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The index of refraction of supercooled solutions determined by the analysis of optical rainbow scattering from levitated droplets

Denis Duft, Thomas Leisner*

Institut für Physik, TU Ilmenau, Ilmenau, Germany

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Abstract

We present a novel method for the determination of the index of refraction of single droplets by light scattering measurements in the region of the first and second order rainbow. An inversion algorithm is proposed which allows to extract the refractive index with high precision from the position and width of both rainbow peaks. The method is applied to determine the index of refraction of supercooled levitated water droplets in the temperature region between 237 K and 273 K.

Keywords: Supercooled solutions; Refractive index; Optical rainbow scattering; Levitated droplets

Supercooled tropospheric and stratospheric clouds have a major impact on the climate of the earth by their various direct and indirect contributions to the energy balance of the atmosphere [1]. Nevertheless, many properties of supercooled liquids are not well established today. This especially holds true for the state of strong supercooling, i.e., when the liquid can no longer be kept in contact with a solid enclosure. Under these conditions experiments have to rely on emulsion samples or contact-free levitation techniques. For atmospheric purposes, the refractive index is the most important property of cloud droplets, as it determines the optical properties of the cloud and therefore its role in the radiation budget of the atmosphere. Furthermore, the refractive index is directly accessed by optical remote sensing techniques, like Lidar, and reliable reference data are crucial for the interpretation of the data collected by these methods. In this contribution, we present a fast and accurate method to determine the index of refraction of levitated supercooled solution droplets which relies on the analysis of the angular dependent light scattering from a spherical microdroplet (phase function measurement). The qualitative principle behind this method can be understood using the classical ray theory of the rainbow, as it is discussed, for example, in Refs. [2,3]. It follows that from a parallel bundle of rays that is refracted from a sphere after undergoing p internal reflections ($p \geq 1$), a maximum density of emerging rays can be found around an angle of extremal deflection, the "rainbow angle" of order p.

According to ray theory, the angular position of the rainbows of order p is given as a function of the refractive index n by:

$$\Theta_p(n) = 2\left\{(p+1)\cos^{-1}\left[\frac{1}{n}\sqrt{1-\frac{n^2-1}{(p+1)^2-1}}\right] - \sin^{-1}\left[\sqrt{\frac{n^2-1}{(p+1)^2-1}}\right]\right\} \qquad (1)$$

In ray optics, the rainbow position is independent of droplet size. If light scattering from spheres is analyzed more carefully using wave theory, the situation becomes more complex. Airy [4] realized that for small droplets the position of the rainbow does depend slightly on the droplet diameter d and that each rainbow is accompanied by additional so-called supernumerary intensity maxima. Later Mie [5] gave an exact solution to the scattering of light by spherical objects. Since then there have been numerous approaches to use the phase function for the determination of the refractive index of droplets. Good surveys can be found in Refs. [2,6,7]. We propose a new method that allows to determine the index of refraction by the measurement of

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* Corresponding author. Tel.: +49-3677-69-3670; fax: +49-3677-69-3672.

E-mail address: thomas.leisner@tu-ilmenau.de (T. Leisner).

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the angular distance between the first and the second rainbow. It uses the width of the rainbow peaks to correct for the size dependence of the rainbow position. We propose an analytical form for the phase function, which can be fitted to experimental data in order to retrieve the refractive index without time consuming Mie calculations. This method is then applied to determine the refractive index of supercooled water down to 237 K.

A closer examination of Eq. (1) reveals that within the interesting range of refractive indices ($1.3 < n < 1.6$) Θ_1 is a monotonously increasing, but Θ_2 a monotonously decreasing function of n. Therefore, it is in principle possible to determine the refractive index from the position of either rainbow, but it is more convenient to use the angular difference between the two rainbows, i.e., $\Delta\Theta = \Theta_1 - \Theta_2$ as experimentally the determination of an angular difference is more accurate and less inflicted by adjustment problems than the determination of an absolute angle. For a realistic range of refractive indices ($1.33 < n < 1.45$), the phase function has to be measured within an angular range of more than 60°. It turns out that the rainbow peaks are more pronounced and more easily analyzed if the incident light is polarized perpendicular to the plane of scattering. Therefore, the remainder of this discussion refers to that case. In the phase function the rainbows can be identified as broad maxima in the angular dependent scattering efficiency. They are superimposed by a fine ripple structure, however, which complicates the determination of the rainbow position. This is illustrated in Fig. 1a, where the calculated phase function for a $d = 80\,\mu$m droplet with $n = 1.34$ is given.

