Temperature Imaging in Liquids using Thermographic Phosphor Particles

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ABSTRACT

Temperature field measurements in liquids are demonstrated using zinc oxide (ZnO) thermographic phosphor particles. The particles are added to the liquid as a tracer. Following laser excitation, the temperature-dependent luminescence emission of the particles is imaged and the temperature is determined using a two-colour intensity ratio method.

In this work, the particle size requirements for accurate temperature tracing in turbulent liquid flows are calculated using a numerical heat transfer model. Spherical 5 µm-diameter particles are shown to have a 95% response time <35 µs in water between 0-100 °C, suitable for accurate tracing in turbulent flows. A method for preparing particle-liquid mixtures using ultrasonic dispersion was developed. The dispersions were characterised using scanning electron microscope imaging and laser diffraction particle sizing, indicating that the particle size is 1-2 µm.

The particle luminescence properties were investigated using spectroscopic and particle luminescence imaging techniques. Using 355 nm laser excitation, the luminescence signal is shown to be the same in water and in air. However, 266 nm excitation is used to avoid spectral overlap between Raman scattering from water and the detected ZnO luminescence emission. It is shown that 266 nm excitation can be used for temperature measurements in water using mass loads as low as 1-5 mg/L, corresponding to measured particle number densities 0.5-2.5x10^{12} particles/m³. In this range, the measured intensity ratio is independent of the mass load. The dependence of the intensity ratio on the laser fluence is also less pronounced using excitation at 266 nm compared to 355 nm. A single-shot, single-pixel temperature precision of 2-3 °C can be achieved over a temperature range spanning 50 °C.

The technique was applied to a convection experiment to measure the temperature fields in a buoyant thermal plume, demonstrating the suitability of these imaging diagnostics for the investigation of thermal convection and heat transfer.

1. Introduction

The ability to measure the fluid temperature and velocity, simultaneously, is essential to study turbulent flows encountered in engineering and in nature. Two prominent examples are turbulent heat transfer between a fluid and adjacent components actively cooled by forced convection; and in turbulent natural convection, where the flow structures encountered in scaled laboratory experiments are relevant to systems of geophysical and astrophysical importance like
the atmosphere, oceans, the Earth’s mantle and in stars including the Sun. In these examples, joint temperature and velocity measurements are needed to determine the heat flux, and to study correlations and the interaction between buoyancy forces and the turbulent flow. Often the fluid in question is a liquid, in which temperature measurement techniques based on thermochromic liquid crystals [1] or laser-induced fluorescence of temperature sensitive dyes (for example rhodamine, see e.g. refs. [2,3]) can be used. The aim of this work is to add a new versatile technique based on thermographic phosphor particles to the existing repertoire of possible solutions for temperature-velocity imaging in liquids.

This thermographic PIV technique was previously demonstrated in gas flows [4,5]. It is based on thermographic phosphors, which are solid materials with temperature-dependent luminescence properties. Phosphor particles are seeded into the flow under investigation. A laser sheet (typically 100’s µm to 1 mm thick) is used to excite the particles in the measurement plane, and their temperature-sensitive luminescence emission is imaged with cameras to determine the particle temperature using a two-colour intensity ratio method. Simultaneously, visible laser light scattered by particles in the same plane is recorded to determine the velocity field using a conventional particle image velocimetry (PIV) approach. Appropriately-sized (typically µm-scale) particles must be used, so that they closely follow the turbulent flow motion, and the particle temperature matches that of the surrounding fluid [5]. This approach permits simultaneous single-shot temperature-velocity imaging [5,6] at fast (multi-kHz) sampling rates [7], with a high (2 K) precision [8], using simple instrumentation and a single tracer.

There are so far only two demonstrations of this temperature imaging concept in liquids. These determined the average temperature distribution in an n-dodecane spray [9], and the temperature fields in burning methanol droplets [10]. The latter study used the phosphor ZnO:Zn but we have recently shown that it is the intrinsic edge emission of zinc oxide (ZnO) itself that is redshifted with temperature, and then used ZnO particles which were not deliberately doped for sensitive temperature measurements in gases [8].

