Precision measurements of refractive index of liquids

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Abstract

We developed a simple interferometric method to measure the refractive index of transparent liquids with precision of the order of 10^{-6}. The main sources of error are analyzed and techniques to minimize these errors are described. A simple way of temperature stabilization of the sample is described. Some measurements of refractive index were performed to test the equipment.

Introduction

Precise measurements of refractive index of liquids can reveal interesting molecular properties of chemical compounds [1] and often the refractive index of liquids is an important input parameter for other measurements such as TIRM (Total Internal Reflection Microscopy) [2]. Commercially available refractometers, such as the Abbe refractometer, are expensive and their precision is usually not much better than 10^{-4} [3]. Several interferometric methods for measuring refractive indices are known in the literature [4, 5]. At the XXIV ENFMC (2001) two groups independently introduced a new and very simple interferometric method of measuring refractive indices of liquids [6, 7]. However, at that time neither of the groups obtained a precision better than $3 \cdot 10^{-5}$. In the present work the sources of error are analyzed and simple methods to minimize the error are described. With the present setup the optical precision obtained was $1.7 \cdot 10^{-6}$. Measurements of the refractive index with such precision would not be of any value without good knowledge of the sample temperature. For solutions based on water the temperature dependence of the index is typically of the order 10^{-4} K^{-1}. This means that the temperature should be known with error smaller than 10^{-2} K. Due to evaporation from the liquid surface it is a difficult task to maintain the temperature constant during the measurement. In this work we describe a simple method to guaranty temperature stability better than $3 \cdot 10^{-3}$K and temperature measurement with an error better than 10^{-2}K.

Experimental Setup

The method for measuring n at a fixed temperature is based on two simultaneous interferometric measurements of mirror displacements. One measures the displacement with a lasers beam traveling in air and the other one measures the same displacement with the laser beam travelling in the liquid sample. The ration of counted interference oscillation of the two beams is then equal to the ration of refractive index of the sample n and of ambient air n_A.

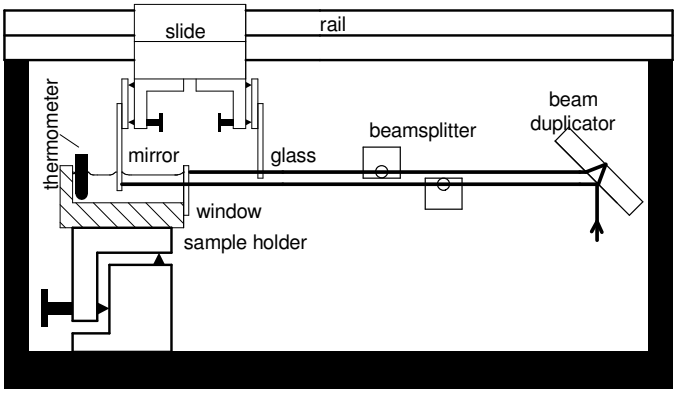


Fig. 1 Experimental setup

Figure 1 shows the experimental set-up. A light beam from a linearly polarized He-Ne laser ($\lambda = 632.8\text{nm}$) is split into two parallel, vertically separated beams by means of a glass plate with enhanced surface parallelism. The upper beam is reflected by a glass plate, which is mounted outside the sample on a slide, and by the surface of the entrance window of the sample holder. The intensity corresponding to the sum of these reflections is registered as the reference signal. The lower beam is reflected by the surface of the entrance window and by a mirror, which is mounted on the same slide and that hangs into the sample. The interference signal of these reflections is registered as sample signal.

These signals are registered by a data acquisition system as a function of time while the slide is slowly being pulled by a clockwork. The number of oscillations is then counted including fractions of oscillations at the beginning and end of the measuring interval.

The precision of this method is limited by three opto-mechanical imperfections:

1) The orientation of the sample holder and the moving mirrors are carefully adjusted such that the reflected beams propagate back into the source. This way the incidence angles on the mirrors are close to 90^o . However, this adjustment has some error. The relation between index, number of counts N , and mirror displacement Δx is therefore

$$2\Delta x = \frac{N_{REF}\ \lambda_0 \cos(\theta+\beta)}{n_A} \tag{1}$$

$$2\Delta x = \frac{N_{SAMPLE}\ \lambda_0 \cos\theta}{n} \tag{2}$$

where λ_0 is the vacuum wave length of the laser light, θ is the angle between the axis of the incoming sample beam and the normal of the mirror surface and β is an additional angular error caused by the non-parallelism of the beam duplication plate. Expanding the cosine up to the second order one gets for the ration of refractive index

$$\frac{n}{n_A} = \frac{N_{SAMPLE}\left(1-\theta^2/2\right)}{N_{REF}\left(1-(\theta+\beta)^2/2\right)} \approx \frac{N_{SAMPLE}}{N_{REF}}\left(1+\theta\beta+\beta^2/2\right) \tag{3}$$

One sees that the main adjustment error θ^2 cancels out. But the beam duplication error β creates a mixed term that brings in a linear adjustment term. Therefore it is important to make sure to have the beams travelling right back into their origin. In the equations (1) and (2) we have not taken into account a possible angle between the Fabry-Perot mirrors. The angle between the Fabry-Perot mirrors is adjusted up to the point where one observes only a single light spot and no longer any fringes.