It is therefore much easier not to evaluate the phase function at a given droplet size, but to average over a small size region. Fig. 1b shows a calculated phase function averaged over a diameter interval of 0.5 μm. The ripple structure is removed and the two rainbow maxima can be clearly discerned. In order to determine the position and width of each rainbow maximum, we fit an analytical function to the rainbow region. The choice of this function is somewhat ambiguous, it turned out that a separate biexponential Fisher–Tipett distribution function [8] for each rainbow peak gives excellent results. Other slanted distributions like extended Weibull or lognormal distributions might give comparable results. The analytical representation of the two Fisher–Tippet peaks is:

$$I(\Theta) = I_0 + A_1 \exp\left[\exp\left(-2\frac{\Theta - \Theta_{c1}}{\omega_1}\right) - 2\frac{\Theta - \Theta_{c1}}{\omega_1}\right] + A_2 \exp\left[\exp\left(-\frac{\Theta - \Theta_{c2}}{\omega_2}\right) - \frac{\Theta - \Theta_{c2}}{\omega_2}\right] \qquad (2)$$

where $I(\Theta)$ is the phase function and the seven free parameters are a constant background I_0 and the amplitude A, position Θ_c and width ω of each of the two rainbow peaks. Depending on the sign of ω the peak can be slanted in either direction. An example of this function is given as a red line in Fig. 1c. Here, the first and second order rainbow have positive and negative width ω, respectively.

In order to evaluate which linear combinations of these seven parameters bear significant information on the droplet size and refractive index, an extensive statistical analysis

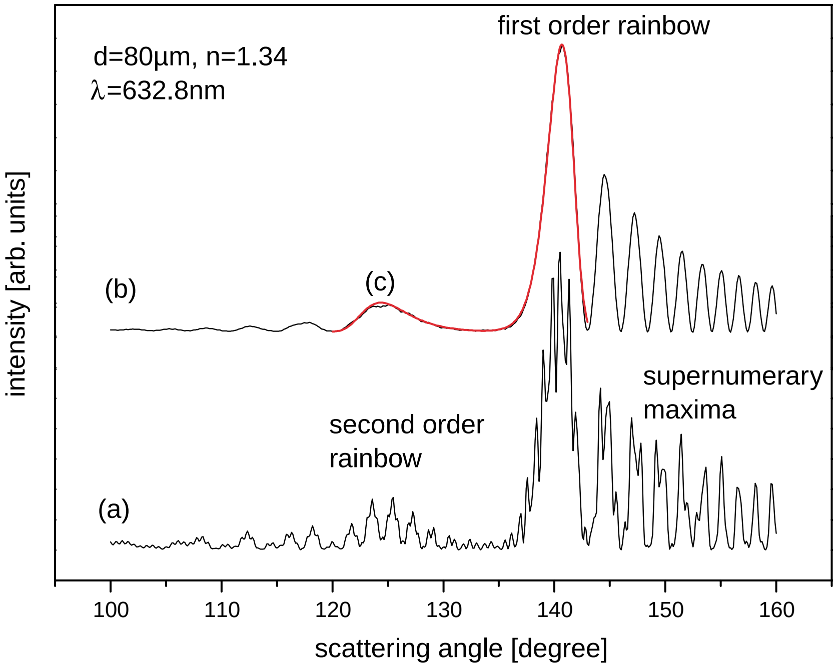

Fig. 1. Light scattering phase functions in the rainbow region (a) $d = 80\,\mu$m droplet according to Mie theory for perpendicular polarization (b) averaged from $d = 80$ to $80.5\,\mu$m (c, red line) fitted analytical function to the rainbow region (cf., text). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

