1 mm. An additional batch was manufactured of pure PTFE as a control. This sample preparation process for PTFE was chosen as it has been verified to produce samples of negligible porosity and high tensile strength, producing samples which can be treated as binary mixtures [21]. However, it should be noted that other published reports using differing sample preparation methods will almost certainly produce varying results, largely because of varying porosity [22].

THz-TDS transmission measurements were carried out on all fabricated samples using a Teraflash Pro (Toptica) spectrometer, purged with dry air. The beam path consisted of four parabolic mirrors ($F/2$, 25 mm mirror diameter, 50 mm effective focal length) orientated in a z-configuration. Sample transmission was measured in the focal plane where samples were placed normal to the beam. The effective refractive index ($n(\nu)$) and effective loss coefficient ($\alpha_{\text{loss}}(\nu)$) in the frequency domain were extracted using Equations 1 and 2 respectively.

$$n(\nu) = \frac{(\phi_s(\nu) - \phi_r(\nu))c}{2\pi\nu L} + 1 \quad (1)$$

$$\alpha_{\text{loss}}(\nu) = \frac{-2}{L} \ln \left[\frac{(n+1)^2}{4n} \frac{E_s(\nu)}{E_r(\nu)} \right] \quad (2)$$

$E_r(\nu)$ and $E_s(\nu)$ are the frequency-dependent field amplitude of the reference and sample signals, respectively. Sample thickness (L) was measured using a micrometre ($\pm 0.001 \text{ mm}$). The maximum measurable loss (α_{max}) is calculated following the procedure laid out by Jepsen et al [23] shown in Equation 3, utilising an experimental measurement of the dynamic range spectrum (DR) of the spectrometer. This equation provides an upper limit to the value of loss which can be measured, which corresponds to the sample signal being attenuated to the level of the noise floor.

$$\alpha_{\text{max}} = \frac{-2}{L} \ln \left[DR \frac{4n}{(n+1)^2} \right] \quad (3)$$

B. Spurious Features in Loss Spectra

Figure 1(a) illustrates the loss coefficient of a solid Borofloat glass sample and a PTFE powder compact, obtained from a single scan of each sample. The loss spectra for the Borofloat sample is plotted up to a maximum frequency of 2.7 THz, at which point the signal falls below the noise floor. These materials exhibit no observable spectral features within the observed frequency range. However, upon analysing mixed media compacts consisting of the Borofloat and PTFE powders, prominent spectral features emerge, which are shown in Figure 1(b), which plots the loss spectra for two different microsphere sizes at 20 % volume concentration. Notably, altering the microsphere size within the compact leads to an increase in the number of spectral features or a shift in those already observed. The frequency locations of these peaks are highlighted by the dashed lines, revealing two peaks for the 125 - 150 μm microspheres, and a single sharp peak for the 90 - 105 μm microspheres. It is important to note that these features fall below the maximum measurable loss that is calculated from the dynamic range and therefore cannot be considered noise.

The real refractive index spectra are plotted in Figure 1(c) for the solid Borofloat glass sample and the PTFE powder compact. The spectrum for PTFE reveals a flat value of refractive index at 1.44, while the Borofloat exhibits a higher refractive index around 2.1 which reduces at higher frequencies. Importantly, both spectra are smooth and do not exhibit any resonance features. In Figure 1(d) the real refractive index for the PTFE and Borofloat composite powder

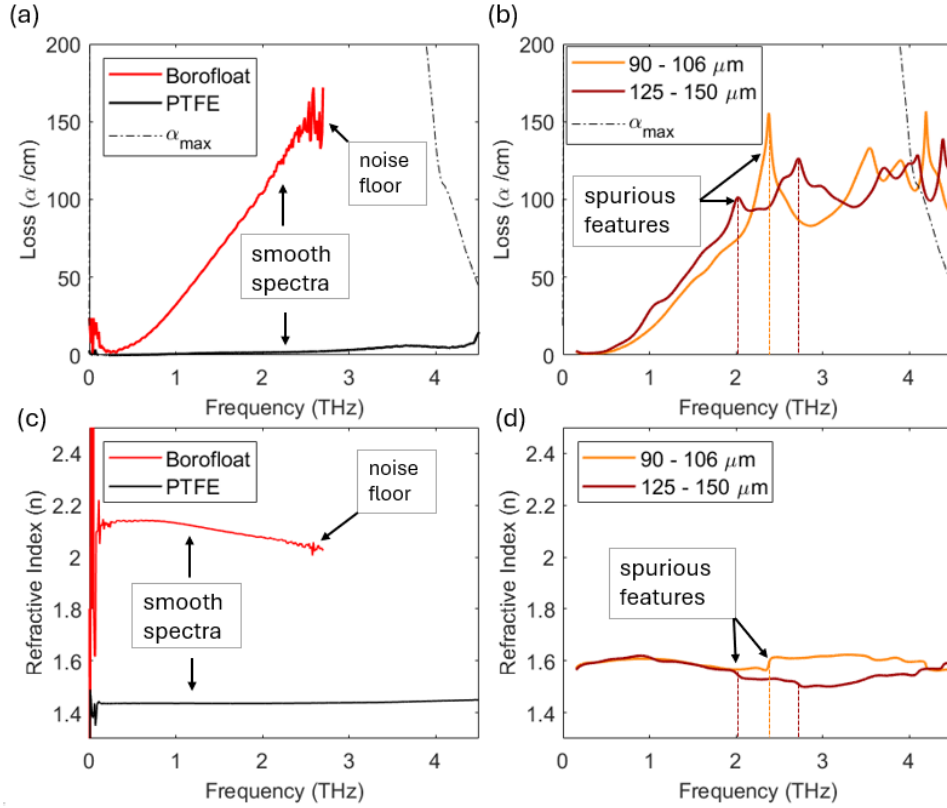


Fig. 1. (a) Loss coefficient of solid Borofloat glass and a PTFE powder compact, both of 1 mm thickness. (b) Loss coefficient spectra of 20 %v/v compacts with varied microsphere size revealing several anomalous features. The maximum measurable loss is depicted as a dashed line. (c) Real refractive index for Borofloat glass sample, and PTFE powder compact sample, revealing smooth flat spectra. (d) Real refractive index of 20 %v/v compacts with varied microsphere size revealing several anomalous features.

compacts are plotted. Overlaid in the dashed lines are the frequency locations of the loss peaks from Figure 1(b). The refractive index for the 90 - 106 μm microspheres is fairly flat however exhibits a sharp jump close to 2.4 THz, which matches the location of the peak in the loss spectrum. At low frequencies, the refractive index for the 125 - 150 μm microspheres is identical to that of the smaller microspheres, however at 2 THz these deviate and the refractive index for the larger microspheres exhibits a small drop, followed by another drop around 2.7 THz. Again, the frequency locations of these refractive index changes matches well with the location of the peaks in loss spectra.

Further exploration of the effect of varying microsphere size is presented in Figure 2(a & b). We highlight here three spectral regions in grey boxes, labelled 1, 2, and 3, as there appear to be three distinct spectral regions where features can be grouped by their shape and locations. Figure 2(a) presents experimental data for microspheres at a range of sizes, all at a concentration of 5 % volume. The first features to note are shown in region 3 around 4.2 THz which appear to remain at a constant frequency location despite changes in microsphere size. These features are relatively small in amplitude with a rounded profile. The next interesting features are highlighted in region 2, located around 3.8 THz, which also appear to remain at a fixed frequency location despite changes in the microsphere size. This feature appears much sharper and taller

than in region 3. Finally, region 1 (between 1 - 3.5 THz) reveals several broad shallow features which appear to change location and amplitude depending on the microsphere size without an obvious trend. To compare these with the plots in Figure 2(b), which plots the loss coefficient for a range of microsphere sizes at 20 % volume concentration, the spectral features in region 3 appear to have vanished, and the features in region 2 have decreased in prominence. In region 1, the features have become much more complex and show multiple peaks at varying frequencies.