2) If the direction of translation is not parallel to the light beams the light spots move on the slide mounted mirrors during translation. In case the glass plates used as mirrors do not have high optical surface quality this movement introduces additional displacements $\delta\Delta x$ and $\delta\Delta x_{REF}$, which are not necessarily equal for the signal and reference beam. We minimized this kind of error using a sliding rail that is much longer than the translation distance used. Parallelism of translation and incident light was then carefully adjusted with translations of about 50 cm and using electronic light detection instead of visual adjustment.

3) The translation of the slide is not a pure translation but may involve some small rotation due to geometrical imperfection of the sliding rail. Let $\vec{\varphi}$ be the rotation vector of this rotation, i.e. a vector pointing along the rotation axis and having modulus of the angle. Let $\hat{n}$ be a horizontal unit vector that is perpendicular to the light beams. Then the displacements Δx of equations (1) and (2) are not equal but differ, to first order, by $d\ \vec{n}\cdot\vec{\varphi}$, where d is the distance of the upper and lower beam. This gives an additional error for the index ratio

$$\delta\frac{n}{n_A} = \frac{N_{SAMPLE}}{N_{REF}}\frac{d\ \hat{n}\cdot\vec{\varphi}}{\Delta x} \tag{4}$$

In our experiment the ratio $d/\Delta x$ is approximately 0.3 so that the resulting relative error of refractive index is $0.3\ \hat{n}\cdot\vec{\varphi}$. Aiming at an overall error of the order 10^{-5} one would like to keep this contribution smaller than say $5\cdot10^{-6}$ which means $\hat{n}\cdot\vec{\varphi} < 1.7\cdot10^{-5}\,\mathrm{rad}$, which is a tight requirement for the straitness of the rail. An elevation of only 1 micron at a distance of 1 cm corresponds to an angle of $10^{-4}\,\mathrm{rad}$! Fortunately the overall error resulting from the three contributions can be measured easily by substituting the liquid sample by air. In this case the deviation of N_{SAMPLE}/N_{REF} from the expected number 1 measures the error. The way we controlled the third kind of error, which results from imperfections of the sliding rail, was simply to look systematically for a portion of the sliding rail where the air to air error was minimal. Fig. 2 shows the beginning and end of the interference signals of an air to air measurement where the overall error was $1.7\cdot10^{-6}$. The

instances of the intensity maxima were determined with the help of quadratic fits around the desired maxima. This method gives, with the number and quality of our data points, a precision of approximately 2% of the oscillation period. This way the error of data analysis in 50355 oscillation is $2 \cdot 0.02 / 50355 \approx 8 \cdot 10^{-7}$, which is small enough for our purpose.

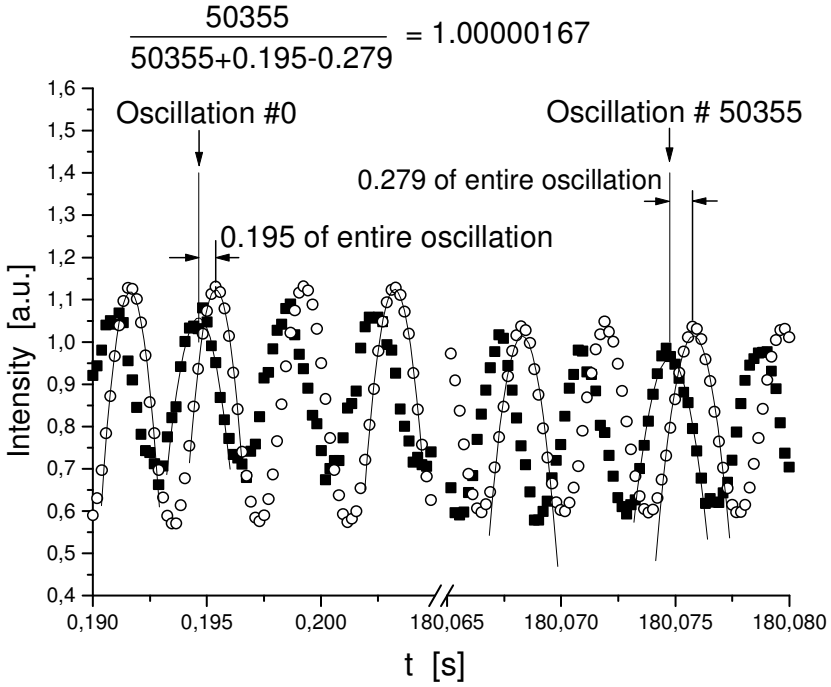


Fig. 2 Initial and final part of an air to air measurement.

