OULU 2009
C 328

ACTA UNIVERSITATIS OULUENSIS

Kai-Erik Peiponen

OPTICAL SPECTRA ANALYSIS OF TURBID LIQUIDS

FACULTY OF TECHNOLOGY,
DEPARTMENT OF ELECTRICAL AND INFORMATION ENGINEERING,
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OPTICAL SPECTRA ANALYSIS OF TURBID LIQUIDS

Academic dissertation to be presented with the assent of the Faculty of Technology of the University of Oulu for public defence in Raahensali (Auditorium L10), Linnanmaa, on 18 September 2009, at 12 noon

OULUN YLIOPISTO, OULU 2009

Acta Univ. Oul. C 328, 2009

Supervised by
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Reviewed by
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ISBN 978-951-42-9167-8 (Paperback)
ISBN 978-951-42-9168-5 (PDF)
http://herkules.oulu.fi/isbn9789514291685/
ISSN 0355-3213 (Printed)
ISSN 1796-2226 (Online)
http://herkules.oulu.fi/issn03553213/

Cover design
Raimo Ahonen

OULU UNIVERSITY PRESS
OULU 2009

Peiponen, Kai-Erik, Optical spectra analysis of turbid liquids
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Acta Univ. Oul. C 328, 2009
Oulu, Finland

Abstract

This thesis is devoted to methods of analyzing optical spectra obtained from turbid liquids, i.e., liquids that are optically very thick and/or scatter light. Data for spectral analysis were obtained with a new, multifunction spectrophotometer developed for industrial liquid samples. One characteristic of the spectrophotometer is that spectral analysis methods can be implemented into the software. Here, the emphasis was on data inversion methods, particularly the Kramers-Kronig analysis and the maximum entropy method, which can be used to gain information on the wavelength-dependent complex refractive index of liquid samples. Relating to such characteristics as density and colour, the complex refractive index also helps to identify the species that form a liquid. The methods were applied to study the internal reflection of light from the prism-liquid interface of the probe and to analyze surface plasmon resonance spectra. This study provided new methods of investigating the optical properties of relatively difficult objects, like offset inks, and of assessing adhesion forces between ink and the substrate system. Another important part of the thesis was the exploration of spectral analysis methods to obtain optical properties of nanoparticles in a liquid matrix. Bounds for the optical properties of multi-component structures in a liquid were considered with the aid of Wiener bounds.

Keywords: complex refractive index, data inversion, nanoparticles, phase retrieval, turbid liquid

Acknowledgements

This thesis is a result of about 10 years research and development of both engineering and theoretical aspects related to the measurement of optical properties of liquids. One important aspect has been to realize devices for industrial environments. During the course of this research the role of liquids that contain nanoparticles has become an important topic. Recently, the global concern of safety of food and beverages that contain nanostructures has stimulated the development of optical sensors for field operation. We are working on such an issue currently in the University of Oulu.

I am very happy that Professor Risto Myllylä supervised me and gave many helpful advises during the course of finalizing this thesis. I wish to thank my colleagues Professor Erik M. Vartiainen, Professor Jarl B. Rosenholm, Professor Martti Toivakka, Adjunct Professor Jukka Räty, Adjunct Professor Jarkko J. Saarinen, PhD Ilpo Niskanen and PhD Evgeny Gornov and MSc Hanna Koivula for nice collaboration.

Finally I express my gratitude to my wife Päivi and my sons Matti and Janne for support and encouragement to finalize a thesis in engineering.

Joensuu, May 2009

List of terms, Symbols and abbreviations

A_z	Scalar component of wave vector
b	Spring coefficient
c	Light velocity in vacuum
e	Elementary charge
E	Electric field
f	Fill factor
H_{123}	Hamaker's constant
I	Irradiance
k	Extinction coefficient
m	Mass
n	Refractive index
N	Complex refractive index
p	Pressure
q	Parameter
r	Reflection coefficient
R	Reflectance
t	Time
T	Absolute temperature
V	Volume
x	Displacement
α	Absorption coefficient
α_{sca}	Scattering coefficient
δ	Phase
φ	Error phase
Γ	Damping factor
ε	permittivity
χ	Susceptibility
μ	Permeability
ω	Circular frequency
ω_p	Plasma frequency
Θ	Angle of incidence
Θ_{sp}	Dip position of SPR reflectance
ATR	Attenuated total reflection
Eff	Effective
K-K	Kramers-Kronig
MEM	Maximum entropy method

List of original papers

This thesis is a summary of research published in the following six papers

I Peiponen K-E, Räty J, Vartiainen EM, Sugiura T & Kawata S (1999) Optical constants of industrial liquids obtained by phase retrieval from reflectometric and surface-plasmon-resonance data. Measurement Science and Technology 10: N145–N148.

II Saarinen JJ, Vartiainen EM & Peiponen K-E (2003) Retrieval of the complex permittivity of spherical nanoparticles in a liquid host material from a spectral surface plasmon resonance measurement. Applied Physics Letters 83: 893–895.

III Peiponen K-E & Gornov E (2006) Description of Wiener bounds of multicomponent composites by barycentric coordinates. Optics Letters 31: 2202–2204.

IV Peiponen K-E & Gornov E (2007) On prediction of optical properties of two- and multiphase nanocomposites for nanomedicine. International Journal of Nanomedicine 2: 799–804.

V Rosenholm JB, Peiponen K-E & Gornov E (2008) Materials cohesion and interaction forces. Advances in Colloid and Interface Science 141: 48–65.

VI Peiponen K-E, Kontturi V, Niskanen I, Juuti M, Räty J, Koivula H & Toivakka M (2008) On estimation of complex refractive index and colour of dry black and cyan offset inks by a multi-function spectrophotometer. Measurement Science and Technology 19: 115601–115606.

Paper I describes the early development of a multifunction spectrophotometer in the Measurement and Sensor Laboratory. The spectrophotometer comprises an SPR sensor, developed in Japan, and utilizes the maximum entropy model (MEM) to resolve the complex refractive index from the wavelength-dependent reflectance of pulping liquor. The idea for this paper originated with the author, while he studied SPR measurement techniques at Osaka University in 1998.

Paper II describes the extraction of complex permittivity or the complex refractive index of insulating nanoparticles in a liquid matrix, which is an issue for nanomedicine and food safety. When using a wavelength scanning SPR sensor, the optical properties of spherical nanoparticles can be extracted using the maximum

entropy method (MEM) and the Maxwell-Garnett effective medium model. It was the author's idea to perform such a study.