has been performed using Mie theory calculations. For that purpose, phase functions have been calculated for 16,000 evenly distributed sample droplets in the experimentally relevant parameter range between $30\,\mu\text{m} < d < 100\,\mu\text{m}$ and $1.32 < n < 1.43$, each averaged over $\Delta d = 0.5\,\mu\text{m}$. Each phase function has been fitted by Eq. (2) and the seven fit parameters have been recorded. We used the method of Singular Value Decomposition [9] to decide which of the fit parameters or which linear combinations of them carry information on the initial droplet size and refractive index. It turns out that I_0 and the amplitudes A_1 and A_2 bear little significant information and that it is sufficient to deduce the rainbow–peak distance $\Delta\Theta = \Theta_{c1} - \Theta_{c2}$ and the averaged rainbow peak width $\omega = (|\omega_1| + |\omega_2|)/2$ in order to achieve an excellent data inversion for the index of refraction. As expected, the droplet size can be extracted only approximately.

By analysis of various low order polynomials in $\Delta\Theta$ and ω, we found that it is sufficient to consider only the linear and quadratic terms, so that our proposed inversion algorithm becomes:

$$n = n_0 + n_\Delta^1 \cdot \Delta\Theta + n_\Delta^2 \cdot \Delta\Theta^2 + n_\omega^1 \cdot \omega + n_\omega^2 \cdot \omega^2 \tag{3}$$

$$d = d_0 + d_\Delta^1 \cdot \Delta\Theta + d_\Delta^2 \cdot \Delta\Theta^2 + d_\omega^1 \cdot \omega + d_\omega^2 \cdot \omega^2 \tag{4}$$

The set of polynomial coefficients that gives the optimal determination of size and refractive index of the droplet is reproduced in Table 1.

Within the parameter interval considered, the so obtained inversion should be accurate (single sigma) to within 8×10^{-5} for the refractive index but only to within $1.5\,\mu\text{m}$ for the diameter of the droplet.

In order to test this analysis experimentally, an electrodynamic levitator [10] has been modified for precise phase function measurements of supercooled solution droplets over an extended angular range. It is of the classic "Paul trap" design [11], consisting of three hyperboloidal electrodes. Horizontal and vertical cross-sections through the trap are given in Fig. 2.

Table 1
Optimal coefficients for the inversion polynomials for size d and refractive index n (cf., Eqs. (3) and (4))

Coefficient	Optimal value	Coefficient	Optimal value
n_0	1.3100	d_0	358.0
n_Δ^1	2.5884×10^{-3}	d_Δ^1	0.941
n_Δ^2	-2.543×10^{-6}	d_Δ^2	-4.0453×10^{-2}
n_ω^1	-3.396×10^{-3}	d_ω^1	-118.2
n_ω^2	1.05×10^{-4}	d_ω^2	11.6

The central toroidal electrode (Fig. 2a) forms a climate chamber with gas inlet and outlet system and optical ports for illumination and observation. In contrast to our previous design [12], its shape has been adapted to allow the integration of two linear charge coupled device (CCD) detectors (Fig. 2b, SONY ILX 511, 2048 pixels, $14\,\mu\text{m} \times 200\,\mu\text{m}$ each) for the phase function measurements in the region of the rainbow angles. The climate chamber is connected thermally to a liquid nitrogen cooled cold finger and its temperature is variable between −100 and 50 °C. The bottom and top endcap electrodes (Fig. 2d and e) carry the AC voltage needed for trapping and superimposed a dc voltage to balance the gravitational force on the droplet. From this voltage, the mass-to-charge ratio of the droplets can be deduced.

The trap is mounted in a vacuum chamber for thermal insulation. Throughout our experiments the trap interior is held at the low temperature of interest and remains under ambient pressure. Individual liquid solution droplets with a diameter of approximately 100 μm are injected through the top electrode from a piezo-driven nozzle (GESIM) which is kept at room temperature. They are charged by induction to a specific charge of about 2.3×10^{-3} C/kg. In the center of the trap they are illuminated by an unfocussed HeNe laser beam (5 mW) polarized perpendicular to the plane of scattering. After rapid (∼200 ms) thermalization to the trap temperature, their diameter shrinks slowly by diffusion limited evaporation. Angular resolved light scattering measurements