In this paper we build on this work and the aforementioned liquid studies by extending the application of ZnO particles to temperature measurements in liquids. An experimental setup for characterising phosphor particles in liquids is developed (Sect. 2). The particle size appropriate for temperature and velocity tracing in liquids is determined and the size distribution and morphology of the particles is investigated (Sect. 3). The luminescence properties of ZnO particles dispersed in a liquid are characterised and compared to gas-phase measurements using the same particles (Sect. 4). The technique is also demonstrated in a convection experiment to image the development of a buoyant thermal plume (Sect. 5).
2. Experimental setup

2.1 Test object

A mixture of deionised water and ZnO particles (96479, Sigma-Aldrich) were contained in a 28 ml (40 mm x 20 mm x 35 mm) fused silica cuvette placed on a heated magnetic stirring plate. Prior to the characterisation and calibration measurements, using a thermocouple it was verified that when heating the dispersion with the stirrer switched on, the temperature was uniform throughout the liquid to within 1 K. For demonstration purposes, to generate a strongly non-uniform temperature field a 10 mm x 10 mm resistance heating block was fixed flat on the bottom of the inside of the cuvette and powered using a direct-current power supply.

2.2 Temperature imaging

Either the third (355 nm) or fourth (266 nm) harmonics of an Nd:YAG laser (GCR-150, Spectra-Physics) were used to excite the particles. Using +500 and -40 mm cylindrical lenses, the beam was formed into a light sheet intersecting the centre of the cuvette as shown in Fig. 1. To determine the laser fluence, the light sheet thicknesses were measured by reflecting the beam using a fused silica window and imaging the fluorescence of a paper target for 266 nm (this method can actually be used for both wavelengths, see ref. [11]), or directly illuminating the sensor of a webcam for 355 nm (see also Fig. 1). A photodiode-based energy-monitoring unit (Energy monitor V9, LaVision), calibrated using a pyroelectric energy detector (ES245C, Thorlabs), was used to measure the energy of the laser on a shot-to-shot basis.

Fig. 1 Setup diagram for characterisation of ZnO particles and temperature imaging demonstration
The particle luminescence emission was detected using two 2x2 hardware-binned interline transfer CCD cameras (Imager ProX 2M, LaVision) fitted with 50 mm f/1.4 objectives (Nikon). The exposure time was 5 µs. However the luminescence lifetime of ZnO, which determines the effective integration time of the measurement, is below 1 ns. A 50:50 plate beamsplitter (46642) and two bandpass filters at 387-11 (84094) and 425-50 nm (86961, all from Edmund Optics) were used to separate and filter the two detection channels. The two cameras were manually aligned using translation stages. Luminescence images were acquired at a rate of 10 Hz. The background (camera offset) was subtracted before applying a cutoff filter >20 counts and smoothing using a 9x9 moving average filter. The in-plane resolution was 450 µm at 90% contrast, as measured using an equivalently-processed image of a resolution target. For characterisation measurements, average luminescence intensities and intensity ratios were extracted from a small region in the centre of the processed images.

2.3 Particle counting

The particle number density was measured using a particle counting system [12]. This consisted of an additional Nd:YAG laser at 532 nm and a third CCD camera. The laser beam was formed into a sheet overlapping the measurement plane. Mie scattering images were processed using Matlab to determine the number of particles, and together with the probe volume size as defined by the measured green light sheet thickness and camera field of view, the particle number density (particles/m³) was determined.