Figure 2(c & d) illustrate the loss coefficients for all concentration levels at two microsphere size distributions (90 - 106 & 180 - 212 μm diameter). Figure 2(c) plots spectra for 90 - 106 μm microspheres, which show in region 1 at low concentrations a fairly flat loss which appears to increase as the microsphere concentration increases. As the microsphere concentration increases further, several broad peaks appear in the loss spectra which become much more pronounced. This behaviour is quite similar for the larger microspheres plotted in Figure 2(d) where low-concentration microspheres display a very broad, weak, feature centred around 1.5 THz, however as the concentration increases this effect grows in amplitude and multiple features become visible. For both microsphere sizes it is clear that in region 2 (around 3.7 THz), and in region 3 (around 4.2 THz), there are features which seem to remain fairly constant in shape, location, and amplitude, as the

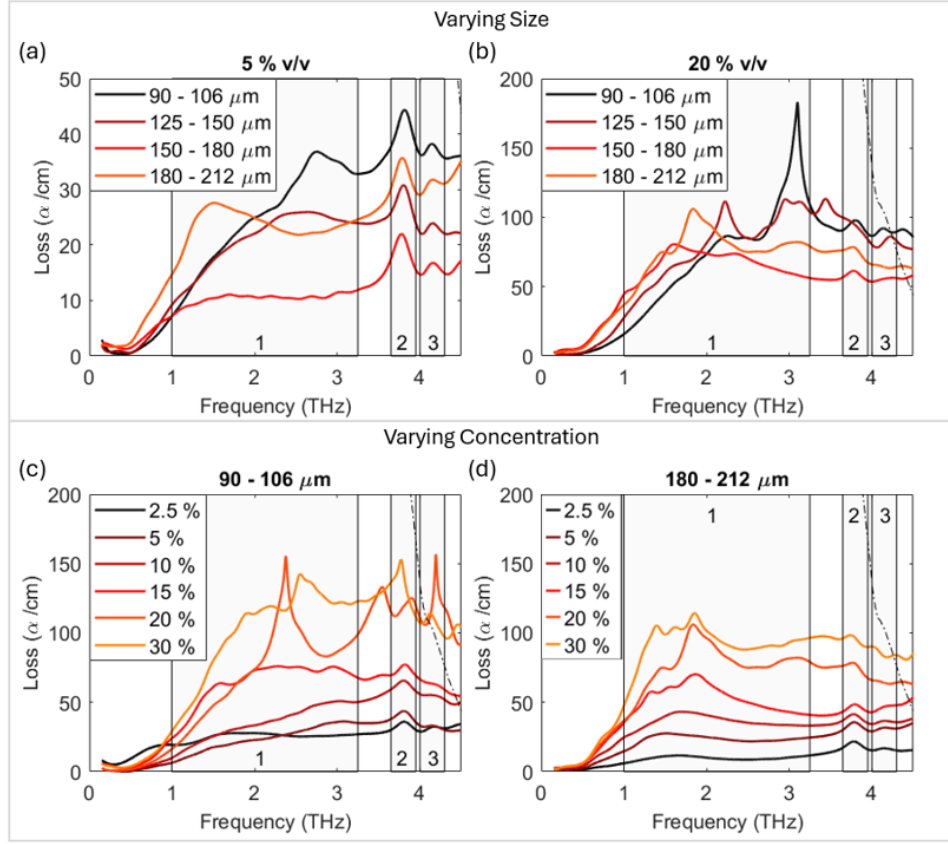


Fig. 2. THz-TDS loss spectra of powder compacts of Borofloat microspheres in PTFE. The maximum measurable loss is depicted as a dashed line. Three spectral regions are highlighted in grey boxes, labelled 1, 2 and 3, grouping together spectral features of similar visual appearance to aid discussion. (a & b) Varying microsphere size, at 5 % and 20 % concentration, respectively. (c & d) Varying microsphere concentration, at sizes of 90 - 106 μm and 180 - 212 μm , respectively.

concentration and size are varied. The cause of these features highlighted in regions 2 and 3 is unknown, however, it is unusual that there is no apparent dependence of the frequency on the microsphere size or concentration.

Figure 3 illustrates the spectral intra-batch uniformity for the 10% v/v compacts within the 90 - 106 μm size range. As evident from the figure, there is considerable intra-batch variation in the spectral profile. This variation is particularly pronounced in region 1, where spurious features exhibit significant differences in both profile and intensity.

Focusing on the spectral features displayed in region 1 (between 1 - 3.5 THz) in Figures 2 & 3, the experimental results demonstrate that spurious spectral features vary in number, position, and profile as the microsphere size and concentration vary. To investigate this phenomenon, we use a ray-tracing simulation to represent the propagation paths of electromagnetic waves through heterogeneous samples.

III. RAY-TRACING SIMULATIONS

A. Modelling Method

Figure 4 presents a schematic diagram showing the geometry in the ray-tracing simulation. A 2D sample of width, W , and depth 1 mm consists of a PTFE matrix with a multitude of randomly distributed Borofloat microspheres. The regions of PTFE and Borofloat are modeled by their complex

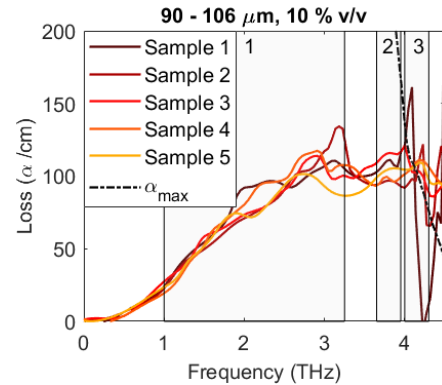


Fig. 3. THz-TDS loss spectra of Borofloat microspheres at 10 % v/v and 90 - 106 μm for each compact. The maximum measurable loss is plotted in a dashed line. We highlight three spectral regions (numbered 1, 2, 3) in which we group together spectral features of similar visual appearance to aid discussion.

refractive indices, as shown in Figure 1(a & c). A bespoke ray-tracing simulation is written in Matlab. Both the refractive index spectra and ray tracing simulation codes are available from the data repository [24]. The simulation traces the paths of individual rays, which emanate from the top surface of the sample with a randomised location on the x-axis and a randomised angle θ normal to the surface. The incidence

angles follow a uniform distribution between $\pm 20^\circ$ in order to approximate the behaviour of a focused beam. It is important to highlight that this is only an approximation, as in reality a Gaussian beam exhibits a flat wavefront at the focal plane, however when modelling this scenario with ray-optics a range of incidence angles are necessary to create a beam which diverges after the focal plane. A ray will trace a straight line through the material until it hits a microsphere, at which point a scattering event occurs and the angle of the ray will be altered. While tracing a path through the microsphere the ray will travel more slowly than in the PTFE owing to the higher refractive index of Borofloat. When the ray emerges from the microsphere it will again speed up and travel in a straight line until it either hits another microsphere or reaches the boundaries of the material slab. Further, the imaginary refractive index is used to model the effects of absorption during propagation. This is achieved by assigning each ray with an initial intensity equal to 1, and calculating after each step how much the intensity has decreased by, depending on the material properties. When the ray eventually exits the slab the exit time of the ray (referred to as time-of-flight) and its intensity are recorded. The time-of-flight values for one million rays are binned, utilising 600 equally spaced bins between 0 and 20 ps, where the intensity of each ray determines its contributing weight in the bin (thereby accounting for absorption effects). The binned data is referred to as the temporal profile. For the case of normal incidence in a homogeneous slab without scattering, all the rays would exit the material at the same time, and therefore the temporal profile would display a single peak, or Dirac delta function. However, it is expected here that the scattering events from the microspheres will create a temporal profile with a broad distribution and possibly exhibit additional features.

1) Geometry Creation:

- 1) Firstly the diameter D of the Borofloat microspheres and their area concentration ρ within the PTFE matrix is defined. A typical value here is 98 μm diameter microspheres with 20 % area concentration.
- 2) Based on the microsphere diameter the width, W , of the slab is determined following the procedure in supplementary section S2. This step is performed to ensure that a 2D sample contains a similar number of microspheres as the 3D scenario from the experiments. The height H of the slab is 1 mm.
- 3) A pixelated slab (an empty matrix M) is generated with pixel size 5 μm , depth 1 mm, and width W .
- 4) The target number N of microspheres is calculated based on the concentration ρ , microsphere diameter D , and slab area.
- 5) A 2D matrix ($2 \times N$) of random numbers is generated which represents the centre points of the Borofloat microspheres in x and y coordinates. Random numbers are generated 0 - 1 following a uniform distribution, then multiplied by the size of the slab in the X and Y dimensions. However, instead of allowing locations for example in the X axis from 0 to W , the limits of the X and Y dimensions here are modified to account for the diameter D of the microspheres to prevent a

microsphere being partly outside the edges of the slab. Therefore the limits are modified to $\frac{D}{2} \leq x \leq W - \frac{D}{2}$, and $\frac{D}{2} \leq y \leq H - \frac{D}{2}$.

- 6) To prevent the un-physical scenario of microspheres spatially overlapping, the distance between each microsphere centre-point and its nearest neighbour is calculated to find any centre-point combinations which are closer than D using the Matlab function 'pdist2'. When any such elements are found, one of the pair is chosen to be redistributed to a new randomised location.
- 7) The previous step is looped repeatedly until the microspheres stop moving, which determines that all microspheres are then non-overlapping and randomly distributed. For concentrations $\leq 30\%$ this method works efficiently and requires only a few iterations to correctly distribute the microspheres.
- 8) Using the array of microsphere centre locations the matrix M is then filled in a binary nature, where pixels of distance from each centre point $\leq \frac{D}{2}$ are filled with 1's (representing Borofloat material), and all other pixels keep a value of 0 (representing PTFE).

