Granular structure determined by terahertz scattering

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Abstract – Light scattering from particles reveals static and dynamical information about the particles and their correlations. Such methods are particularly powerful when the wavelength of the light is chosen similar to the sizes and distances of the particles. To apply scattering to investigate granular matter in particular—or other objects of similar submillimeter size—light of suitable wavelength in the terahertz regime needs to be chosen. By using a quantum cascade laser in a benchtop setup we determine the angle-dependent scattering of spherical particles as well as coffee powder and sugar grains. The scattering from single particles can be interpreted by form factors derived within the Mie theory. In addition, collective correlations can be extracted as static structure factors and compared to recent computer simulations.

Light scattering with visible light is fundamental for the way humans perceive their environment: Scattering makes the sky blue, milk white, and some gem stones appear in brilliant colors [1]. Within and beyond the visible part of the electromagnetic spectrum, light scattering has also for long been a versatile method for the characterization of media comprising discrete objects, from atoms and molecules [2], to colloidal suspensions and proteins [3], up to aircraft and astronomical objects [4]. X-rays, visible light, microwave radiation or radio waves allow for most sensitive measurements by scattering when the particle sizes and distances are of the order of the wavelength of the scattering light [4]. With practical laser sources now emerging in the terahertz region, light scattering with wavelengths between 30 $\mu$m and 1 mm becomes possible [5]. As these wavelengths match typical particle sizes in granular media [6,7] as well as bubbles sizes in typical foams [8], but also sizes of cells and unicellular organisms [9], suitable setups as well as methods for interpretation shall unlock the potential for terahertz light scattering in these areas. In the following, we present a bench-top light-scattering configuration using terahertz radiation, and demonstrate it for the investigation of granular particles between 80 $\mu$m and 1 mm in diameter. By suitable interpretation of the scattering intensities, we determine the particle sizes and for high densities identify the correlations among the particle positions in a static structure factor. The results demonstrate the possibility to investigate structures on previously unattainable length scales by scattering techniques in the terahertz region.

The statistical physics of granular matter has seen rapid progress in recent years: In addition to macroscopic measurements, experiments with direct imaging in two dimensions [10] or tomography in three dimensions [11] allow for analyses on the scale of individual particles. Many computer simulation studies provide testable predictions for particle packings or reveal intriguing structural anomalies [12]. Below the length scales of typical granular particles lies the realm of colloidal suspensions where light scattering has emerged as a reliable technique for the investigation of such structural properties and phase transitions [13]. Scattering offers the principle advantages of a) being able to monitor the time evolution of the measured system, b) a good resolution of both larger and smaller length scales with reliable statistics, and c) the \textit{in situ} measurement of three-dimensional samples. Hence, the use of scattering techniques is desirable also for granular matter. THz extinction spectra obtained from samples...
comprising granular media have already indicated the sensitivity of the extinction to particle size and packing density [14–17]. However, such measurements are superpositions of spectroscopic features of the sampled materials as well as scattering effects, and therefore difficult to interpret. The measurement of the angular dependence of scattered intensities at a single wavelength leads to sensitivity to geometric features of the sample alone.

The development of terahertz quantum cascade lasers (QCLs) [18,19] make experiments feasible that are in close analogy to static light scattering (SLS) setups which apply visible light. In SLS, lasers provide collimated, monochromatic, high-intensity radiation. Common solvents like water, organic liquids and air are transparent, and background light is easily shielded by lightproof containers. Using THz radiation imposes several constraints not present in experiments with visible light: Many media including ambient air are highly absorbing over large regions of the THz spectrum, and strong background radiation from thermal emission at room temperature has to be faced [5]. To overcome these constraints we use 1) a transmission window of air at 3.4 THz, 2) thin, effectively two-dimensional samples and 3) lock-in detection of the signal. Consequently, we obtained a versatile bench-top experiment for angle-resolved scattering experiments (see fig. 1). The capabilities of the setup are demonstrated in the following to characterize spherical particles with diameters from 80 μm to 1000 μm as well as technical grade coffee powder and sugar grains.

First, polystyrene and polyethylene spheres are used with nominal diameters of 80 μm (“PS 80”), 250 μm (“PS 250”), 500 μm (“PS 500”), and 1000 μm (“PE 1000”). From microscopy images we obtained the particle radius $a$, the standard deviation $\sigma$ and the polydispersity $PD = \sigma / a \cdot 100$ of the PS and PE particles. The size ratios $x = 2\pi \cdot a / \lambda$ and the phase shifts $\rho = 2\pi \cdot |m - 1|$ were calculated using $a$ and literature values for the complex refractive indices relative to air $n_{PS} = 1.59 - 0.002$ and $n_{PE} = 1.54 - 0.0014$ [20]. The number of illuminated particles followed from the cross-section of the laser beam of 3 mm$^2$ and the packing fraction of 0.55 determined from microscopy images. The scattering vector is determined by the scattering angle $\theta$ and the wavelength in air $\lambda$, $q = 4\pi / \lambda \cdot \sin(\theta / 2)$. From the packing density and the beam cross-section, the number of illuminated particles was estimated (see Supplemental Material in [21] for the description and determination of parameters). Table 1 summarizes the characteristic parameters.

A custom-made QCL, obtained from the Paul-Drude-Institut für Festkörperelektronik, Berlin, provided linearly polarized THz radiation with an average wavelength in air of 87.2 μm. The polarization direction was always chosen perpendicular to the scattering plane. We measured in 1.5° steps from $-20^\circ$ to $100^\circ$ around the sample with an angular resolution of 2.6° using a Golay cell. A thin PE foil supported the particles with an angle of 20° to the primary beam to allow asymmetric measurements up to scattering angles of 100°. Background intensity measurements with empty PE foil showed scattering up to 20°; the full width at half-maximum was determined to 14.1°. These values are comparably large due to the roughness of the adhesive film. The obtained scattering spectra from particles were corrected and normalized for background and drift in detector response and QCL power.