Also the original idea for papers Paper III and IV came from the author, who made use of the concept of barycentric coordinates to deal with the Wiener bounds of nanocomposites and multiply subtractive Kramers-Kronig relations. Particular attention was paid to cases where the optical and geometric properties of nanostructures are either unknown or supposed to change as a function of time.

Paper V is a review article devoted to colloids and interfaces. The author came up with the idea of applying modified Kramers-Kronig relations and Wiener bounds to the study of ink and incorporating Hamaker's constant into the analysis. The study involves chemical and optical issues that have importance for ink setting during the printing process.

The author is responsible for the idea of Paper VI, while Dr I. Niskanen performed the measurements. This paper reports on the assessment of the optical properties of heat set offset inks.

The author contributed substantially to the writing of Papers I-VI. As the principal author, he had the responsibility of writing Papers I, III, IV and VI.

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Original papers

1 Introduction

The most famous liquid is water, which is the source of life. Without water, there would not be living features on the Earth. Fortunately, in Finland we have innumerable natural water bodies, such as lakes, rivers, costal waters and, naturally, ground water, which is a crucial source of drinking water. It is easy to make visual observations of a water sample taken, for example, from a brook. One important characteristic is colour, which may be due to natural colorants, such as the soil and the amount of solid material in the sample. Colour is produced by light absorption, whereas solid particles become visible through light scattering. In science, a turbid sample, be it in a liquid or solid phase, indicates that there may be simultaneous absorption and scattering of light. In engineering, a turbid liquid that contains solid particles, either in water or any other liquid matrix, is called a suspension, because non-solvable solid particles experience sedimentation as a function of time. The particles of a suspension are typically relatively large. However, since small nanoparticles have a particle diameter of about 1- 10 nm, they tend to float without sedimentation. This type of system is called a colloid.

In this thesis, the phrase "turbid liquid" is used to cover all possible cases of two or multiphase liquids that may absorb and/or scatter a probe light. Why would we want to probe a turbid liquid with a light wave? There are several reasons to do so. First of all, optical measurement techniques, such as optical spectroscopy, yield information on the probed medium. For example, utilizing the concept of refractive index allows one to obtain information on the density of the medium under study. If the medium has spectral features at a certain spectral range, it is generally possible to recognize this medium. Moreover, if the medium is a composite or represents a multiphase system, such as a solid state-liquid system, it is possible to recognize a particular component or components by inspecting the transmission, reflection or scattering spectrum from a sample. This involves investigating the height, half width and location of the spectral peak. Unfortunately, this type of spectral analysis is often insufficient for the comprehensive description of the optical properties of a medium. Luckily, other types of method exist that can be used to extract more spectral data. Different spectral analysis methods are referred to as chemometrics. To get an idea of more advanced spectral analysis methods, suffice to say that the conventional measurement of light transmission in a homogenous liquid sample, based on scanning the wavelength of a spectrophotometer, provides information on absorbance and colour, but does not yield the refractive index of the liquid.

However, by measuring light reflection from the same samples, we may resolve the refractive index using the Kramers-Kronig relation (K-K) (Kronig 1926, Kramers 1929). An alternative method for the same purpose is the so-called maximum entropy method (MEM) (Peiponen *et al.* 1999).

In this thesis, I consider methods of extracting the complex refractive index of turbid liquids using K-K relations, MEM and other methods for internal reflection spectra. Providing motivation for the research is a long-term project seeking to realize novel optical sensors, such as the multifunction spectrophotometer, developed in collaboration between the Measurement and Sensor Laboratory of the University of Oulu and the University of Joensuu, and appropriate data analysis methods for the inspection of liquid quality in industrial and natural environments. Some progress has already been reported in book form (Räty *et al*. 2004 and Peiponen *et al*. 2009) and as a dissertation (Niskanen 2008). Here, I combine internal reflection spectra with surface-plasmon-resonance (SPR) measurements and data analysis to study the properties of pulping liquid. Another issue addressed here involves using SPR spectral analysis in conjunction with MEM for the investigation of nanoparticles in a liquid matrix. The latter issue has importance for the sensing of liquids in such fields as nanomedicine. Furthermore, I shall discuss spectral data obtained from offset inks with the multifunction spectrometer (Niskanen 2006). Techniques based on reflection have a long history in the measurement of optical properties of liquids (Partington 1960, Batsanov 1966, Kortum 1969, Harrick 1979, Mirabella 1993). Due to recent developments in light sources and detectors and new device innovations, this field is undergoing continuous progress. As a result, various commercial optical sensors are in routine use in industrial environments, such as process refractometers, used to monitor the condition of liquids. In addition to optical probes, the dielectric properties of liquids can be monitored using lower frequencies ranging from THz radiation to as low as 10^{-6} Hz (Kaatze 2008).

2 Basic thermodynamic properties of turbid liquids

Liquid is a medium which takes a fixed volume in a container, but does not have a fixed shape. Apart from liquid crystals, liquids have a rather high density and present an amorphous structure in normal conditions. It is quite typical that liquids flow easily from a higher potential to a lower one. The viscosity of a liquid depends naturally on its temperature and, in the case of suspensions, also on the inertia of the solid stuff. Increasing the temperature induces stronger random motion among the molecules comprising the liquid and a reduction of friction between these molecules and those representing the environment.

Pure substances, such as pure water, allow predicting their thermodynamic condition. Doing that requires the application of basic thermodynamic variables, namely, absolute temperature T, pressure P, volume V and mole number, i.e., the amount of substance present. Quite often, the amount of substance present remains constant and, in the absence of chemical reactions, a state description can be made using the so-called state equation, which couples the state variables. For instance, a constant amount of pure liquid has the relation

$$F(p,V,T) = 0. \tag{1}$$

State equation (1) presents a surface in the pVT space. Unfortunately, for binary or multi-mixtures, such as suspensions or colloids, it is usually not possible to arrive at a simple state equation that could be used to predict their thermodynamic state in a turbid condition. For example, the system may not be in a steady state during sedimentation. And after sedimentation, the density of solid particles is higher in the volume they occupy. Assessing accurately the volume of the solid particles and the heat exchange rate of such a complex system are very difficult undertakings. Nevertheless, we can always predict some basic properties of turbid liquids from the laws of pure substances. The laws of energy conservation and entropy hold for any complex liquid system. Therefore, we know that the introduction of heat to a turbid liquid will increase its temperature and affect thermal expansion and viscosity. Thermal expansion is a fundamental parameter, as it controls the liquid's density. Density, in turn, is important, because it relates to the refractive index of the medium. Thus, it is relatively easy to believe that thermal properties, not only in turbid liquids, but in media at large have an impact on their optical properties. Perhaps the most striking example is the critical opalescence of water. A change

from a liquid to a solid state may also bring about a phase change from an amorphous state to a crystal state. When this occurs, an optically isotropic system may switch to an anisotropic system that is birefringent. A multimixture also increases optical complexity, and this complexity is most typically observed as light scattering from the mixture, regardless of its thermodynamic condition.