2.4 Spectroscopy

Two setups were used for spectroscopic investigations of ZnO particles. For measuring the excitation spectrum, a fluorescence spectrometer (RF-5301PC, Shimadzu) was used. The device houses a 150 W xenon lamp and monochromator for excitation, monochromator and photomultiplier tube (PMT) for detection, and an additional PMT to automatically compensate for the excitation light power. The ZnO particle dispersion could be placed inside the sample holder in a cuvette which was continuously stirred using a magnetic stirrer. An additional filter (387-11 nm, see above) was placed on the detection line for additional rejection of scattered excitation light. The background was recorded using deionised water as a reference and subtracted from the results. For the measurements presented here, the signal-to-background ratio was greater than 10 across the investigated wavelength range (250-370 nm).
To obtain luminescence spectra, ZnO powder was contained in a ceramic crucible and excited at either 355 or 266 nm using the pulsed Nd:YAG laser described above. The laser beam diameter was adjusted using an iris and reflected onto the sample using a dichroic mirror appropriate for the excitation wavelength (LaserOptik). Luminescence was collected using an f/4 lens; spectrally dispersed using a 300 mm focal length f/4 spectrometer (Acton SP-2300i, Princeton Instruments) with a grating groove density of 300 g/mm and entrance slit width of 100 µm; and detected using an interline transfer CCD camera (Imager ProX 2M, LaVision) with an exposure time of 5 µs. The transmittance of the complete detection system was calibrated using the reference spectrum of a tungsten halogen lamp (LS-1, Ocean Optics).

3. Particle size and particle mixture preparation

3.1 Particle tracing properties

The inherent accuracy of the measurement technique depends on the time it takes for the particles to respond to changes in the fluid temperature and velocity. The matter has previously been addressed for gas flows [5], normally using properties for air. Here the analysis is extended to liquids.

The finite difference numerical model previously developed by our group (see ref. [5]) was used to solve the heat conduction equation to evaluate the particle response time to a step change in the liquid temperature. This approach is able to account for local temperature-dependent fluid properties, a finite fluid volume i.e. insulated system boundary conditions, and radiative heat transfer to the surroundings. The temperature dependent properties of water, which is the liquid used in these experiments, were included in the model to account for changes in the thermal conductivity over the working temperature range (0-100 °C). However a semi-infinite medium, i.e. with the temperature of the liquid fixed far from the particle (100 µm), was considered because of the low particle number densities of $10^{11}-10^{12}$ particles/m$^3$ used in these experiments and the high specific heat capacity of water. Radiative heat transfer was also not included owing to the near-ambient temperatures under consideration.

The calculated response times are adequately fast for many turbulent liquid flows of interest: $\tau_{T,95%} < 35$ µs for spherical ZnO particles with a diameter of 5 µm in water between 0-100 °C. The particles can be significantly larger in a liquid than in a gas, where in air for example, particles with a diameter of 1 µm have to be used to achieve a similar response time at 20 °C. The numerical model captures the thermal inertia of the fluid via the time dependent term in the heat conduction equation for the fluid. We note that a simple lumped capacitance approach [13]
which solves the time-independent heat equation in the fluid, as employed in ref. [14], may not be sufficiently accurate. This is because the increased volumetric heat capacity of liquids means that the thermal diffusivity of e.g. water, is much lower than that of air. This point will be explored in more detail in a forthcoming article.

For the velocity response time, the equation of motion for a spherical particle in a fluid has to be solved. Since in water the particle Reynolds number is below unity for slip velocities up to 0.1 m/s for particles with a 5 µm diameter, Stokes’ drag law can be used. We then assumed that the fluid and particle densities are equal and solved for velocity difference to yield the particle velocity relaxation time:

$$\tau_{U,95\%} = \frac{\rho_p d_p^2}{4 \mu_f}$$

where $\rho_p$ is the particle density, $d_p$ is the particle diameter, and $\mu_f$ is the fluid dynamic viscosity.

For gases, normally $\rho_p >> \rho_f$ is assumed and so $\rho_f ~ 0$, but for liquids this is not so and the added mass and pressure gradient terms are retained in the equation of motion. This has the effect of increasing the factor to $\frac{1}{4}$ in the $\tau_{U,95\%}$ expression. The absolute particle density appears in the expression, indicating that neutrally-buoyant particles in air respond faster than denser neutrally-buoyant particles in, for example, water. The dynamic viscosity of water is nearly two orders of magnitude higher than for air, so as for temperature the particles can be considerably larger in liquids and still offer adequate tracing capability. For spherical ZnO particles 5 µm in diameter, $\tau_{U,95\%} = 35 \mu s$ in water at 20 °C. Typically the temperature-dependence of the dynamic viscosity is more pronounced in liquids and this should be considered if using larger particles in highly turbulent liquid flows.