The intensity of the radiation scattered by the particles exhibits variations with angle and particle size. Figure 2 shows the measured intensities for scattering angles from $\theta_{\text{min}} = 12^\circ$ up to $\theta_{\text{max}} = 100^\circ$. In a first step to interpret the measured variations, we compare the experimental data with theoretical predictions for scattering from single spheres. From this we shall obtain quantitative information on the particle size and discuss the systematic deviations from theory in terms of correlated particle positions. The phase shifts $\rho$ produced by the particles (see table 1) exceed the assumption underlying Rayleigh-Gans-Debye (RGD) theory by far: $\rho < 1$ is commonly used in SLS measurements [22], while phase shifts and size ratios larger than 1 indicate a much better applicability of the approximative theories of anomalous diffraction by van de Hulst (vdH) [4]. We calculated scattered angle-dependent intensities according to RGD and vdH as well as the Mie theory. Fitting of the data was performed using Matlab codes (www.mathworks.com). Scattering amplitudes

| Name       | $a$ (μm) | PD (%) | $x$ | $\rho$ | $n_{ill}$ |
|------------|---------|-------|----|--------|-----------|
| PS 80      | 40.3    | 9.2   | 3.028 | 3.57   | $\approx 250$ |
| PS 250     | 109.5   | 5.1   | 8.327 | 9.83   | $\approx 40$   |
| PS 500     | 286.1   | 4.6   | 21.65 | 25.55  | $\approx 5$    |
| PE 1000    | 500     | N/A   | 37.85 | 40.88  | $\approx 2$    |

Table 1: Characterization of polystyrene (PS) and polyethylene (PE) particles by particle radius $a$ and polydispersity (PD) measured by light microscopy, size ratio $x$, phase shift $\rho$, and the number of illuminated particles $n_{ill}$. PD cannot be given reliably for only two illuminated 1 mm PE particles.

![Fig. 1: (Color online) Setup for THz scattering from granular matter. A beam from a quantum cascade laser (QCL) operating at 3.4 THz is chopped in a lock-in configuration to suppress thermal background radiation. The incoming beam is scattered from a quasi-two-dimensional granular sample at variable angle $\theta$. A Golay cell is used as a detector.](www.mathworks.com)
The scattering problem was calculated using three terms of the vdH series [4]. The Mie solution to the anomalous diffraction were calculated using the first diameter are probed and deviations are expected. For the smaller spheres, PS 80 and PS 250, deviations by correlations among the particle positions can be expected. The most pronounced effect of interference of light scattered from particles with correlated positions is the suppression of scattering at small scattering angles [3]. This can be observed in the scattering spectra of PS 80 and PS 250. Arrows in fig. 2 indicate where the respective scattering angles correspond to a length scale of the particle diameter, sin(\(\theta^* / 2\)) = \(\lambda / (4a)\). Smaller scattering angles, \(\theta \lesssim \theta^*\), hence describe length scales larger than the particle diameters. The Mie prediction for single-sphere scattering alone overestimates scattered intensities at these angles. For our thin samples this suppression can be described by the structure factor \(S(q)\), the Fourier transform of the point pattern representing the particle positions [3].

The scattered intensity \(I_{sca}\) becomes the product of the single-sphere scattering amplitude \(P(q)\) and the structure factor \(S(q)\): \(I_{sca}(q) \propto P(q) \cdot S(q)\), where \(q\) is the modulus of the scattering vector.

We divide the scattered intensity by the result of the Mie prediction for scattering from a single sphere \(P_{Mie}(q)\) to get an estimate of the structure factor. Figure 4 shows the result for this calculation along with the prediction of the Baus-Colot theory for the structure factor of two-dimensional hard-disc liquids with an area fraction of 0.6 [25]. The position of the first maximum and the asymptotic behavior of the structure factor for small \(q\)-values agree well with the analytical prediction for hard-disc fluids. Additional fluctuations in the experimental structure factor arise from the limited number of configurations probed in the static experiments. To compare the measured structure factor with the simulation, we estimate from fig. 2 [12] that the predicted anomaly \(S_q \propto q\) is found for wave vectors \(qd \lesssim 3\) in the simulation. As seen in the left panel of fig. 4, in the experiment the wave vectors for the 80 \(\mu m\) particles start around \(qd \gtrsim 1\) allowing for enough overlap to give a first estimate about \(S_q\).
In conclusion, we demonstrated a versatile setup for THz scattering together with the necessary methods for interpreting the signals. With this setup, particle sizes and static structure factors can be determined reliably for packings of typical granular particles. The setup is also suitable for other particulate systems such as foams, emulsions, and cells; and it is elaborated above what specific constraints such samples need to respect to allow for effective scattering. How to extract information on the particle level from the measured scattering signals is shown in detail for granular matter. Hence, by closing the gap between the infrared and the microwave part of the electromagnetic spectrum, a window opens for scattering methods to determine structural properties of particle packings and particulate systems of a wide variety.

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Fig. 4: (Color online) Experimental structure factors from THz scattering. Structure factors of the samples are determined by $S(q) = I_{exp}(q)/I_{th}(q)$ and shown together with the Baus-Colot (BC) prediction for hard-disc fluids with a packing fraction of 0.6. The scattering vector is scaled with the particle diameter.

Fig. 5: (Color online) Background-corrected (see text) scattered intensities of coffee powder (left) and sugar grains (right). Curves indicate least-square fits of Mie theory calculations used to determine the particle sizes.
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