Practical optical measurements must always take account of the temperature of the object to be measured. Pressure, on the other hand, is not often a big issue. Problems arise in industrial environments, when the temperature of the optically inspected target fluctuates, or the ambient temperature changes either regularly or irregularly as a function of time. This highlights the significance of the correct calibration of the optical sensor to ensure its reliability as an on-line gauge, for instance. Another typical problem that occurs when measuring minute optical changes in an object is that even a small temperature variation induces a large change in the measured optical parameter. In view of these practical problems, the results we usually get are estimates, not accurate information. Fortunately, industrial inspections tend to allow a degree of tolerance in the accuracy of the measured optical quantity. Sometimes, there are no other means of obtaining information on the optical properties of a system than to use general bounds such as Wiener bounds (Wiener 1912), which are used in this dissertation to investigate nanoparticles in a liquid matrix.

3 Frequency-dependent complex refractive index of a medium

In this section, I consider the interaction of light with an insulator and define complex refractive index and other relevant quantities that are useful for optical materials research.

3.1 Light interaction with an insulator

When an electromagnetic field, such as light in this study, interacts with a medium, it disturbs the medium's electron and atom system. In this section, we shall concentrate on the interaction of light with the electron system, which is relevant for the visible-UV spectral range. When a light wave encounters an insulator, the wave's external field induces a dipole moment. This is a plausible restriction for turbid liquids without any metallic particles in the liquid matrix. However, the concepts presented here are also valid for metals and semiconductors. At any rate, when a light field polarizes electrons, it induces a dipole moment. As a result of oscillations of the electric field, single electrons are subject to electric-field driven oscillation. Newton's second law allows us to arrive at the following equation of motion:

$$m\frac{d^2x}{dt^2} + m\Gamma\frac{dx}{dt} + bx = -eE_o \exp[-i\omega t] \,, \tag{2}$$

where m is the mass of the electron, x is displacement, t is time (consider the situation at the origo of a Cartesian coordinate system, which permits the spatial dependence of the electric field to be omitted), Γ describes the friction experienced by the oscillator, b is the spring constant, -e is the charge of the electron, E_o is the amplitude of the electric field and ω is the circular frequency of the light field. Electron motion equation (2) can be solved using an exponential trial function similar to that on the right-hand side of Eq. (2). Thus, we get

$$x(t) = -\frac{eE_o}{m}\frac{\exp[-i\omega t]}{\omega_o^2 - \omega^2 - i\Gamma\omega}, \tag{3}$$

where $\omega_o = \sqrt{b/m}$ is the natural frequency of the oscillator and i is an imaginary unit. Note the complex form of the solution.

The dipole moment of the oscillator is equal to –ex(t*)*. To describe the macroscopic polarization of electrons, we utilize polarization (P) given by

$$P = -\rho e x \quad , \tag{4}$$

where ρ is the number density of electrons. According to the theory of electromagnetism, we also have

$$P = \varepsilon_o \chi E, \tag{5}$$

where χ is the electric susceptibility of the medium and ε_o is the permittivity of vacuum. With the aid of Eqs. (3)-(5), we get

$$\chi(\omega) = \frac{\rho e^2}{m\varepsilon_o} \frac{\omega_o^2 - \omega^2}{(\omega_o^2 - \omega^2)^2 + \Gamma^2\omega^2} + i\frac{\rho e^2}{m\varepsilon_o} \frac{\Gamma\omega}{(\omega_o^2 - \omega^2)^2 + \Gamma^2\omega^2} \quad . \tag{6}$$

Obviously, electric susceptibility is a complex function in the presence of dissipation of energy. Dissipation is due to the friction term, i.e., the second term on the right hand-side of (2).

Permittivity and susceptibility of the insulator are coupled by the relation

$$\varepsilon = \varepsilon_o (1 + \chi) \, . \tag{7}$$

The simple model can be generalized such that susceptibility builds up from different the resonances of different electron groups. In this case, susceptibility can be presented by the expression

$$\chi(\omega) = \frac{e^2}{m\varepsilon_o} \sum_j \frac{\rho_j}{\omega_{oj}^2 - \omega^2 - i\Gamma_j\omega} \quad . \tag{8}$$

Fig. 1 shows simulations of the corresponding real and imaginary parts of complex permittivity at three resonances. Note that the imaginary part of complex permittivity is always positive, whereas the sign of the real part is not definite.

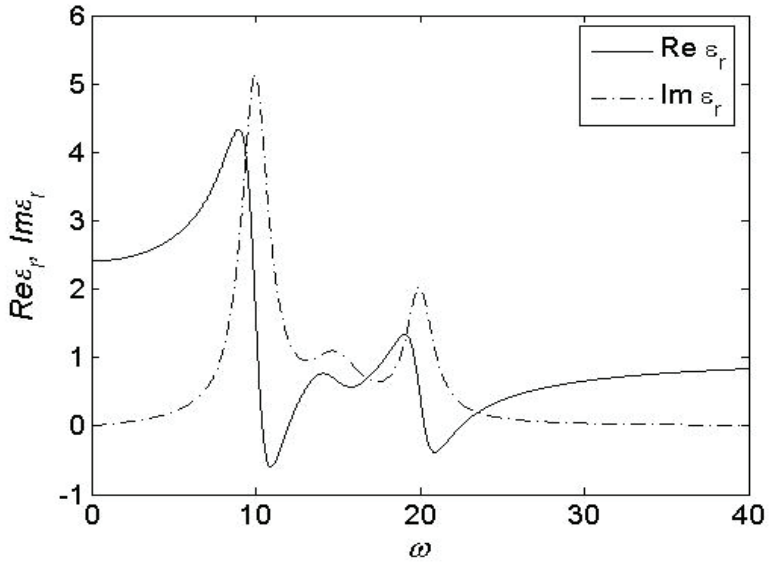

Fig. 1. Real (solid line), and imaginary (dotted line) part of permittivity. Local maxima of the imaginary part correspond to three resonance angular frequencies. The variable is the angular frequency given as 1/s.