The particle diameter is normally a critical parameter due to its quadratic dependence, especially when seeding solid particles into gas flows. We conclude that due to the differing properties of liquids and gases the constraints on the particle diameter are relaxed considerably for liquids. Larger particles can be used while still obtaining accurate results.

3.2 SEM imaging and particle size measurements

When adding ZnO particles to the liquid, agglomerates so large as to be visible to the eye were clearly present and these could not be removed by simply stirring the sample. Therefore, the particle-water mixtures were dispersed using an ultrasonic homogeniser (Sonopuls UW2070, Bandelin). The particle size distributions with and without this treatment were characterised
using laser diffraction measurements (Mastersizer 2000, Malvern Instruments), as shown in Table 1. The median particle diameter based on volume does not change significantly \((d_{v,50} \approx 1-2 \, \mu m)\) and is suitable for flow tracing purposes, but the plot in Fig. 2 shows that the distribution without ultrasound is bimodal, containing a number of very large particles in the range 10-100 \(\mu m\). Therefore ultrasonic dispersion was routinely used for the following experiments to prepare the particle-water mixtures, using successive dilutions of an initial mixture down to mass loads in the range 1-5 mg/L used for the actual measurements (see Sect. 3.3).

<table>
<thead>
<tr>
<th></th>
<th>(d_{v,10} (\mu m))</th>
<th>(d_{v,50} (\mu m))</th>
<th>(d_{v,90} (\mu m))</th>
</tr>
</thead>
<tbody>
<tr>
<td>without ultrasound</td>
<td>0.79</td>
<td>1.65</td>
<td>3.54</td>
</tr>
<tr>
<td>with ultrasound</td>
<td>0.58</td>
<td>1.20</td>
<td>2.42</td>
</tr>
</tbody>
</table>

**Table 1** \(d_{v,10}\) the median and \(d_{v,90}\) particle sizes with and without ultrasonic dispersion

**Fig. 2** Left: Particle size distribution of ZnO powder, with and without ultrasonic dispersion. Right: SEM image of ZnO powder following ultrasound treatment

A qualitative overview of scanning electron microscope (SEM) images of the particles shows that the primary particles are sub-micron, on the scale of 100’s nm. The image in Fig. 2 indicates that after ultrasonic dispersion the primary particles remain agglomerated, and that the particles have projected sizes in the range 1-2 \(\mu m\). The particle sizing measurements (Fig. 2) can be expected to contain some inaccuracy since the particles are not homogeneous spheres, an assumption underlying the Mie theory that the device utilises. However, the SEM image also supports the picture that ultrasonic dispersion produces a particle size distribution favourable for flow tracing: in the range 1-2 \(\mu m\), and free of large agglomerates. Due to improved drag characteristics and an increased ratio of particle surface area to particle volume, the time
responses for both velocity and temperature respectively are therefore expected to be even faster than the calculations above.

3.3 Particle mixture preparation

The particle-sizing measurements indicate that ultrasound dispersion is necessary to remove large agglomerates, and so the following procedure was used to generate the liquid-particle dispersion. First, 20 mg of ZnO particles were added to 40 ml deionised water. In this dense initial dispersion containing large agglomerates the ultrasonic homogeniser (see above) was used for two minutes, after which the mixture appeared homogeneous and turbid. This was then diluted in two subsequent steps to the required mass load (1-5 mg/L), which appears completely clear to the eye in an ordinary one litre laboratory beaker.

3.4 Particle counting measurements

Using the previously developed particle counting system [12] it is possible to directly measure the particle number density and therefore know how many particles contribute to the measured luminescence signal. This system was used to measure the number of particles for a fixed mass load of 1 mg/L in a dilution prepared using the procedure described above. For this measured mass load, the particle number density is $4.8 \times 10^{11}$ particles/m$^3$. From repeated measurements using new dilutions, the particle number density varied by only ±12% of this mean value. Measured mass loads were used to obtain the required particle number densities and unless stated otherwise the particle number densities for all subsequent experiments described below are subject to this small error.