2) Ray-Tracing:

- 1) A ray starts at the upper surface of the slab, with a randomised location x in the $\hat{x}$ axis, and a randomised incident angle θ normal to the surface. To prevent the ray from starting too close to the horizontal edge and hitting the side of the slab, the x values are limited to a uniform distribution between $\frac{1}{4}W \leq x \leq \frac{3}{4}W$. The incident angles are uniformly distributed between $\pm 20^\circ$ to provide a range of incident angles. The y location at the upper surface of the slab is defined as 0. The ray is assigned an initial intensity $I = 1$, which will be used to model the effects of absorption while passing through the slab.
- 2) A line is generated using the parameters (x, y, θ) which provides the direction of propagation in an analytical formulation. The line is converted to a list of pixel locations that it passes through.
- 3) A ray then starts to move along this path, pixel by pixel. At each step, the time taken to traverse the pixel is calculated using the pixel dimension (5 μm) divided by the speed (c/n), and added to a counter which will be used to sum the total time-of-flight for the ray. The intensity I at each step is reduced according to the imaginary refractive index k and the distance traveled (equal to the pixel size).
- 4) When the ray moves into a new pixel, if it detects that it has entered a Borofloat microsphere (if $M_{i,j} = 1$) then the angle of propagation θ is altered according to the randomised distribution function AniRand. The propagation angle is now 'locked' while the ray is inside the microsphere which means the ray angle cannot change again; the lock only will be released once the ray exits the microsphere. AniRand is a customised function that returns a randomised angle between $\pm 180^\circ$ with a specific probability distribution (discussed in detail in supplementary section S1). The AniRand function

was obtained by modelling in COMSOL the angular distribution of scattered intensity for a $200\ \mu\text{m}$ diameter microsphere at a range of frequencies. This function is then utilised in the ray tracing model for all microsphere sizes.

- 5) In the case of very large scattering angles it is possible the ray will immediately leave the microsphere, and therefore will be back-scattered. In this scenario the ray will incur a time increase of 30 fs as the simulation will detect the ray was present inside a single pixel of the microsphere (at pixel size of $5\ \mu\text{m}$).
- 6) The ray will continue to move through the microsphere along its newly defined line, with the time-of-flight through each pixel now taking slightly longer owing to the increased real refractive index of Borofloat compared to PTFE.
- 7) When the ray exits the Borofloat microsphere it continues to travel at the same angle. The lock on the angle is now removed, ready for a new interaction with a microsphere if it occurs.
- 8) Steps 4, 5, 6, and 7 are repeated until a ray is detected to have reached a boundary of the slab. If the ray exits the slab on the top or side surfaces then its existence is ignored. If the ray exits on the lower surface of the slab then its total time-of-flight and intensity are recorded.

3) Data Processing:

- 1) A total of 1 million rays are traced through the sample as this is shown to provide a stable result.
- 2) The time-of-flight of each ray is binned, utilising 600 equally spaced bins between 0 and 20 ps, where the intensity of each ray determines its contributing weight in the bin, thereby accounting for absorption effects. The binned data gives the temporal profile of rays traced through the sample.
- 3) A Fourier transform is used to convert the temporal profile into the frequency domain.

The ray-tracing simulation relies on random starting points, averaged over many iterations. The sample geometry is created using a random seed S_{geo} which allows for an identical microsphere placement to be reproduced, or varied, depending on whether the seed number is kept constant or changed. Similarly, the ray-tracing uses a random seed S_{ray} which initialises the random number sequence for the ray's initial location and scattering angle. For example, if two simulations were performed with the same values of geometry seed S_{geo} , and the same values of ray-tracing seed S_{ray} , then the Borofloat microspheres would be in identical locations and the rays would be traced along identical paths in both simulations. It is important to define these seed numbers as controllable variables to allow for repeatability and performance testing within the simulations. By changing the value of S_{geo} when generating the sample the microspheres will appear in different locations, which is similar to the real-world experiment where multiple samples are created with the same parameters of microsphere size and concentration. By changing the value of S_{ray} the rays will be initialised with different locations and angles. Ultimately it is important that enough rays are used

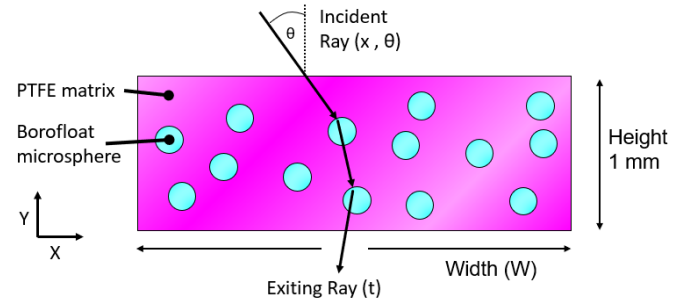


Fig. 4. Schematic diagram of geometry for the ray-tracing simulation. The sample consists of a slab of PTFE with randomly placed Borofloat microspheres. Rays begin at randomised locations on the top surface of the slab and are traced through, slowing down and deflecting when they travel through the Borofloat. The exit time and intensity of the rays are recorded to generate the temporal profile.

such that the simulation becomes insensitive to the value of S_{ray} , so by simulating with varying numbers of rays N and varying the ray seed we find how many rays are needed to become insensitive to S_{ray} . It is found that 1 million rays are sufficient to generate temporal profiles which are insensitive to the ray-tracing randomisation seed. A flow chart of the ray tracing simulation, and data analysis pipeline, is provided in Figure 5 to simplify the explanation of the methodology.

B. Results of Ray-Tracing Simulations

1) *Time Domain Spectra:* Figure 6 presents the temporal profiles obtained from experimental measurements and simulations. The simulated temporal profiles are shifted backwards by 3.33 ps to account for the time it would take a ray to traverse a distance of 1 mm in vacuum. Therefore the time $t = 0$ in the simulation figures refers to the time that a ray would exit the sample if the medium had a refractive index of unity. For the $98\ \mu\text{m}$ diameter microspheres in Figure 6(a) it can be seen that at low concentrations of 2.5 % the temporal profile displays a sharp peak at 1.4 ps followed by a much smaller second peak. As the concentration of the Borofloat microspheres is increased the height of the second peak gradually increases, and additional peaks become visible. The peaks remain at fixed locations equally spaced by 0.21 ps (highlighted by the overlaid grey lines). Further, at the highest concentrations of 20 and 30 % the first peak becomes the non-dominant feature as subsequent peaks become larger. Also the temporal profile starts to display a broad distribution superimposed behind the sharp peaks, which has gradually tails off over a duration of 1 ps.

An equivalent dataset from the experimental measurements is produced by normalising the frequency-domain sample spectra against the air reference measurement, and then transforming into the time domain via an inverse Fourier transform to produce the experimental temporal profile. This provides the sample response, which is analogous to the temporal profile presented for the simulated datasets. Figure 6(b) presents the experimental temporal profile for $98\ \mu\text{m}$ diameter microspheres. At 2.5 % concentration the temporal profile shows a sharp peak at 1.4 ps. As the concentration increases the

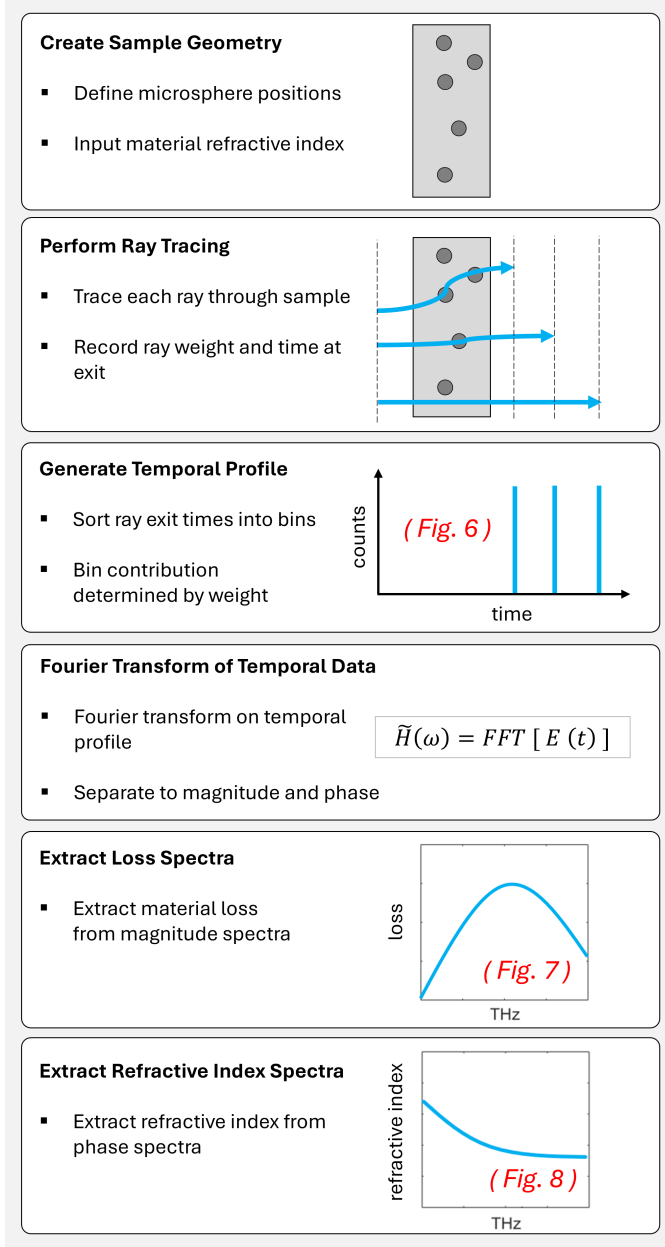


Fig. 5. Flow chart depicting each stage of the ray tracing simulation and data analysis pipeline, highlighting the steps involved to produce subsequent figures.

temporal profile becomes broader and the location of the peak moves further forward in time, reaching 2.1 ps for 30 % concentration. This matches well with the simulated data for 30 % concentration.