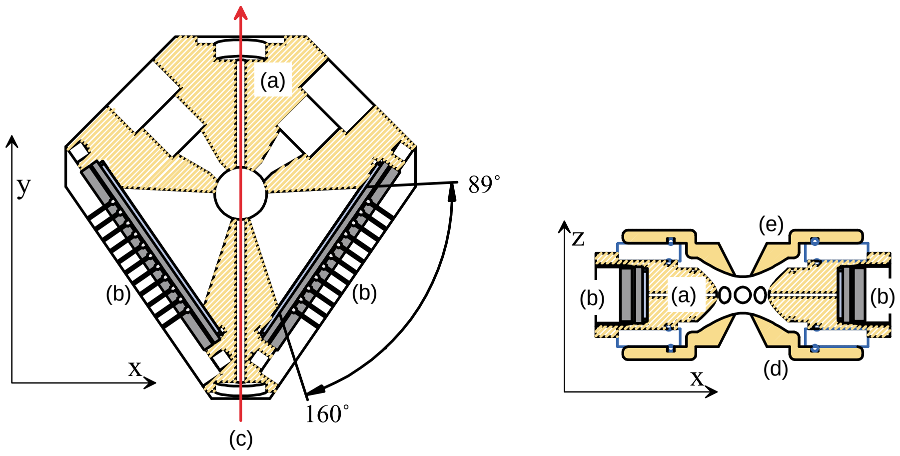

Fig. 2. Schematic horizontal and vertical cross-section through the levitator: (a) central electrode and climate chamber, (b) linear CCD detectors, (c) illuminating laser beam, (d) bottom and (e) top endcap electrode.

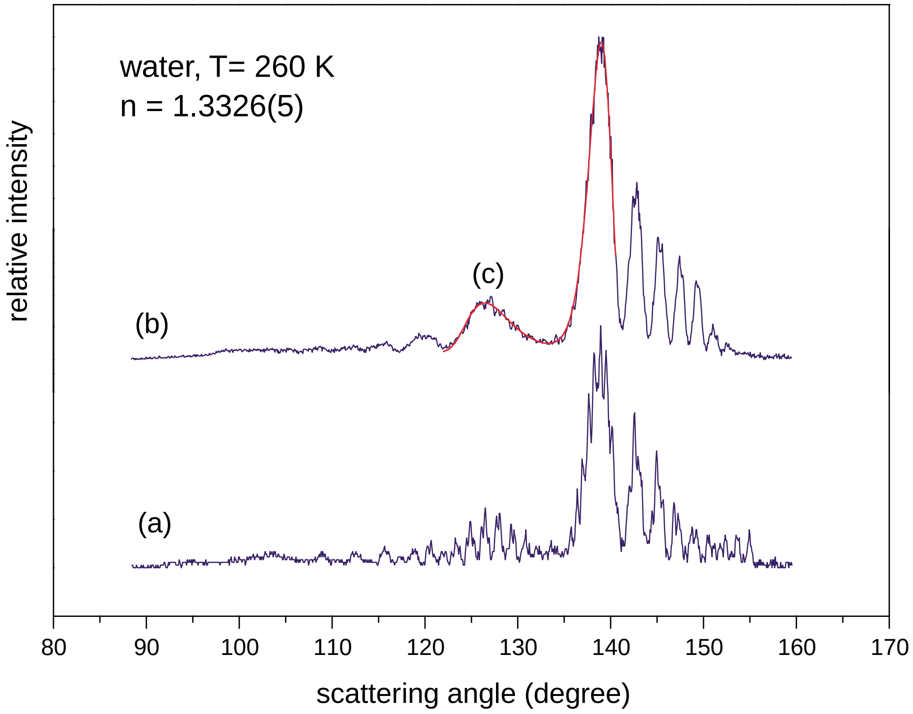

Fig. 3. Experimental phase functions in the rainbow region (a) $d \sim 91\,\mu$m droplet, perpendicular polarization (b) averaged from $d = 91$ to $90\,\mu$m (c, red line) best fit to the rainbow-regions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