4. Results and discussion

4.1 Interference from Raman scattering

The previous gas-phase temperature measurements with ZnO particles used 355 nm excitation [8]. Using this wavelength and a laser energy of 3 mJ/pulse, a series of initial test measurements were carried out, first with an empty cuvette, and a second with deionised water only. The first of these tests revealed no signal in either channel, but in the second test, a weak signal could be detected in the 425-50 nm channel. The 425-50 interference filter has an optical density (OD) >5 at 355 nm. To ensure this signal was not laser light scattered at 355 nm an additional notch filter
blocking 355 nm (also OD >5) was temporarily installed, but this did not reduce the signal intensity. An integrated fibre-optic-coupled CCD spectrometer (BRC641E, BW-Tek) was used to measure the spectrum of the signal, revealing a peak at 404 nm as shown in Fig. 3. The spectral location of the interfering signal suggests it is Raman-scattered 355 nm laser light corresponding to the water O-H stretch at 3400 cm⁻¹. This was confirmed by installing a polarisation filter (Hoya) on the 425-50 nm detection channel and measuring the ratio between the polarised and depolarised components of the signal. Our value of 0.3 is similar to the Raman scattering depolarisation ratio in liquid water measured in ref. [15] (0.2 at 3400 cm⁻¹).

Fig. 3 Left: Measured spectrum (not to scale) of the Raman scattering from water at ~404 nm generated using 355 nm laser light. The emission spectra of ZnO particles at 23 °C using 266 and 355 nm excitation (this study), and 355 nm excitation at 95 °C [8] are also shown, along with the transmission curves of the interference filters used in this study. Right: Excitation spectrum of ZnO particles dispersed in water, normalised to 355 nm.

Fig. 3 also plots the emission spectra of ZnO, indicating that spectral discrimination of the Raman signal on the detection side is difficult to achieve. Choosing a different filter combination to avoid integrating the spectrum around 404 nm would severely compromise the signal level for measurements in the temperature range 0-100 °C. The short-lived edge luminescence emission has a lifetime of 100’s ps, which also precludes temporal discrimination using ns laser pulses. Even using a polarisation filter on the appropriate channel, the depolarised component of the Raman scattering would still be transmitted.

However, it is possible to make use of an attractive feature of thermographic phosphors, which is that they usually have a broad absorption band. Instead of the third harmonic of an Nd:YAG laser, using the fourth harmonic at 266 nm to excite ZnO would shift this Raman line to ~293 nm, which is well-separated from the ZnO edge luminescence and outside the passbands of both filters (see Fig. 3). This is a simple means to avoid generating the Raman signal at a
wavelength directly overlapping the ZnO edge emission, and was the approach adopted for all subsequent measurements.

4.2 Excitation and emission spectra

Measurements were performed to identify differences between excitation at the UV Nd:YAG harmonics at 355 and 266 nm. A dispersion of ZnO particles in a 3 ml cuvette was placed inside the fluorescence spectrometer. A continuous scan monitoring the ZnO edge emission peak at 387 nm is shown on the right in Fig. 3. The luminescence signal is normalised to 355 nm. Using the continuous output of the xenon lamp the excitation efficiency at 266 nm is about 55% of the 355 nm value.

The luminescence emission was also measured using pulsed (10 ns) excitation at 355 and 266 nm with the Nd:YAG laser, at a fluence of 1.2 mJ/cm². The results shown on the left in Fig. 3 are for aggregated powder placed in a crucible. The spectra are normalised to indicate that there is little difference in the lineshape or emission peak position using different excitation wavelengths. The Raman scattering peak and the temperature-shifted ZnO emission spectrum at 95 °C are also shown, to illustrate the spectral overlap. It should be noted that the relative signal level using 355 or 266 nm excitation determined by such a test is not a reliable indicator of the signal from an individual ZnO particle due to multiple scattering effects in the bulk powder, and this evaluation is left for measurements in water.