The simulated data for the 196 μm diameter microspheres in Figure 6(c) reveals a similar behaviour to the smaller microspheres, however in this case the sharp peaks have a wider spacing of 0.42 ps, and the first peak remains the largest in magnitude at all concentrations as compared to the other peaks. It is also noted that unlike the 98 μm microspheres, the temporal profile for the 196 μm diameter microspheres do not display such a broad background distribution but is mostly comprised of sharp peaks. Figure 6(d) plots the

experimental data of the 198 μm diameter microspheres. At 2.5 % concentration the spectrum shows a sharp peak at 1.4 ps. At 5 % concentration a second peak appears, with a separation of 0.3 ps between the two peaks, and this remains present also for 10 and 15 % concentrations. For the 30 % concentration sample the spectrum displays a steep slope to the background signal which is likely caused by a phase unwrapping error owing to the characteristic low frequency noise present in THz TDS systems [25].

Overall, when comparing the simulated and experimental temporal profile, it is seen that for both diameter microspheres sizes at low concentration the spectrum is dominated by a single sharp peak, however as the concentrations increase the spectrum broadens and becomes delayed in time. For both experimental samples at 2.5 % there are multiple small sharp peaks however the separation of these are very close to the temporal resolution of the experimental data and therefore these should be viewed with skepticism.

2) *Loss Spectra*: Figure 7 presents frequency domain loss spectra for simulated and experimental data at a range of microsphere sizes and concentrations. For the simulated spectra, the frequency domain loss is obtained by taking a Fourier transform of the temporal profile, normalising this against a simulated air reference, and then converted to a value of loss following Equation 2. Simulated loss spectra for 5 samples are presented for each combination of concentration and microsphere size, where the randomised locations of the microspheres within the simulation are varied for each sample to simulate the effects of intra-batch variation. Similarly, the experimental data presents spectra for 3 samples at each combination of microsphere concentration and size, where the samples are made to identical recipes but present spectral variations owing to the distribution of Borofloat microspheres.

Figure 7(a) presents simulated loss spectra for the 98 μm diameter microspheres at a range of concentrations. The temporal profile for this dataset (Figure 6a) revealed multiple sharp peaks evenly spaced with a separation of 0.2 ps. It is known that when performing a Fourier transform of a time domain signal consisting of two Dirac delta functions separated by Δt , the frequency domain amplitude will display a dip in amplitude at a frequency of $f_0 = 1/(2 \times \Delta t)$, which for a value of 0.21 ps will result in an expected spectral features located at 2.4 THz. A dip in amplitude equates to an increase in loss, and therefore peaks in the loss spectra are expected at f_0 . This frequency value f_0 has been highlighted on the graphs in a grey dashed line. It can be seen that for low microsphere concentrations, the loss spectrum displays a very broad, shallow peak that increases in strength when going from 2.5 to 15 % microsphere concentration. The loss peak appears to be located at the expected frequency f_0 . Interestingly, as the concentration increases the behaviour changes and it can be seen that at higher concentrations of 20 and 30 % the loss spectra begin to show large intra-batch variation. Further, instead of a single loss peak there is a splitting effect where peaks occur either side of the f_0 frequency.

Figure 7(b) presents the frequency domain loss spectra for experimental measurements of 3 samples at each microsphere concentration. It can be seen that at low concentration of

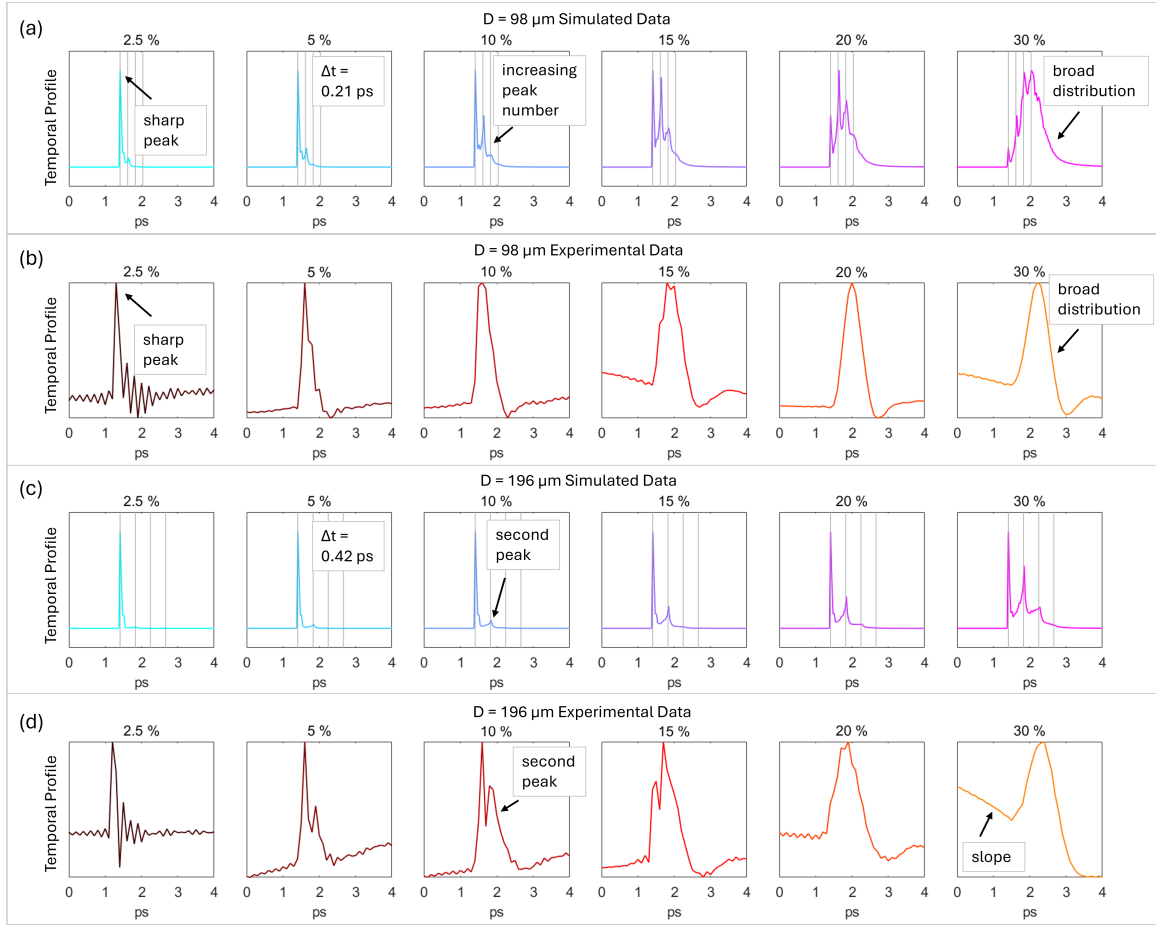


Fig. 6. (a) Simulated ray-counts and (b) experimental system response for varying microsphere concentrations at 98 μm diameter. (c) Simulated ray-counts and (d) experimental system response for varying microsphere concentrations at 196 μm diameter.

2.5 % there is a flat spectral response, however as the concentration increases the loss starts to increase, especially at higher frequencies. At 15 % concentration several pronounced peaks in the loss become present, which are closely located around the highlighted frequency value of 2.4 THz. As the concentration increases further the spectra become more complicated as multiple features appear and the intra-batch variation increases. There is also clear evidence of the spectral splitting effect for the 30 % concentration samples, where peaks occur symmetrically either side of the f_0 frequency.

Figure 7(c) presents loss spectra for microspheres simulated at 196 μm diameter. The location of the expected resonance frequency is highlighted as $f_0 = 1.2$ THz, based on the temporal peak separation of 0.42 ps that was observed in the simulated temporal profiles in Figure 6(c). It can be seen that for low concentrations there is a shallow peak located around 1.2 THz which grows in strength as the concentration increases. At 20 % the intra-batch variation starts to increase as the strength of the peak shows variation between samples. By 30 % concentration the intra-batch variation has increased further and there is some variation in the frequency location of the peak. Overall the plots of the simulated results at 196 μm diameter show less complicated spectra as compared to the 98 μm diameter microspheres, and less intra-batch variation.