Clearly, the imaginary part in Fig. 1 resembles spectral features that can be observed, for example, in the transmission spectrum of a medium. Indeed, the imaginary part of permittivity is intimately connected with the absorbance of the medium being studied, while the real part of permittivity is closely linked to the dispersion of light.

3.2 Wave equation

Maxwell's equation can be used to derive the wave equation for an electric field in free space as follows:

$$\nabla^2 E = \frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial y^2} + \frac{\partial^2 E}{\partial z^2} = \mu_o \varepsilon_o \frac{\partial^2 E}{\partial t^2} \quad , \tag{9}$$

where μ_o is the permeability of vacuum. The wave equation presents a monochromatic harmonic plane wave that propagates with the velocity

$$c = \frac{1}{\sqrt{\mu_o \varepsilon_o}} . \tag{10}$$

When a light wave propagates with the velocity v in a lossless medium with a refractive index n, we can write

$$n = \frac{c}{v} . \tag{11}$$

We now generalize relation (11) to hold for a medium that absorbs light. To revise equation (10) to hold for an insulating medium, we write

$$\nabla^2 E = \mu\varepsilon \frac{\partial^2 E}{\partial t^2} \tag{12}$$

and define the complex refractive index N, given by

$$N = n + ik = \sqrt{\frac{\varepsilon}{\varepsilon_o}\frac{\mu}{\mu_o}} = \sqrt{\mu_r \varepsilon_r} , \tag{13}$$

where n is the ordinary real refractive index and k is known as the extinction coefficient of the medium. The solution of (12) for wave propagation along the x-axis is

$$E(x,t) = E_o \exp[iKx - \omega t] , \tag{14}$$

where K is a complex wave vector defined by

$$K = \frac{\omega}{c}\sqrt{1+\chi} . \tag{15}$$

We observe that the solution of the electromagnetic wave equation for a wave propagating in an insulator is

$$E(x,t) = E_o \exp\left[-\frac{\omega}{c}kx\right]\exp\left[i\left(\frac{\omega}{c}nx - \omega t\right)\right]. \tag{16}$$

It is obvious that the first exponential term in (16) describes attenuation of the electric field while it propagates in the positive x- direction. The second exponential term, on the other hand, describes wave propagation at a velocity

equal *to c/n*. Hence, the complex refractive index couples absorption and the dispersion of light.

The qualitative model above can be generalized to hold for metals merely by setting the natural frequency equal to zero in Eq. (3). In addition, the model for an optically isotropic insulator can be generalized to hold for birefringent insulators. In such a case one has to consider three-dimensional electric-field driven oscillators that have different spring constants along the axes of the Cartesian coordinate system.

In transparent or semi-transparent liquids, a typical optical measurement involves recording the transmission spectrum from the sample. If there is no light scattering from a homogeneous liquid, one can utilize the Beer-Lambert law

$$I = I_o \exp(-\alpha d), \tag{17}$$

where I_o denotes the incident irradiance, I is the measured irradiance, α is the absorption coefficient of the liquid and d is the thickness of the sample. The absorption coefficient and extinction coefficient are coupled by the relation

$$k = \frac{c\alpha}{2\omega}. \tag{18}$$

In the case of a turbid, light scattering liquid, we can use a generalization of Eq. (17) which reads

$$I = I_o \exp(-\alpha - \alpha_{sca})d, \tag{19}$$

where α_{sca} is the attenuation coefficient due to light scattering. Unfortunately, this coefficient is usually difficult to treat theoretically, when the shape of the particles is irregular, and a densely packed system may not allow light to penetrate sufficiently through a thick sample. In the case of spherical particles, one can use the Mie (Bohren & Huffman, 1983) scattering model for measured transmittance data.

3.3 Fresnel's formulas for reflectance

The most convenient method of analyzing the reflection spectra of liquids involves using Fresnel's formulas for reflectance of s- or p-polarized light as follows:

$$R_s(\omega) = \left| \frac{\cos\theta - \sqrt{N'^2(\omega) - \sin^2\theta}}{\cos\theta + \sqrt{N'^2(\omega) - \sin^2\theta}} \right|^2 \tag{20}$$

and

$$R_p(\omega) = \left| \frac{N'^2(\omega)\cos\theta - \sqrt{N'^2(\omega) - \sin^2\theta}}{N'^2(\omega)\cos\theta + \sqrt{N'^2(\omega) - \sin^2\theta}} \right|^2, \tag{21}$$

where Θ is the angle of incidence and N' is the relative complex refractive index. The concept of relative index is important, because we are interested here in the internal reflection spectroscopy of liquids. In this thesis, the incidence medium is usually the probe window of a prism. Relations (20) and (21) hold for homogenous and non-scattering media. In turbid liquids, however, certain limitations apply. When a prism is used to probe the optical properties of a liquid, it provides a smooth surface that is essential for ensuring the validity of Fresnel's formulas. As the previous section showed, sometimes the only way of getting a transmittance signal from a turbid liquid is to dilute it, i.e., to change its optical properties. This contrasts with the reflection measurement mode, which does not impose a need to manipulate the sample. In the vicinity of the critical reflection angle, the signal is obtained from a thin layer at the interface of the probe face and the turbid liquid. As a result, light scattering may not be such a big issue as in transmission measurements.