In order to determine n with precision of the order 10^{-5} the index of air cannot be considered to be one. The following empiric formula [8] was used to determine n_A

$$n_{AIR} - 1 = A \cdot P \frac{1 + P[B - C(T - T_0)]}{1 + D(T - T_0)} - EP_{H_2O} \qquad (5),$$

where P is the ambient air pressure, T is the ambient temperature and P_{H_2O} is the partial pressure of water in the ambient air. The constants *A* to *E* and T_0 are

$A = 3.836849 \cdot 10^{-7}$ Torr^{-1} $\qquad$ $B = 0.801 \cdot 10^{-6}$ Torr^{-1}

$C = 1.30 \cdot 10^{-8}$ Torr^{-1}K^{-1} $\qquad$ $T_0 = 273.15$ K

$D = 3.6610 \cdot 10^{-3}$ K^{-1} $\qquad$ $E = 4.84539 \cdot 10^{-8}$ Torr^{-1}

The indices of ambient air were determined from measurements of *P, T* and P_{H_2O} with typical error smaller than $\delta n_{AIR} \approx 6 \cdot 10^{-7}$

The index measurements do not only require high opto-mechanical precision. It is also required that the temperature of the sample is known with considerable precision. As the temperature coefficients of most liquid samples are of the order of $\partial n / \partial T \approx 10^{-4}$ K^{-1} a measured index with 6 significant digits is only meaningful if the temperature is declared with precision of the order of $\delta T \approx 0.01$ K. In our measurements the sample is kept in a stainless steel vessel of approximately 6 mm thick walls and the sample surface is exposed to ambient

air. Evaporation at the sample surface can create considerable temperature gradients in the sample. These gradients show up once the slide is being pulled so that the immersed mirror mixes liquids of different temperatures leading to fluctuations of the measured temperature. To minimize these effects we cooled the sample holder approximately to the temperature at which liquid water would be in equilibrium with the atmospheric partial water pressure. This way the evaporation at the sample surface is minimized. With this setup the measured temperature stays stable during the 3 min. measurements better that $3 \cdot 10^{-3}$ K.

The temperature was measured with a F3141 platinum resister using a four wire configuration with the multimeter HP34401Av. The time constant of the thermometer was $\tau = 24\ s$.The thermometer had been calibrated with a triple-point cell.

Several measurements of solutions of Na Cl in H_2O were performed and the results showed high degree of consistency.

Discussion

With the present experimental equipment we obtained a precision of $1.7 \cdot 10^{-6}$ in the optical measurement. This value can probably be decreased still substituting the homemade rail by a precision machined one. This substitution is planned. The software that was used to count the fringes introduces an error of the order 1/10 fringes during the determination of fractions of fringes at the beginning and end of the measuring interval. This causes an error of the order of 10^{-5} which can easily be removed using the quadratic fitting procedure, which was used in Fig. 2. The method has one basic drawback; it is relatively difficult to measure at a given temperature. The best way to obtain the refractive index at a desired temperature T is to measure at an arbitrary temperature T_{ARB} and to measure with a separate experiment the index change that occurs in the transition from T_{ARB} to T. This can be done interferometrically with very high precision without any moving parts.

Acknowledgements

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References

[1] M.E.Manzur, E.Romano, S.Vallejo, S. Wesler, F. Suvire, R.D. Enriz, M.A.A. Molina: *Analysis of Dielectric properties of cytosine in aqueous solution* Journal of Molecular Liquids 94 87-96 (2001)

[2] D.C. Prieve, F. Luo, F. Ianni: *Brownian Motion of a Hydrosol Particle in Colloidal Force Field*, Faraday Discuss. Chem. Soc. 83, 297-307 (1987)
H. Chew, D.S. Wang, M. Kerker: *Elastic Scattering of Evanescent Electromagnetic Waves* Appl. Opt.18 2679-2687 (1979)
G. Zocchi, Mechanical measurement of the unfolding of a protein Europhys. Lett 35 (8), 633-638 (1996)

[3] K.L. Ono: *Medida do índice de refração de sólidos e líquidos com o Refratômetro de Abbe*, USP Instituto de Física

[4] M. Angelis, S. Nicola, P. Ferraro, A. Finizio, G. Pierattini: *Liquid Refractometer Based on Interferometric Fringe Projection*, Opt. Comm. 175, 315-321, 2000

[5] V.N. Kumar, D.N. Rao: *Using Interference in Frequency Domain for Precise Determination of Thickness and Refractive Indices of Dispersive Materials*, Opt. Soc. Am. 12, 1559-1563, (1995)

[6] T. Passamani, B. F. da Silva, J. P. da Silva, P.C. de Oliveira: *Laser Refractometer of Liquids with a Double-Beam Michelson Interferometer*, XXIV ENFMC (2001)

[7] R. B. Santiago Heto, J.P.R.F. de Mendonça, B.Lesche: *Uso da técnica interferométrica para medida do índice de refração absoluto*, XXIV ENFMC (2001)

[8] C.O. Owens: Optical Refractive Index of Air: Dependence on Pressure, Temperature and Compositon, Appl. Opt. 6, 51 (1967)
S. Mc Murtry, J. D. Wright, D.A. Jackson, *Sensing applications of low-coherence fibre-optic interferometer measuring the refractive index of air* Sensors and Actuators B 72 69-74 (2001)