Figure 7(d) presents loss spectra for experimental data of 196 μm diameter microspheres, with the resonance frequency of 1.2 THz highlighted in the grey dashed line, as expected from simulations. Again, the loss shows a flat response at low concentrations which increases as the concentration increases. For the 5 % samples a peak in loss can be seen close to the grey dashed line, and these features increase in strength as the concentration increases. The 30 % concentration samples display large peaks in loss located very close to the highlighted frequency f_0 .

When comparing the simulated and experimental loss spectra, it can be seen that in all cases the loss increases as the microsphere concentration is increased, and that peaks in loss are present around the highlighted frequency locations. In both simulation and experiment the number of spectral features increases with microsphere concentration, and it is seen that smaller size microspheres result in larger intra-batch variation in the loss spectra.

3) Refractive Index Spectra: Figure 8 presents the real component of refractive index for the simulated and experimental measurements calculated using Equation 1. The simulated temporal profiles are normalised by generating an equivalent temporal profile that would be produced by an air reference measurement, which is a Dirac delta function.

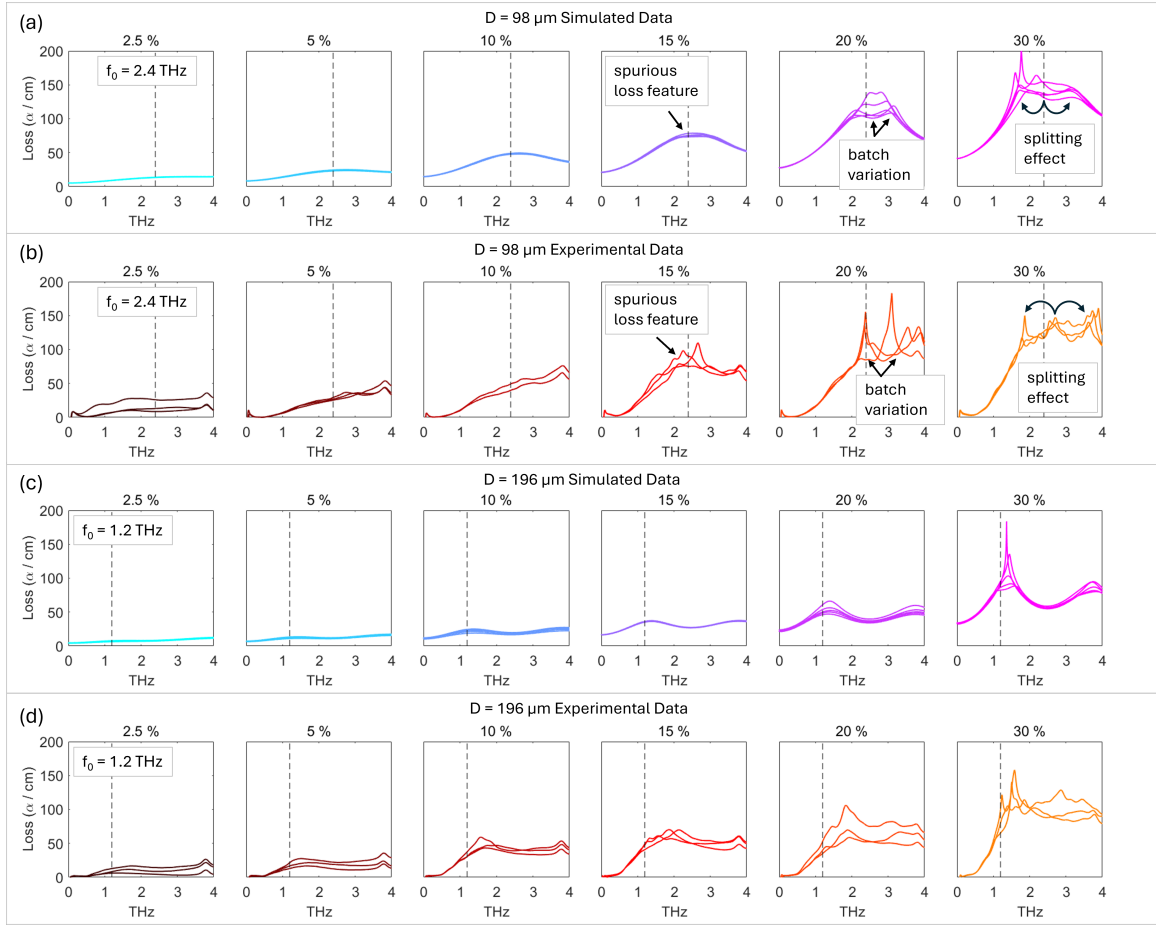


Fig. 7. (a) Simulated and (b) experimental loss spectra for varying microsphere concentrations at $98 \mu\text{m}$ diameter. (c) Simulated and (d) experimental loss spectra for varying microsphere concentrations at $196 \mu\text{m}$ diameter.

The experimental measurements are normalised against a reference measurement taken in air. The grey dashed lines of expected resonance frequencies f_0 are overlaid on the plots. For comparison, it should be noted that the refractive index of bulk PTFE is 1.44 with minimal variation over the plotted frequency range, while that of Borofloat is significantly higher ~ 2.1 at 1 THz and decreases to a value of ~ 2 at 3 THz.

Refractive indices of microspheres simulated at $98 \mu\text{m}$ diameter are plotted in Figure 1(a) which show that at low concentrations the refractive index is close to 1.4 (similar to that of PTFE) and as the concentration increases so does the refractive index at low frequencies, however at higher frequencies it slopes downwards and stays close to 1.4. For the 20 % concentration spectra there is an increase in intra-batch variation and the presence of a weak spectral feature close to the highlighted frequency of 2.4 THz. At 30 % concentration the spectral feature is much more pronounced and shows a bifurcation point where the spectra appear to split into two distinct profiles close to 1.6 THz. Although this feature is at a lower frequency than that highlighted in the dashed grey line, it matches well with the location of the loss peaks observed in Figure 7(a) for the same concentration of microspheres, which may occur at lower frequencies owing to the spectral splitting effect.

The experimental refractive index spectra for the $98 \mu\text{m}$ diameter microspheres (Figure 1b) reveal a similar trend where the refractive index starts close to 1.4 and increases as the microsphere concentration increases. However, for the experimental spectra the refractive index is much more flat when plotted against frequency as compared to the simulations. The experimental measurements of 15 and 20 % samples reveal spectral features close to 2.4 THz, however they are not present in all samples.

Simulations of the $196 \mu\text{m}$ diameter microspheres are presented in Figure 1(c). The spectra show an increase in refractive index at low frequencies as concentration increases, which tend towards a values of 1.4 at higher frequencies. For concentrations of 20 and 30 % there are resonance features around 1.5 THz (slightly higher frequency than the dashed line at f_0), however unlike the $98 \mu\text{m}$ microspheres, the $196 \mu\text{m}$ microspheres show a lower degree of intra-batch variation and do not present any bifurcation features.

The experimental measurements of the $196 \mu\text{m}$ microspheres in Figure 1(d) show a large degree of variation. Concentrations of 10 % and above show a dip in refractive index close to 1.5 THz, which is similar to the simulations. At the highest concentration of 30 % there is a bifurcation point at 1.2 THz where two of the spectra increase in refractive index,