Some rather general methods (Humphreys-Owen, 1961) exist that can be used to resolve the complex refractive index using the light reflection measurement technique and relevant data analysis methods. Azzam's theory (Azzam 1979), for example, offers a useful and very practical approach, when the oblique angle reflectance of both *s*- and *p*-polarized light can be measured. However, we make use of the Verdet sign convention (Holm 1998), in which the reflection coefficient, which is a complex number, can be expressed for the electric field of *s*- and *p*-polarized light as follows:

$$r_s = \frac{\cos\theta - \sqrt{N'^2 - \sin^2\theta}}{\cos\theta + \sqrt{N'^2 - \sin^2\theta}} \tag{22}$$

and

$$r_p = \frac{N'^2 \cos\theta - \sqrt{N'^2 - \sin^2\theta}}{N'^2 \cos\theta + \sqrt{N'^2 - \sin^2\theta}}\ , \tag{23}$$

where $N' = n+ik$ is the relative complex refractive index of the light absorbing sample. If we set

$$q = \sqrt{N'^2 - \sin^2\theta}, \tag{24}$$

Eqs. (22) and (23) can be expressed in another way, namely

$$r_s = \frac{\cos\theta - q}{\cos\theta + q} \tag{25}$$

$$r_p = \frac{(q^2 + \sin^2\theta)\cos\theta - q}{(q^2 + \sin^2\theta) + q}. \tag{26}$$

Then we get a useful equation

$$r_p = r_s \frac{r_s - \cos 2\theta}{1 - r_s \cos 2\theta}. \tag{27}$$

The above formalism is valid throughout the whole electromagnetic spectrum. Being able to measure reflectance, we take the squared modulus on both sides of Eq. (27) and finally get

$$R_p = R_s \frac{R_s + \cos^2 2\theta - 2\sqrt{R_s}\cos 2\theta \cos\varphi_s}{1 + R_s \cos^2 2\theta - 2\sqrt{R_s}\cos 2\theta \cos\varphi_s}\ , \tag{28}$$

where φ_s is the phase of the s-polarized reflected light, defined as follows:

$$r_s = \sqrt{R_s}(\cos\varphi_s + i\sin\varphi_s) \tag{29}$$

From Eq. (28) we can solve the phase angle

$$\cos\varphi_s = \frac{R_s^2 - R_p + R_s(1 - R_p)\cos^2 2\theta}{2\sqrt{R_s}(R_s - R_p)\cos 2\theta}. \tag{30}$$

The complex refractive index can be solved as follows:

$$N = n + ik = n_p \sqrt{\sin^2\theta + \left(\frac{1 - r_s}{1 + r_s}\right)\cos^2\theta} \quad , \tag{31}$$

where n_p is the refractive index of the probe prism.

Eqs. (30) and (31) were exploited in *Paper VI* for the calculation of the complex refractive index of dry offset inks. Naturally, these inks were in a liquid phase to start with, but the samples were prepared in such a way as to simulate heat set off-set printing. Unfortunately, the recipe of a printing ink is typically a secret matter. This was also the case of inks studied in paper VI. Resolving of the components of an ink is not an easy task, but a partial solution for a particular magenta ink was presented in (Preston *et al.* 2002).

3.4 Surface plasmon resonance and reflectance

A plasmon is a collective oscillation of electrons in metals, and the rigorous description of the phenomenon is based on quantum mechanics. Surface plasmons exist at the metal boundary, and they can be produced in some cases by an external electric field. Let us first consider the volume plasmon using the concepts of classical electromagnetism. The relative permittivity of an insulator can be qualitatively described with the aid of (6) and (7). In the case of metals, there is no restoring force keeping conduction electrons confined in the vicinity of the nucleus. In other words, the spring coefficient $b = 0$. This, in turn, means that also $\omega_o = 0$. If we substitute this information into Eqs. (6) and (7), we get the relative complex permittivity of the metal in question (ε_{mr}). The resulting relations are called Drude dispersion formulas, and they are

$$\begin{aligned} \mathrm{Re}\{\varepsilon_{mr}\} &= 1 - \frac{\rho e^2}{m\varepsilon_o}\frac{1}{\omega^2 + \Gamma^2} \\ \mathrm{Im}\{\varepsilon_{mr}\} &= \frac{\rho e^2}{m\varepsilon_o}\frac{\Gamma}{\omega(\omega^2 + \Gamma^2)}. \end{aligned} \tag{32}$$

A metal's plasma frequency (ω_p) is defined by the relation $\mathrm{Re}\{\varepsilon_{mr}\} = 0$. This happens when $\omega >> \Gamma$, and plasma frequency is given by the definition

$$\omega_p^2 = \frac{\rho e^2}{m\varepsilon_o}. \tag{33}$$

According to (32) and (33), it holds that

$$\begin{aligned} \mathrm{Re}\{\varepsilon_{mr}\} &= 1 - \frac{\omega_p^2}{\omega^2} \\ \mathrm{Im}\{\varepsilon_{mr}\} &<< 1. \end{aligned} \tag{34}$$

Real metals exhibit a dip in reflectance in the vicinity of the plasma frequency. Volume plasmons, which are fluctuations in charge density, can be observed using a beam of electrons for excitation.

We are here interested in surface plasmon resonance (SPR), which can be induced by a light beam. As far as the application of light sensing and prism reflectometry to surface plasma waves is concerned, Kretchmann and Räther (Kretchmann 1968, Kretchmann & Räther 1971, Räther 1988) are essential reading. Also Homola's review (Homola *et al*. 1999) is useful in this context.

The oscillation of surface charge fluctuations cannot ordinarily be excited by light. To circumvent the problem, Otto (Otto 1968 &1969, Kretschmann and Räther 1968) proposed the exploitation of a prism and a thin metallic film to generate surface plasma waves using p-polarized light. This allows resonance-related information to be obtained by observing reflectance above the critical angle of reflection in the ATR mode. At a specific angle of incidence, reflectance has a dip due to the fact that the light beam couples most effectively into the metal film. This resonance angle depends on the complex permittivity of the metal film, the optical properties of the liquid to be studied and the refractive index of the prism. Now, the theory is somewhat more complicated here than in the case of bulk metal above. Reflectance can be derived by inspecting multiple light reflections in an ambient-film-substrate system (Azzam & Bashara 1977). The expression of reflectance is as follows:

$$R_p(\theta) = \left| \frac{r_{pm}(\theta) + r_{ml}(\theta)\exp\left[2iA_z(\theta)d\right]}{1 + r_{pm}(\theta)r_{ml}(\theta)\exp\left[2iA_z(\theta)d\right]} \right|^2, \tag{35}$$

where r_{pm} is the electric field reflection coefficient at the prism-metal film interface, r_{ml} is the corresponding coefficient at the metal-liquid interface, d is the thickness (typically around 50 nm) of the metal film and A_{z} is a scalar component of the wave vector normal to the metal film surface. The electric field reflectance is

$$r_{pm} = \frac{\frac{A_{z,prism}}{\varepsilon_{prism,r}} - \frac{A_{zm}}{\varepsilon_{mr}}}{\frac{A_{z,prism}}{\varepsilon_{prism,r}} + \frac{A_{zm}}{\varepsilon_{mr}}} \tag{36}$$