4.3 Luminescence signal

The first aim was to answer the question: is the signal per particle the same in air as in water? For air, this data is already available from the previous study using the same ZnO particles [8]. To obtain similar data in water, a dispersion of ZnO particles was prepared and illuminated using the laser at 355 nm. Simultaneously, the laser energy was measured on a shot-to-shot basis. The average signal in the 387-11 nm detection channel was calculated for each laser shot and is plotted as a function of laser fluence in Fig. 4.
For comparison, the same detection channel was considered for both air and water experiments (387-11 nm filter). The data were compared at a fluence of 40 mJ/cm² and $1 \times 10^{11}$ particles/m³. The laser sheet thickness, which changes the number of particles contained in the probe volume and therefore the luminescence signal, was also accounted for. Though the same f/1.4 camera objectives were used in each study, different CCD cameras were used and so the ADC conversion factors, quantum efficiency and hardware-binned pixel size, as well as the magnification, were all accounted for according to the equation presented in ref. [11]. The calculation shows that for ZnO using 355 nm excitation, the measured signal per particle for air and water is the same (to within 6%). A single ZnO particle emits ~$3 \times 10^6$ photons using a fluence of 40 mJ/cm² using a 10 ns laser pulse at 355 nm. This result is to be expected since we do not anticipate any influence of the environment on the luminescence emission, or significant variation in the absorption of laser light by the particles stemming from the different refractive indices of air and water.

The SEM images (Fig. 2) show that after ultrasound treatment the particles remain irregularly-shaped agglomerates, and the particle sizing measurements (Fig. 2) indicate that larger agglomerates are broken up. These measurements of the luminescence signal per particle show that the signal per particle in air and in water is very similar using 355 nm excitation, suggesting that the size of the ZnO agglomerates using ultrasound in water or seeding in a gas flow is similar. In our experience, we have found that seeders for gas flows that produce a high degree of centrifugation, high velocities leading to high shear forces, and agitation of the particle bed produces an aerosol free of large agglomerates, with improved spatial homogeneity and temporal consistency. It would seem that larger agglomerates are effectively broken up by these
processes and the resulting dispersion is similar to that produced using ultrasound treatment in a liquid.

The second aim was to check the luminescence signal per particle using 266 nm. For this, the mass load was kept same as for the 355 nm measurements described above. As previously mentioned, the number density for a given measured mass load is subject to a ±12% error. Therefore to improve the accuracy of the excitation wavelength comparison, the scattering signal from the particles at 532 nm was monitored using an additional CCD and the average signal from each dataset was used to correct for small variations in the particle number density. The measurements were also corrected for the UV laser sheet thickness.

The results are displayed in Fig. 4, showing that the signal is approximately a factor two lower for 266 nm excitation. The saturation behaviour is also prominent, where the rate of increase of the luminescence emission decreases with laser fluence. This finding is consistent with studies of ZnO [8] and BAM:Eu$^{2+}$ [11,12] particles in air.

For the same laser fluence, there are ~25% fewer excitation photons at 266 nm than at 355 nm, partly explaining the difference in the signal obtained using the two excitation wavelengths. The room temperature absorption spectrum in ref. [16] shows the absorption coefficient is very similar at 266 and 355 nm (~2.7x10$^5$ cm$^{-1}$). Together with these measurements of the signal per particle at each wavelength (which correspond well to our measured excitation spectrum) this may suggest that the quantum efficiency at 266 nm is lower than at 355 nm. Nevertheless, if necessary the lower signal using 266 nm excitation can be regained by increasing the mass load of particles in the liquid.

4.4 Seeding density effects

The dependence of the intensity ratio of the particle number density was investigated. The band gap of ZnO particles is at 3.37 eV [17], corresponding to ~368 nm, and the room temperature luminescence emission peak is shifted only slightly to ~385 nm. Therefore there is some overlap between absorption and emission and so luminescence could be reabsorbed by particles on the detection path. For example, with the filters used here this effect would dominate in the 387-11 nm channel, so the intensity ratio might be expected to increase with the particle number density.

This was checked for a range of mass loads in the range 1-5 mg/L, corresponding to particle number densities between 5x10$^{11}$ and 2.5x10$^{12}$ particles/m$^3$, by measuring the average intensity ratio using the two-colour thermometry system. The results shown on the left in Fig. 5 indicate that there is no trend in the intensity ratio, within the uncertainty of the measurement.
(4% in the intensity ratio, considering 2% camera linearity). Any changes in the particle number density during experiments are therefore supposed to have no effect on the measurement accuracy.