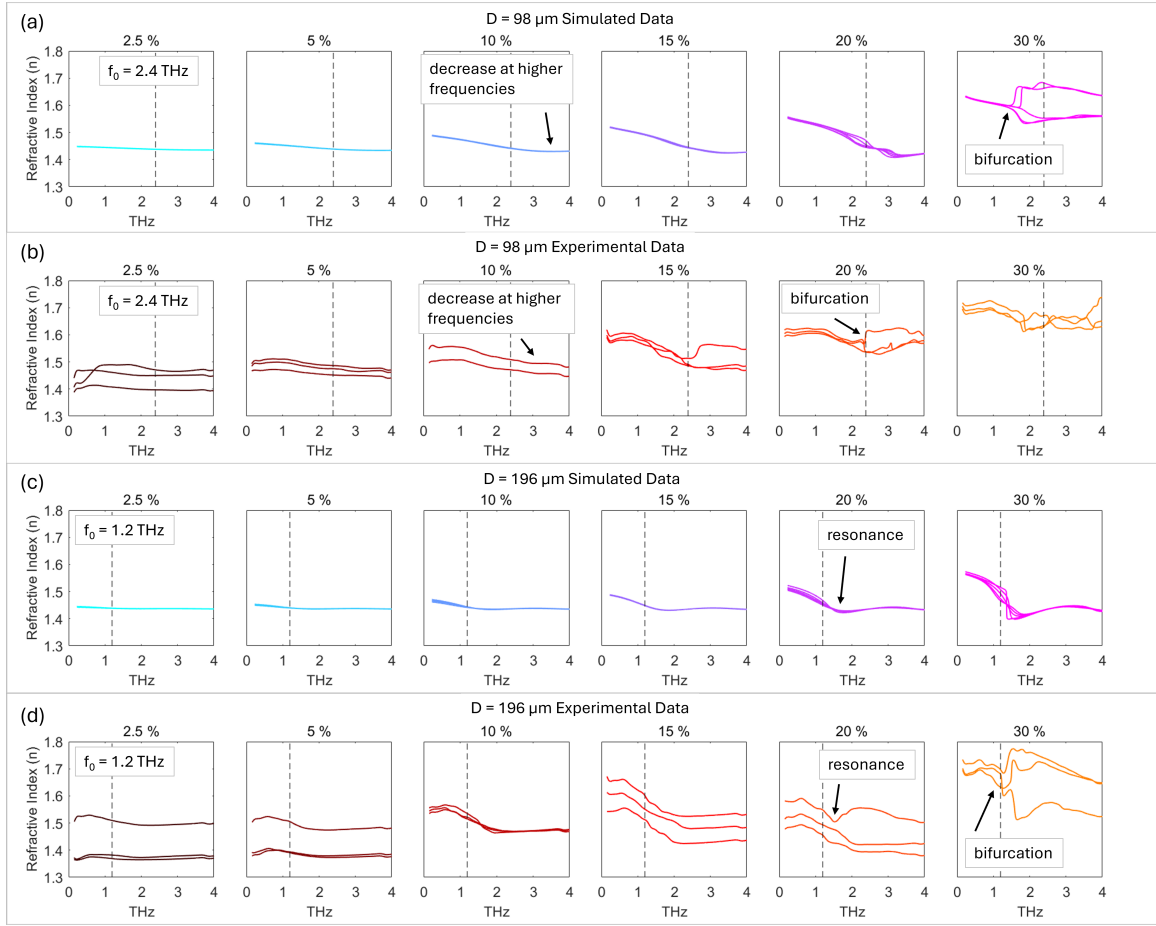


Fig. 8. (a) Simulated and (b) experimental refractive index spectra for varying microsphere concentrations at $98 \mu\text{m}$ diameter. (c) Simulated and (d) experimental refractive index spectra for varying microsphere concentrations at $196 \mu\text{m}$ diameter.

while one of the samples exhibits a decrease in refractive index.

It should be highlighted that the cause of these bifurcations in the phase spectra is currently unknown. It is possible that they are due to phase unwrapping errors where large changes in phase are present, or that there is a physical mechanism at play. Qualitatively, the bifurcations in refractive index do appear to coincide with samples which display a splitting effect in the loss spectra (those at microsphere concentrations of 20 and 30 %). Further, it can be seen in Figure 6 that for these high concentration samples the first peak in the temporal profiles transition from the dominant to non-dominant feature as subsequent peaks grow in amplitude, which possibly begin to compete with each-other in defining the resonance.

For both microsphere sizes, the experimental refractive indices show a larger degree of variation as compared to the simulations. Further, especially at low concentrations, the experimental refractive index falls below 1.44 which is the value for the bulk PTFE. This value must therefore be erroneous, and is possibly the result of porosity within the sample.

C. Origin of Spectral Features

The simulated temporal profiles presented in Figure 6 reveal the presence of multiple sharp peaks with a separation that depends on microsphere size but not microsphere concentration. The peak separation is 0.21 ps for the $98 \mu\text{m}$ diameter microspheres, and 0.42 ps for the $196 \mu\text{m}$ diameter microspheres. Based on the real refractive index of PTFE and Borofloat it is found that the peak separation values correspond extremely closely to the time delay that would be expected for a ray passing through a Borofloat microsphere, compared to through PTFE. To confirm this hypothesis, the ray-tracing simulation is modified to record the number of times each ray scatters (passes through a microsphere). Rays are then sorted according to their scattering number, and temporal profiles are overlaid for each value of scattering event number S . The modified simulation does not include the effects of absorption.

Figure 9(a) plots the simulated temporal profile for Borofloat microspheres of $98 \mu\text{m}$ diameter at 20 % concentration. The black dashed line plots the temporal profile for all rays traced through the sample, which displays several sharp peaks with a separation of 0.21 ps. Superimposed on this plot are the temporal profiles calculated for rays that are sorted by the number of microspheres that they have interacted with. It can be seen that each of the peaks in the black dashed line is

produced by rays that have grouped together in time based on the number of microspheres that they have interacted with (the number of scattering events). For this data-set only the scattering events from $S = 0$ up to $S = 4$ are plotted; higher order events will occur, however it can be seen that after $S = 4$ the contribution to the overall temporal profile is diminishing. From this plot it can be concluded that the sharp peaks in the simulated temporal profile are caused by rays becoming grouped together in time based on the number of scattering events they have undergone. The temporal separation of these peaks is therefore determined by the optical path length difference between a microsphere and the surrounding medium.

A major implication of this result is that the temporal peak separation does not depend on the microsphere concentration, but instead on the microsphere diameter and refractive index difference between microsphere and matrix.

Spurious spectral features are known to occur for granular mixtures of large diameter microspheres (several tens to hundreds of microns in diameter), however these features disappear for smaller microspheres [13]. To investigate this behaviour, microspheres are simulated at $12 \mu\text{m}$ diameter at 20 % concentration, and their temporal profile is plotted in Figure 9(b). Firstly it can be seen from the black dashed line that the temporal profile for all rays traced through the sample is much smoother than for the large diameter microspheres, and there are no sharp peaks present. The colored lines plot the temporal profiles for rays sorted by the number of scattering events they have undergone, from values of $S = 0$ to $S = 15$. There is no upper limit to the number of scattering events that can occur, yet only the first 15 are plotted here to avoid the graph becoming over-crowded. It can be seen that the peaks for these individual temporal profiles are much closer together than for the large diameter microspheres. Further, the rays undergo an increased number of scattering events on average as compared to in the larger diameter microsphere sample.

D. Spectral Splitting Effect

Figure 6 revealed that when microsphere concentration increases, the simulated temporal profile displays an increasing number of peaks. In the loss spectra in Figure 7 for simulations and experiments it was seen that the increased concentration also correlates with the presence of multiple peaks, and the loss spectra increasing in complexity. To explain this effect we plot in Figure 10(a) time domain signals which contain two, three, four, and five Dirac delta functions, to mimic the effect of multiple peaks at fixed temporal distance. The peaks have a separation of 0.21 ps , identical to that observed in simulations of $98 \mu\text{m}$ microspheres. Figure 10(b) presents the amplitude spectra in the frequency domain. For the case of two Dirac delta functions it can be seen that in the frequency domain a feature appears with the dip at $f_0 = 1/2\Delta t = 2.4 \text{ THz}$, followed by another dip at 7.2 THz . The frequency spectrum is only plotted up to 10 THz , but this repeating pattern will continue infinitely in the frequency domain. However, when the time domain signal contains three Dirac delta functions at equal spacing the frequency domain spectra change and two dips appear symmetrically around the frequency f_0 . As the

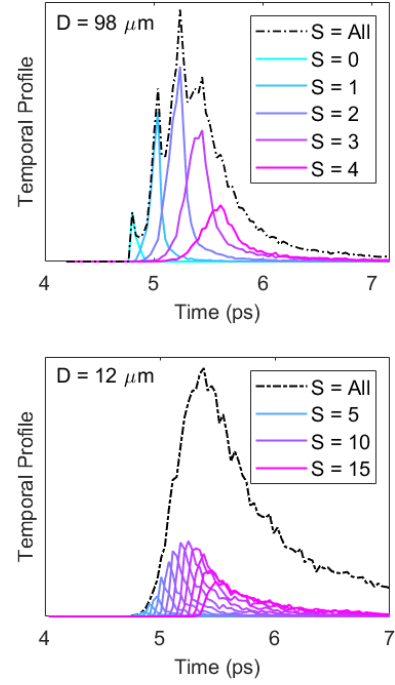


Fig. 9. The modified ray-tracing simulation records the number of scattering events S that each ray undergoes. Temporal profiles are then produced for each sub-set of rays according to scattering number. Microspheres simulated with 20 % concentration at (a) $98 \mu\text{m}$ diameter exhibit several sharp peaks, while (b) $12 \mu\text{m}$ diameter microspheres exhibit a smooth broad distribution. For the $12 \mu\text{m}$ microspheres the scattering events are plotted in integer steps from 0 to 15. The modified ray-tracing simulation does not include absorption effects.

number of Dirac delta functions increases further it can be seen that the dip continues to split into an increasing number of smaller dips, while remaining symmetrically located around the initial frequency f_0 . When compared to experimental and simulated results a similar effect is observed where the presence of additional peaks in the time domain leads to a splitting effect in the loss spectra, which occurs symmetrically around the central frequency. Unfortunately, the frequency domain of the experimental data is limited to 4 THz by the dynamic range of the THz TDS instrumentation. If measured over a wider frequency range, we predict the experimental measurements for the $98 \mu\text{m}$ diameter microspheres would reveal a similar profile to those in Figure 10(b) with one dip located at 2.27 THz , followed by another at 7.2 THz etc.