$$r_{ml} = \frac{\frac{A_{zm}}{\varepsilon_{mr}} - \frac{A_{z,liq}}{\varepsilon_{liq,r}}}{\frac{A_{zm}}{\varepsilon_{mr}} + \frac{A_{z,liq}}{\varepsilon_{liq,r}}}, \tag{37}$$

where $\varepsilon_{\text{prism, r}}$ is the relative permittivity of the prism, ε_{mr} is the complex relative permittivity of the metal and $\varepsilon_{\text{liq,r}}$ is the complex relative permittivity of the liquid. The wave number is defined as follows:

$$A_{zj} = \left[\varepsilon_{jr} \left(\frac{\omega}{c} \right)^2 - A_x^2 \right]^{1/2}, \tag{38}$$

where

$$A_x = n_{prism} \frac{\omega}{c} \sin\theta. \tag{39}$$

The minimum of the reflectance curve corresponds to the surface plasmon resonance, which can be obtained at an angle θ_{sp}

$$n_{prism} \sin\theta_{sp} = \text{Re}\left\{ \sqrt{\frac{\varepsilon_{mr}\varepsilon_{liq,r}}{\varepsilon_{mr} + \varepsilon_{liq,r}}} \right\}. \tag{40}$$

This relation is widely used for the assessment of the refractive index of non-absorbing liquids, since the permittivity of the metal is usually known and the angle of surface plasma resonance can be experimentally detected. In the case of an absorbing liquid, the half width and the depth of the dip depend on the extinction coefficient of the liquid. In the vicinity of the dip, reflectance can be approximated using a Lorentzian line model (Chen & Chen 1980 and 1981), which makes it possible to estimate, for example, the permittivity of the metal film and its thickness, together with their uncertainty (Tilkens *et al.* 2000). Kano and Kawata (Kano & Kawata 1994) investigated ways of enhancing the absorption-sensitivity

of surface-plasmon sensors by optimizing the thickness of the metal film. Unfortunately, in severe industrial measurement environments, thin metallic films are usually subject to wear, which may lead to erroneous measurement results.

Using surface plasmon resonance (SPR) for material sensing has proven a very sensitive technique for the detection of small changes in the refractive indexes of media in the gaseous (Nylander *et al.* 1982–83) and liquid phase (Löfås *et al.* 1991). Nowadays, some measurement techniques based on SPR employ, for example, a grating configuration instead of a prism to detect physico-chemical changes in media. Thus, SPR has become a valuable tool for such applications as the analysis of dynamic biological interactions with biomaterials (Vanderberg 2000, Green *et al.* 2000). In laboratory conditions, the detection of surface plasmon resonance can be used to obtain the refractive index, and hence information about the concentration of the constituents of "ill-behaved" industrial liquids, such as turbid pulping liquor (described in *Paper I*), pigment slurries (Peiponen *et al.* 2000) or milk (Jääskeläinen *et al.* 2001).The optically thick liquids of Paper I were similar as those used in (Räty *et al.* 1998). That is to say synthetic commercial lignin dissolved in NaOH, and commercial red food-colouring matter dissolved in water. Inspecting lubricants at a high pressure by SPR is also possible (Wong *et al.* 2005). *Paper II* extracted optical properties of nanoparticles in a liquid matrix using a wavelength-scanning SPR configuration. Recently, a review on retrieval of optical properties of nanoparticles in liquid matrix by maximum entropy model was published in (Saarinen *et al*. 2009).

Matsubara (Matsubara *et al.* 1988) has introduced a device, which makes use of a convergent light beam, which does away with the need to rotate the prism. This technique has also been exploited in commercial devices (Homola *et al.* 1999), although it suffers from the limitation that only a relatively narrow refractive index range can usually be covered. Johansen (Johansen *et al* 2000) suggested that it is (numerically) possible to achieve a resolution better than 10^{-9} refractive index units (RIU).

Another technique, also based on Kretschmann's configuration, keeps the angle of incidence fixed and uses a wideband white light source for SPR generation instead (Zhang & Uttamchandani 1988). In that mode, only a certain wavelength of the used spectral range will couple to a surface plasma wave related to a specific constituent of the analyte. A multi-wavelength technique for the assessment of optical constants of liquids has been proposed by Yee (Jung 1995, Karlsen 1995), and by Lavers and Wilkinson (Lavers & Wilkinson 1994). The choice of metal and wavelength for surface-plasmon resonance sensors has been

also investigated (de Bruin *et al.* 1992). Due to the high sensitivity of SPR sensors to the refractive index of media, they are also sensitive to temperature changes, which has to be considered in practical applications (Chiang *et al.* 2001). Nowadays, a handheld SPR sensor is available (Feltis *et al.* 2008), and an automated SPR imaging system is underway (Ruemmele *et al.* 2008)

3.5 Effective medium theory

Nanoparticle research is vitally important for nanomedicine and biosciences (Lazarides & Schatz 2000, Lazarides *et al.* 2000). In bio assaying, for instance, quantum dots are used for monitoring purposes (Han *et al.* 2001, Alvisatos 2004, Eastman *et al.* 2006). Also the development of nanoparticles as targeted drugs for tumors is experiencing a strong upswing. Another increasingly significant field of nanoparticle application is the utilization of nanostructures within the food industry (Weiss *et al.* 2006, Luykx *et al.* 2008) As a result of these developments, there is a clear need to develop optical sensing and imaging techniques for monitoring nanoparticles in liquid environments.

This thesis considers the effective medium theory of liquids which contain optically linear nanoparticles. What this usually means is that light scattering can be neglected, especially if the volume concentration of nanoparticles is low and they do not form aggregates, i.e., there is no agglomeration. Originating from research that started at the beginning of the 20th century (Maxwell Garnett 1904 & 1906), the idea of the model is that there is a host medium (in this study a liquid) and an embedded inclusion (nanoparticles) consisting of spherical particles. Such solid nanospheres can be either insulators, metals or semiconductors. Moreover, we assume that there is no interaction between the inclusion particles, meaning, for example, that the fill fraction (f) of nanospheres is relatively low f << 1. Some studies related to nanocomposites has placed the upper limit of fill fractions as high as $f = 0.5$ (Boyd *et al*. 1996). We deal with the effective permittivity (ε_{eff}) of a system and refer once again to the classical theory of electromagnetism (Jackson 1962) and particularly to a well-grounded pedagogic paper (Aspnes 1982), which presents the derivation of the effective medium expression of permittivity for a two-phase Maxwell Garnett nanocomposite. It holds that

$$\frac{\varepsilon_{eff} - \varepsilon_h}{\varepsilon_{eff} + 2\varepsilon_h} = f \frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + 2\varepsilon_h}, \tag{41}$$

where ε_h is the complex permittivity of the host, and ε_i is the complex permittivity of the inclusion.