![Graph of mass load vs. intensity ratio](image1.png)

**Fig. 5** Cross-dependencies of the intensity ratio. Left: Intensity ratio measured for different mass loads of ZnO particles dispersed in water. Right: Intensity ratio against laser fluence. The 266 nm results were measured in water as part of this study and the 355 nm results are from ref. [8].

4.5 Excitation laser fluence

The previous study using ZnO particles in air found that there was a dependence of the intensity ratio on the excitation laser fluence at 355 nm [8]. This was checked for the 266 nm excitation adopted for the measurements in water. Single shot intensity ratios were evaluated from each instantaneous image and the laser energy was measured on a shot-to-shot basis. These results are shown on the right in Fig. 5. Also, in this plot the results using 355 nm excitation in air are reproduced for comparison.

The results indicate that there is also some dependence of the intensity ratio on the laser fluence when using excitation at 266 nm. However, the dependence is less prominent. Between 5 and 20 mJ/cm² the ratio increases by 55% for 266 nm excitation as opposed to a 75% increase using 355 nm. 266 nm excitation is in this respect beneficial, since for a fixed variation in the laser energy, the induced variation in the measured intensity ratio is lower. For the temperature measurement, there is then less demand on the correction employed for spatial and temporal variations in the fluence, as discussed in [8].

We consider two possible explanations for the different dependencies of the intensity ratio on the laser fluence with 355 and 266 nm excitation wavelengths. On the one hand, if laser-induced heating is primarily responsible for the behaviour, since the difference between
excitation and emission wavelengths is larger using 266 nm excitation more energy would be dissipated in the particles as heat, leading to a stronger dependence of intensity ratio on laser fluence. In comparing the trends, these results are therefore somewhat surprising. On the other hand, ref. [8] showed that the increase in the intensity ratio with laser fluence was in part due to the high excitation irradiance. For the same laser fluence there are less photons at 266 nm, and so the photon irradiance is lower. This may affect the density of excited centres in each particle, causing a spectral shift of the luminescence emission [16] and thereby altering the relative trend in the intensity ratio with laser fluence.

It should be noted that although the emission spectrum of the bulk ZnO powder is very similar using each excitation wavelength (Fig. 3, left), in particle-water dispersions the absolute value of the intensity ratio is different for each excitation wavelength (Fig. 5, right). However, different cameras and fields of view were employed in each case. Variations in camera gain or the effective filter transmission curves in different imaging configurations might be responsible for this difference in the absolute intensity ratio values.

4.6 Temperature calibration

To calibrate the intensity ratio against temperature, a particle-water dispersion (5 mg/L) was continuously stirred and heated using the heating plate. At various intermediate temperatures, sets comprising of 100 images were acquired with the 266 nm laser energy set at 10 mJ/cm² (800 µm light sheet thickness). Intensity ratio images were divided by an average intensity ratio image at room temperature as a correction for spatial non-uniformity in light collection efficiency and spatial variation in the laser fluence. Pulse-to-pulse fluctuations in the laser energy were continuously measured using the energy monitor. To obtain the temperature calibration, at each temperature a linear fit through the laser fluence-intensity ratio data was made, and so for a fixed fluence, the temperature calibration points shown in Fig. 6 could be extracted. A quadratic fit through these points is also shown. The mean deviation of the calibration points from the fit is 0.3 °C, and the maximum deviation is 0.6 °C. The sensitivity, which at 24 °C is ~0.7 %/°C, is across the range 20-70 °C very similar to that obtained using 355 nm excitation in air using the same filter combination [8].
Since the temperature within the cuvette is uniform, the same images used for the calibration were also used to assess the temperature precision. Pulse-to-pulse fluctuations in the laser energy were continuously measured using the energy monitor, allowing correction of each single shot image using the laser fluence-intensity ratio data of Fig. 5. The calibration curve was used to convert the corrected intensity ratio fields into temperature. The single-shot precision (the average standard deviation of the processed pixels in each instantaneous temperature image) was 2.9 °C at 25 °C (1.0% of the absolute temperature) and 2.1 °C (0.6%) at 72 °C, for an in-plane spatial resolution of 450 µm. The reason for the improved temperature precision with increasing temperature is the improved sensitivity with increasing temperature using this filter combination. The shot-to-shot standard deviation of the average temperature was 1.4 °C (0.5%) at 25 °C.