E. Effect of Microsphere Size

To illustrate the effect of microsphere size, Figure 11(a) plots the temporal profile for microspheres simulated with varying diameters at 5 % concentration. In the time domain (Figure 11a) for the largest diameter of $100 \mu\text{m}$ it is clear that two distinct peaks are visible. As the diameter of the microspheres is decreased more peaks appear and the spacing between the peaks is reduced. For the case of 10 and $20 \mu\text{m}$ microspheres there are no longer distinct peaks visible, and instead, the temporal profile has become a smooth broad distribution.

Figure 11(b) plots the loss spectra in the frequency domain. It can be seen that for the $100 \mu\text{m}$ microsphere, there is a

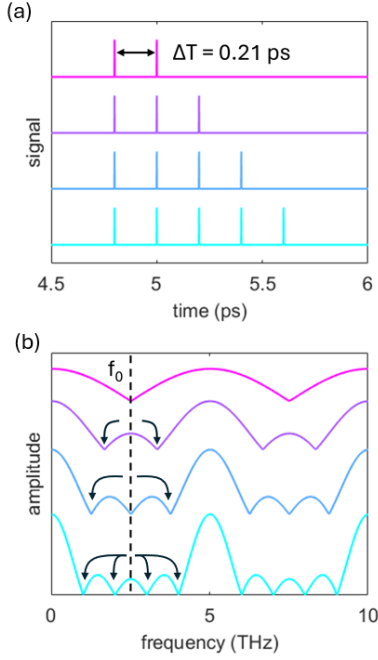


Fig. 10. (a) Time domain and (b) frequency domain of signals containing increasing number of Dirac delta functions at 0.21 ps separation. For two Dirac delta functions the amplitude spectra displays a dip at a frequency $f_0 = 1/2\Delta t = 0.24$ THz, which repeats with a period of $2f_0$. As the number of Dirac delta functions increases the amplitude dips split symmetrically around the central frequency f_0 , as highlighted by the curved arrows, where the number of splitting features increases with the number of Dirac delta functions.

peak present in the amplitude around 2.4 THz which is due to the multiple peaks in the temporal profile. As the microsphere size is decreased the peak in loss is no longer visible, as it has likely moved beyond the plot limit of 4 THz. It can also be seen that the loss is larger at high frequencies, and that this effect becomes stronger as the microsphere size decreases.

The real refractive index spectra are plotted in Figure 11(c). It can be seen that for the large $100\ \mu\text{m}$ diameter microspheres the refractive index is close to that of PTFE at 1.44, with a slight decrease at higher frequencies. As the diameter of the microspheres is reduced the real refractive index is seen to increase at all frequencies, however the dispersion (the decrease in refractive index from low to high frequencies) becomes more exacerbated. This result highlights that despite the concentration of the two constituent materials in the sample remaining constant, the microsphere size still plays an important role in the refractive index spectra.

Experimental loss spectra for microsphere sizes of 41 and $98\ \mu\text{m}$ are presented in Figure 11(d). The $98\ \mu\text{m}$ microspheres display several peaks in the loss spectrum, although for the smaller $41\ \mu\text{m}$ microspheres the spectrum is much smoother, which is in general agreement with the simulations. However, the main difference to note is that the simulations reveal the loss increases for smaller microspheres, while the experiments show the opposite trend where the loss decreases for small microspheres. Figure 11(e) presents the refractive index for experimental measurements, showing that the refractive index at low frequencies is higher when the microsphere size is

increased. Again, this is the opposite trend as compared to the simulation results.

Overall, when simulating microspheres with diameters less than $100\ \mu\text{m}$ it is seen there is no longer a good agreement between simulation and experiment, and any conclusions drawn from the simulations should be viewed with skepticism. This divergence of simulation and experiment may be due to the simulation method becoming invalid when the microsphere size becomes far smaller than the incident wavelengths. In this regime diffraction may become an important effect, which is not accounted for in this ray tracing simulation. In any case, the simulation cannot completely encapsulate reality, and it is useful to know the boundaries in the parameter space in which the simulation begins to diverge from experiment.

F. Analytical Formulation of Loss Spectra

The loss peaks displayed in Figure 7 for experimental results and simulations are the product of a destructive interference effect when a pulse transmitted through the PTFE matrix becomes out of phase with a pulse transmitted through the microsphere. The expected frequency f_0 at which this feature is observed can be easily found as a function of microsphere diameter D , matrix refractive index n_1 , and microsphere refractive index n_2 . The first pulse is transmitted through distance D of the matrix after time $t_1 = Dn_1/c$, where c is the speed of light. Similarly, the second pulse which travels through the microsphere will take time $t_2 = Dn_2/c$, resulting in a time difference $\Delta t = (n_2 - n_1)D/c = \Delta n D/c$. To achieve destructive interference, the two pulses must arrive with a π phase shift, therefore Δt must equal $T/2$, where T is the time period of the wave. Alternatively, this can be written with the frequency of the wave, $\Delta t = 1/2f_0$. This is rewritten as a function of frequency in Equation 4.

$$f_0 = \frac{c}{2\Delta n D} \quad (4)$$

Figure 12 plots the refractive index difference between microsphere and matrix (Δn) which would be required to produce a spectral feature at a given frequency and microsphere diameter. In the black line, we overlay the Δn which corresponds to the case of Borofloat microspheres in a PTFE matrix, where we plot the minimum (0.58) and maximum (0.7) refractive index difference within the observable frequency range to account for the dispersion of the Borofloat. The plotted values of Δn have been limited to a maximum value of 1 to aid the visual representation of the graph. By following the overlaid lines it can be seen that the expected spectral frequency f_0 is inversely proportional to the microsphere diameter, and that when microspheres are less than $50\ \mu\text{m}$ in diameter the spectral feature is expected at a frequency of 5 THz or more.

Further, we compare this analytical formulation to experimental results by plotting the loss peak frequency for various microsphere sizes at 5 % concentration. The 5 % concentration is utilised here as it is shown to produce spectra that are less likely to undergo the spectral splitting effect. The horizontal error bars on the data points correspond to the particle size distribution as quoted by the manufacturer. The experimental

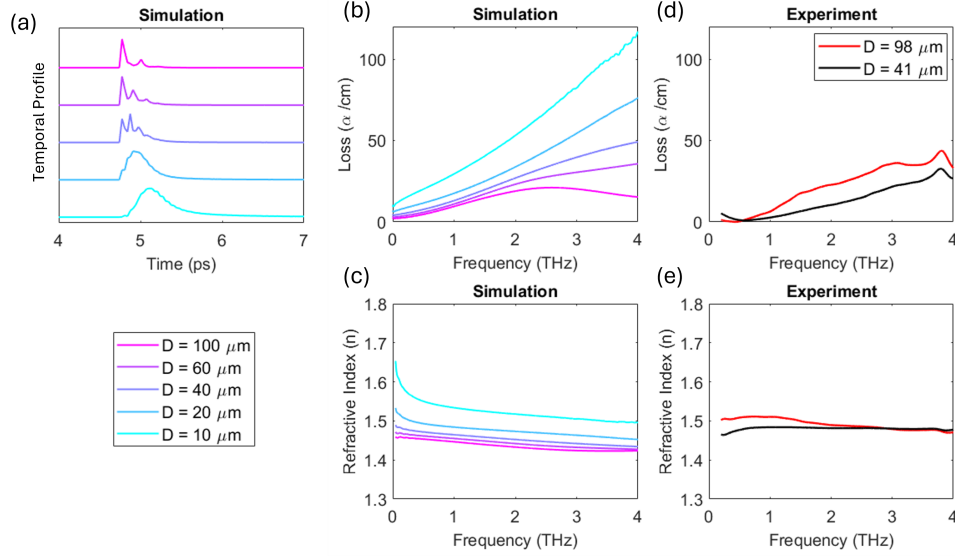


Fig. 11. (a) Time domain, (b) loss, and (c) refractive index spectra for microspheres simulated at 5 % concentration with varying microsphere diameter. Experimentally measured (d) loss and (e) refractive index spectra for microspheres at 98 and 41 μm diameter.

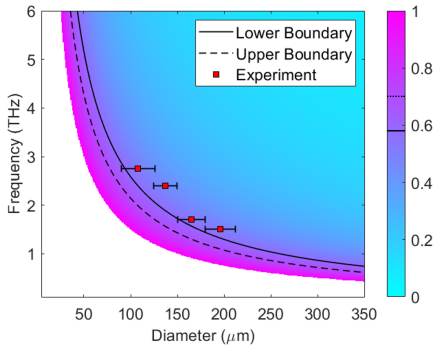


Fig. 12. Refractive index difference between matrix and microsphere Δn is plotted against spectral frequency f_0 and microsphere diameter utilising Equation 4. The upper and lower values of Δn plotted in black corresponds to the case of Borofloat microspheres surrounded by PTFE matrix. Experimental loss-peak frequencies for samples at 5 % concentration of plotted in red squares.

data points are obtained from samples with a fixed value of Δn and therefore it is expected that these data points should follow an inverse proportionality between frequency and microsphere diameter. The data points indeed do seem to follow this inverse proportionality trend however there are limited data points from which to draw a conclusion. While the data points do not lie within the upper and lower bounds for the refractive index difference, the lower edge of the error bars do fall within this expected range.