In optical spectroscopy, information is usually obtained about the effective complex refractive index (N_{eff}) of the system. This information makes it possible to determine the effective permittivity of a liquid with the aid of (41). Furthermore, if ε_h and f are known, one can obtain information on ε_i from (42)

$$\varepsilon_i = \frac{\varepsilon_h \left[2(\varepsilon_{eff} - \varepsilon_h) + f(\varepsilon_{eff} + 2\varepsilon_h)\right]}{f(\varepsilon_{eff} + 2\varepsilon_h) - (\varepsilon_{eff} - \varepsilon_h)}. \tag{42}$$

Since we usually wish to find out the complex refractive index of the inclusions, i.e., $N_i = n_i + i\, k_i$, we have to solve n_i and k_i using (42). It is also possible to monitor f, if both the permittivity of the host and inclusion is known. A Maxwell-Garnet model was applied in *Paper II* to extract the permittivity of nanoparticles in water. In that study, reflectance was recorded as a function of wavelength using an SPR configuration.

The shortcoming of the Maxwell-Garnett effective medium theory is that it requires a low fill fraction. In addition, no information is available concerning nanosphere size. One way of generalizing the Maxwell-Garnett model to include the concept of size (Ruppin 2000) is to employ the Mie scattering theory. The size dependence of the refractive index of metal nanoparticles in a suspension, such as gold (Scaffardi & Tocho 2006), is of vital importance in both engineering and nanomedicine (Haes & Van Duyne 2004).

3.6 Wiener bounds

A simple way to estimate the true complex permittivity, and hence the complex refractive index of any effective medium, is to make use of Wiener bounds (Wiener 1912) for permittivity. The idea is that the effective permittivity of a medium is between two ultimate limits of full screening and no screening of the nanostructures (Aspnes 1982). In the case of J different components, Wiener bounds read as

$$\varepsilon_{eff} = \sum_{j=1}^{J} f_j \varepsilon_j \,, \tag{43}$$

and

$$\frac{1}{\varepsilon_{eff}} = \sum_{j=1}^{J} \frac{f_j}{\varepsilon_{eff}}, \tag{44}$$

where f_i are the fill fractions, $\sum_{j=1}^{J} f_j = 1$ and ε_j is the complex permittivity of the j: th component. These bounds hold for composites regardless of the composition and structure. Mathematical and graphical methods to estimate strict bounds for the complex effective permittivity of a two-phase composite are described in (Bergman 1980, Milton 1982, Aspnes 1982). The case of multicomponent media is treated in (Golden, G. Papanicolaou 1985) with the aid of several complex variables. Strict bounds are usually obtained by assuming that nanoparticles are spherical and isotropic. Since this is not always true, Wiener bounds often only provide rough bounds for permittivity. Dealing with nanomedicine, *Paper III* and *Paper IV* applied Wiener bounds in conjunction with barycentric coordinates to estimate the permittivity of nanoparticles. In addition, *Paper V* introduced the use of Wiener bounds at an imaginary frequency.

4 Spectra analysis by dispersion relations

4.1 Kramers-Kronig relations

In linear optical spectroscopy, the dispersion relations approach is based on the theory devised by Kramers and Kronig (Kramers 1927, Kronig 1926), who were able to link the real and imaginary parts of linear susceptibility. Underlying Kramers-Kronig (K-K) dispersion relations is the principle of causality, which stems from the time order of cause and response in a system. In optics, the cause is an incident electromagnetic field and the response typically polarization of electric charges. In the frequency domain, the principle of causality for the linear susceptibility χ of a medium can be described by the following mathematical expression:

$$\chi(\omega) = \int_0^\infty \chi(t) \exp[i\omega t] dt \,, \tag{45}$$

where ω is the circular frequency of electromagnetic radiation, t is time and i is an imaginary unit. Obviously, the conversion from the time domain to the frequency domain is carried out by a half Fourier transform. The lower bound of the integration is zero, because the response of the system $\chi(t)$ occurs later than the cause. Because the cause has to be a real function of time, Eq. (45) yields a complex function $\chi(\omega)$. The real part represents dispersion and the imaginary part dissipation of light in the medium. Thus, K-K relations couple the real and imaginary parts and are mutually dependent. Further, Titchmarsch theorem (Nussenzveig 1972) gives a rigorous proof for the connection of causality and K-K relations for an insulator (see also Lucarini *et al*. 2005). Causality and K-K relations in the time domain have been investigated in (Waters *et al*. 2005). An alternative analysis method to K-K relations is the conjugate Fourier-series approach introduced in (King 1978).

One crucial assumption justifying the validity of K-K relations in linear optics is that the complex refractive index and reflectivity are holomorphic (= analytic) functions in the upper half of the complex frequency plane (Lucarini *et al.* 2005), but they can possess a discrete number of poles in the lower complex frequency plane, and *vice versa*. A second assumption expresses the requirement of a sufficient fall-off of the complex optical function at high frequencies. Finally, the third assumption is that the real part of the complex function is an even and the

imaginary part an odd function of frequency. This can be seen from Eq. (1) for linear susceptibility. Replacing the circular frequency by a negative variable, we get $\chi(-\omega) = [\chi(\omega)]^*$, where * stands for a complex conjugate. The symmetry property follows directly from the separation of the real and imaginary parts of the Eq. (45). The requirements stated above are usually fulfilled, and one can apply complex contour integration for the derivation of K-K relations (Peiponen *et al.* 1999).

The first step in contour integration is to get the Hilbert transforms, which we give below for any physical quantity presented as a complex function $u+iv$, which fulfils the three assumptions above. The pair of Hilbert transforms is

$$u(x') = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{v(x)}{x - x'} dx$$

$$v(x') = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{u(x)}{x - x'} dx\,, \tag{46}$$

where x typically represents the energy or alternatively circular frequency of radiation. The symbol "P" means that the integral is calculated using a limiting process called Cauchy principal value. The role of the Cauchy principal value is that the singular point x' is approached in a symmetric way from the left and right in the limiting process during integration over the real axis. K-K relations are obtained after using the symmetry property of the complex function. Then the integration is from zero to infinity. Note, however, that if we know the symmetry of the relevant function, we can also use Hilbert transforms. What advantage K-K relations have over Hilbert transforms is that they tend to offer a better convergence for the other partner in a pair of dispersion relations.