5. Temperature imaging demonstration

The resistance heating block was fixed inside the cuvette, which was filled with a dispersion of particles. The 266 nm laser light sheet intersected the centre of the cuvette. Starting from a uniform room temperature, the heating block was switched on, while luminescence images were continuously acquired at a rate of 10 Hz. These were processed to produce temperature images using the previously recorded calibration curve.
A time sequence of the evolving temperature field is shown in Fig. 7. A plume forms above the block and rises upward due to buoyancy. The plume increases in temperature and grows, forming a convective current within the cuvette. This 10 Hz sampling rate is sufficient to resolve the flow behaviour in time, but only every 5th image of the later part of the recording is shown in Fig. 7. The temperature difference is ~50 °C, and a high measurement precision (<1%) can be maintained over this range. A video of the plume development will be available online as supplementary material [18].

6. Conclusions

Calculations were performed to establish a suitable particle size for flow tracing in liquids, showing that spherical ZnO particles 5 µm in diameter have response times for temperature and velocity below 35 µs in water at 20 °C, fast enough for most turbulent liquid flows of interest. SEM images of particle-water mixtures following ultrasonic dispersion indicated that the particles remain in an agglomerated form with a projected size on the scale of 1-2 µm. This supported the results of the laser diffraction particle sizing measurements which showed that ultrasonic dispersion is essential to remove large agglomerates. The number of particles was directly measured for a given mass load finding that, using the developed dispersion method, 1 mg/L corresponds to a particle number density 4.8x10^{11} particles/m³. The particle luminescence
properties were characterised using spectroscopic and particle luminescence imaging techniques, determining that:

- Using 355 nm laser excitation, the luminescence signal is the same in water and in air. A single ZnO particle emits $3 \times 10^6$ photons using a fluence of 40 mJ/cm$^2$, using a 10 ns laser pulse at 355 nm.
- In water, 355 nm excitation generates Raman scattering at ~404 nm which spectrally overlaps the ZnO luminescence emission.
- The interfering Raman scattering can be avoided by using 266 nm radiation (the fourth harmonic of an Nd:YAG laser) to excite ZnO.
- Compared with 355 nm excitation, the collected luminescence signal per particle is a factor two lower using 266 nm.
- Compared with 355 nm excitation, the dependence of the intensity ratio on laser fluence is lower using 266 nm.
- The intensity ratio is independent of the mass load in the range 1-5 mg/L, corresponding to particle number densities between $5 \times 10^{11}$ and $2.5 \times 10^{12}$ particles/m$^3$.

The technique was successfully used to measure the temperature field in a thermal plume developing above a resistance heating block. It is straightforward to use the same tracer particles for PIV, enabling simultaneous velocity measurements. The diagnostics have a short integration time (~ns), can be applied at kHz repetition rates, have a good spatial resolution of the order 100’s μm, and could be used to measure over a broad temperature range (>100 °C) while maintaining a good precision (2-3 °C), serving as a useful addition to laser diagnostics for temperature-velocity imaging in liquids.

Future work in this area should focus on the following:

- To further investigate the dependence of the luminescence signal and intensity ratio on the laser fluence using 266 nm excitation in air, and acquire spectrally-resolved measurements of water-particle mixtures using 355 and 266 nm excitation.
- An additional helpful outcome of this study is related to the fact that characterising phosphors on a single particle basis is essential to find new, useful phosphors and design thermographic PIV experiments. This work that shows liquids are a good medium in which to measure the signal per particle, the quantity of interest, because only a small amount (<0.1 mg for the 28 ml cuvette used in this study) of powder is needed for a simpler experiment, compared with the requirement for much larger (order 100 g)
quantities of particles for the seeders typically used for gas flows. Experiments like these can be used to perform carefully controlled investigations of single phosphor particles to systematically investigate the effect of e.g. particle size, host compound, dopant/sensitiser concentration and other important parameters related to particle morphology and phosphor composition.

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