IV. DISCUSSION

The simulations here have shown that rays passing through heterogeneous samples consisting of PTFE with Borofloat microspheres are grouped together in time according to the number of microspheres that the ray has passed through (number of scattering events), creating distinct pulse peaks in the time domain. These peaks have a separation Δt which

depends on the microsphere diameter but not microsphere concentration. The time delay between peaks observed in the simulations matches to the expected delay of rays passing through a discrete number of Borofloat microspheres, where $\Delta t = \Delta n D / c$ (c is the speed of light in vacuum, and Δn is the difference in real refractive index between microsphere and matrix, and D is the diameter of the microsphere). When the time domain signals are transformed into the frequency domain, the distinct pulses in the time domain result in dips in the amplitude spectrum (or peaks in the loss spectrum), which are located at a frequency $f_0 = 1/(2\Delta t)$.

However, as the concentration of microspheres increases, the number of pulse peaks in the time domain increases and this results in multiple peaks in the loss spectrum owing to the spectral splitting effect demonstrated in Figure 10. When the microsphere size decreases the rays undergo many scattering events. The rays are still grouped together in the time domain according to the number of scattering events, however the spacing between the peaks is significantly reduced and the distributions for each scattering number are broader, resulting in a smooth temporal profile. In this case, the lack of sharp features in the time domain means there are no sharp peaks in loss.

It should be noted that for microspheres below 100 μm diameter the simulations and experimental results begin to diverge. Although both simulations and experiments show that smaller microspheres produce smoother loss spectra without peaks, the simulations suggest loss increases as microsphere size decreases, while experiments show the opposite behaviour. It may be the case that for small microspheres the ray tracing method utilised in the simulations is no longer representative of reality, and other effects may become dominant at such small length scales such as diffraction. This may be because the modelling of scattering angles in the simulation utilises an identical scattering distribution regardless of microsphere size, and although this produces a good agreement

to experiments for larger microspheres, it becomes invalid for smaller objects. This provides an interesting avenue for future work to determine the microsphere sizes at which different scattering regimes become dominant.

There have been many studies investigating the role of sample preparation techniques (such as compaction pressure and relaxation times) in producing pellets with minimal variation in spectral properties. However, even for the case of ideal samples simulated to contain an exact microsphere concentration, without porosity, and with an exact known thickness, we find through simulations that intra-batch variations exist and can result in dramatic differences in loss and refractive index spectra. The simulations reveal that these differences are due to the spatial locations of the scattering microspheres within the sample, therefore highlighting that the samples do not contain enough microspheres to become insensitive to their individual placement.

As has been shown in the simulations in Figure 11, it is possible to remove any sharp features in the loss spectrum by using microspheres of small diameter ($< 40 \mu m$) whereby the pulse peaks in the time domain become blurred together into one smooth distribution.

Alternatively, instead of removing these anomalous spectral features, it may be advantageous to utilise them to quantify sample morphology, for example, to determine the size and concentration of microspheres by recognising patterns in the measured spectra. This may be achieved through techniques such as principal component analysis, or machine learning.

For future work, there are several possible improvements to the modelling method which could be investigated to see their effects in comparison to experimental results. When initialising the rays we utilise a range of angles with a uniform distribution to model a focused beam, however this could be more accurately modelled by including an intensity distribution to reduce the intensity of larger angles. Further, we plan to investigate via simulations and experimental measurements, the possible changes in loss spectra that are produced by utilising a focused or collimated THz beam.

Finally, it should be noted that the simulations here appear to explain only part of the experimental results. Namely, in Figure 2 the spectral features in region 1 are well explained by the simulations here, however, those shown in regions 2 and 3 are still unexplained. We believe these features may be understood from effective medium theories [16], [26], [27], and require future investigations. These features occur close to the upper frequency limit of the THz TDS instrument, where the signal-to-noise ratio is very low, and therefore may require additional techniques such as air-plasma THz sources or Fourier-Transform spectroscopy.

V. CONCLUSION

Spurious features in the loss spectra of compacted granular samples were previously reported in samples consisting of Borofloat and PTFE. Individually these materials display no spectral features within the measured frequency window, however, when combined in granular compacts, strong loss features were present, which were observed to change with Borofloat microsphere size and concentration.

Here, by performing extensive experimental measurements of Borofloat and PTFE compacts, alongside ray-tracing simulations, we have presented a theoretical framework to explain the physical cause of this phenomena. We show that rays passing through these heterogeneous samples become grouped together in time, depending on the number of microspheres that they have interacted with. This grouping effect creates distinct pulse peaks in the time domain with a separation depending on the microsphere size and refractive index difference between microsphere and matrix. When transformed into the frequency domain, these temporal peaks create dips in amplitude (or peaks in loss), which shift to higher frequencies as the microsphere size decreases. Simulations reveal that by reducing the microsphere size below $40 \mu m$ diameter the sharp peaks in the temporal profile disappear, and in the frequency domain the peaks are removed from the loss spectra.

In conclusion, we have employed ray-tracing simulations to demonstrate how scattering in granular materials can produce spurious loss features in THz time-domain spectra. This is the first time, to our knowledge, that a detailed explanation has been given for such features, based on different path lengths arising from multiple scattering events as rays travel through the granular material. The proposed explanation is supported by modelling and validated by extensive experimental results. Moreover, we show that the model can be used to estimate the size and concentration of scattering objects. Consequently, spurious spectral features in THz spectra caused by scattering can be used as an analysis tool for granular materials, rather than merely an undesirable source of errors. Such analysis can be applied to product testing and non-destructive evaluation in many industries such as pharmaceuticals, agriculture, mining, and soil contamination.

VI. DATA AVAILABILITY STATEMENT

All the data associated with this paper are openly available from Zenodo [24] under a Creative Commons Attribution (CC BY) license. For the purpose of open access, the author has applied a Creative Commons Attribution (CC BY) license to any Author Accepted Manuscript version arising from this submission.

VII. CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Jon Gorecki: Writing – original draft, Writing – review & editing, Visualization, Methodology, Conceptualization, Investigation, Software. **Keir Murphy:** Writing – review & editing, Methodology, Conceptualization, Investigation. **Daniel Markl:** Writing – review & editing, Supervision, Funding acquisition. **Andrew Burnett:** Writing – review & editing, Methodology. **Mira Naftaly:** Writing – review & editing, Supervision, Conceptualization, Methodology.

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Jon Gorecki is from London, UK. He studied an undergraduate degree in Physics, followed by a PhD from the Optoelectronics Research Centre, both at the University of Southampton. He currently works at Imperial College London, developing optical instrumentation for biological applications.

Keir N. Murphy was born in Kilmarnock, United Kingdom, in 1997. He earned a BSc (Hons) in Chemistry from the University of the West of Scotland in 2019, followed by a PhD in Pharmacy and Biomedical Science from the University of Strathclyde in 2024. His doctoral research focused on Terahertz spectroscopy and analytical method development. Currently, he is a Technical Specialist at the University of Manchester, where he operates and maintains the CUSTOM Terahertz Scanning Near-Field Optical Microscopy (THz-SNOM) facility.



Daniel Markl received the B.Sc. and M.Sc. degrees in Information and Computer Engineering from the Graz University of Technology, Graz, Austria, in 2010 and 2012, respectively. He obtained the Ph.D. degree in Chemical Engineering from the Graz University of Technology in 2015. In 2016, he joined the Terahertz Applications Group at the University of Cambridge as a Postdoctoral Research Associate. In 2018, he was appointed as a Chancellor's Fellow and Lecturer at the University of Strathclyde in the Strathclyde Institute of Pharmacy and Biomedical Sciences (SIPBS). Since 2023, he has been a Professor in Pharmaceutical Product Engineering at the University of Strathclyde and, since 2022, an Associate Director at CMAC, an international centre for advanced pharmaceutical manufacturing. His research focuses on the development of self-driving labs and advanced measurements systems for drug product development and manufacturing.



Andrew D. Burnett received the Ph.D. degree in electronic and electrical engineering from the University of Leeds, in 2008, after completing his studies in chemistry with forensic science at the University of Bradford, in 2004. Since 2008, he continued his work at the Leeds, first, as a Postdoctoral Fellow in electrical engineering to understand the THz spectral properties of protein crystals before moving to the Faculty of Biological Sciences at Leeds in 2011 after receiving an EPSRC Postdoctoral Fellowship. In 2015, he moved to the School

of Chemistry, firstly as a Teaching Fellow for Physical Chemistry, and then in 2017 as an EPSRC Early Career Fellowship. Since 2022 he has been Associate Professor in the School of Chemistry at the University of Leeds. His research focuses on the development of linear and non-linear THz spectroscopic techniques and the understanding of THz spectra of solids through density functional theory calculations.

Mira Naftaly is at the National Physical Laboratory, UK, where she does THz measurements