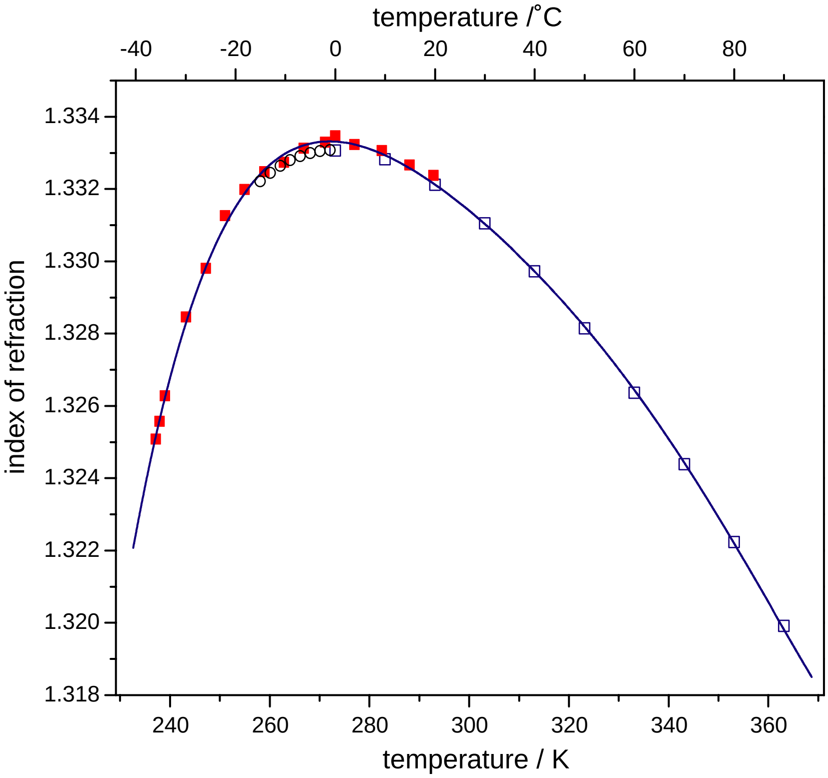

Fig. 4. Index of refraction of water in the temperature range between 240 and 365 K. Full squares: levitated droplets, this work; open circles, Ref. [13]; open squares, Ref. [14]. The solid line is a polynomial fit of fifth degree to all data sets.

are performed by means of the two linear CCD detectors at a rate of about 100 Hz. The pixel numbers of the raw data have to be converted to scattering angles. For this purpose, the geometrical shape of the trap and the light detector has to be known with high accuracy. We have determined a geometry factor by comparing the measured phase function of water droplets at room temperature to Mie calculations using the well established refractive index of water at room temperature and 632.8 nm wavelength. The so derived geometry is then used throughout our experimental temperature range. It differs from the geometry derived from the size of our trap and the CCD sensor by about 7%. This discrepancy is somewhat larger than expected from machining errors and its origin is still under investigation. The measured phase functions are averaged over a diameter interval of about 1 μm in order to remove the ripple structure, as discussed above. A typical experimental example is shown in Fig. 3.

First and second order rainbow are clearly discernable and their position and width are determined by fitting a function according to Eqs. (2) and (3). They are then used to determine the refractive index as a function of trap temperature. This procedure is repeated for falling temperatures of the trap in order to obtain the temperature dependent refractive index of the supercooled solution, until the limit of rapid homogeneous nucleation of the water is reached.

The power of this method is illustrated in Fig. 4, where the refractive index of water at 632.8 nm is given as a function of temperature between 237 and 297 K. The anomaly of water with a maximum in density and refractive index slightly above 0 °C is clearly visible. Our data (closed squares) reproduce nicely the reference data in the temperature interval between 258 and 293 K (open circles, open squares, adapted from Refs. [13,14]) but extend into the previously inaccessible region down to 237 K.

The method described herein provides an accurate and fast way of measuring the refractive index of levitated microdroplets. The proposed inversion of the phase function does not require Mie calculations and is therefore fast enough to be performed in real time. It relies, however, on phase function averaging by the evaporation of the droplet. If this is not feasible, an alternative version of the technique might be employed which uses a slight tuning of the wavelength of the laser light source instead.

In the mean time, we have applied this method to determine the refractive index of more liquids of atmospheric interest, namely, supercooled sulfuric acid solutions and supersaturated ammonium sulfate solutions. The results will be reported in a subsequent publication.

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