In the transmission measurement, the transmittance $T = I/I_o$, where I_o is the incident light and I is the transmitted intensity of light, recorded as a function of probe wavelength. Since the thickness of a sample is usually known, and by assuming that the sample is homogenous, we may exploit the Beer-Lambert intensity law (17) and (18) to invert the extinction coefficient data.

Fig. 2 shows transmission data for some red wine samples from eight different countries (Mutanen *et al.* 2007). Some of these wines can be recognized due to their spectral features. Nevertheless, the red wine colour, which can be calculated from the transmission data, is subject to temporal change.

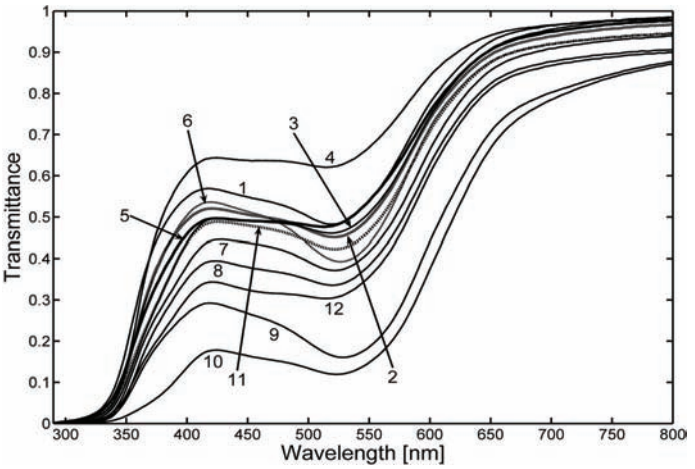

Fig. 2. Transmittance of some commercial red wines from 8 different countries. 1 Italy, " & 3 Spain, 4- 6 France, 8 Portugal, 9 Argentina, 10 Chile, 11 USA, and 12 South Africa.

Although the transmission measurement is one of the most basic measurements in materials research, it will not provide direct information about the absolute refractive index of a sample. However, the refractive index is directly proportional to the concentration of the research object, such as a liquid sample. Therefore, knowing the refractive index is very important, and this knowledge can be used, for example, to monitor the sugar and salt concentration of liquids. A number of commercial devices, known as refractometers, have been developed for such purposes, but these devices do not provide information on the wavelength-dependence of the refractive index. Light absorption and dispersion are coupled together, meaning that, if we measure a change in light absorption, we may also expect dispersion of light. In linear optical spectroscopy, it is the principle of causality that rules light absorption and dispersion. Hence, if we have a general rule that couples light absorption and dispersion, we may estimate dispersion by measuring the absorption of light, and *vice versa.* This rule indicates a pair of Kramers-Kronig relations. The pair of K-K relations that connects the extinction coefficient and the real refractive index n of a medium involves only a change in the real refractive index, as can be observed from the K-K relations below

$$n(\omega') - 1 = \frac{2}{\pi} P \int_0^{\infty} \frac{\omega k(\omega)}{\omega^2 - \omega'^2} d\omega \tag{47}$$

and

$$k(\omega') = -\frac{2\omega'}{\pi} P\int_0^{\infty} \frac{n(\omega)-1}{\omega^2 - \omega'^2} d\omega \cdot \tag{48}$$

Fig. 3 exemplifies a change in the extinction coefficient and refractive index of the red wine samples shown Fig. 2. Data for Fig. 3 were calculated from data shown in Fig. 2 using Eqs. (18) and (47). Optical properties can be used in the quality monitoring of red wine and in checking the authenticity of a wine (Mutanen *et al.* 2006).

K-K analysis is normally restricted to the use of Eq. (47). Nevertheless, we have recently emphasized the utilization of relations (47) and (48) for cross-checking both the validity of the data and the success of the K-K analysis. Progress on mathematical methods for the calculation of K-K relations is discussed in (Lee 1996, Lee & Sindoni 1997, King 2002, Cohen *et al.* 2005).

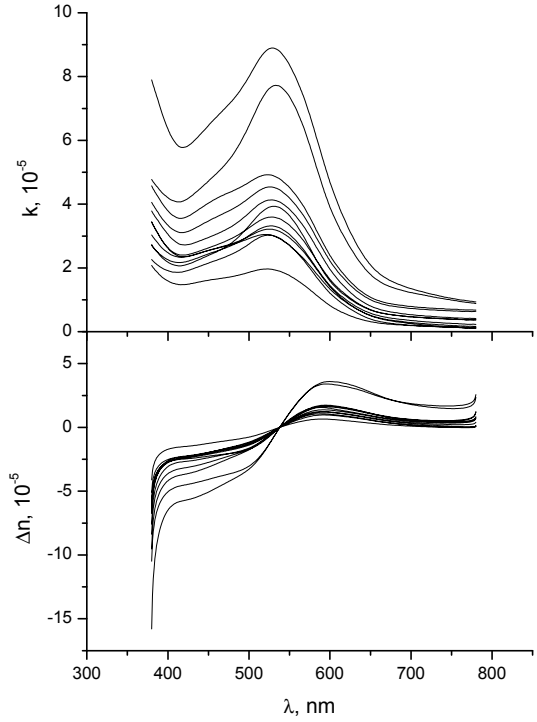

Fig. 3. Real refractive index change and extinction coefficient of some commercial red wines.

The transmission measurement incorporated within the K-K relation (47) is a powerful method for the spectral analysis of solid, liquid, and gaseous phases, if the studied medium is optically not very dense or thick. Information on the complex refractive index, $N = n + ik$, provides a more comprehensive picture of the overall optical properties of a medium than transmittance only. Once we know N, it is easier to assess, for example, the optoelectronic properties of semiconductors used for light sources and detectors. Moreover, if we wish to know how much radiation a metal reflects, information on N is certainly crucial. Note that due to the definition of K-K relations, they can be expected to remain valid over the whole spectral range.

Present computer technology makes it possible to implement an algorithm, running on the PC of a spectrophotometer, which is capable of calculating the refractive index change of a medium immediately after the measurements. However, there is the well-known problem that one can only measure data in a finite frequency range, while K-K relations require utilizing a semi-infinite frequency range. Therefore, the application of conventional K-K relations necessitates extrapolating the spectrum beyond the measured range, which may lead to errors (Peiponen &Vartiainen 1991). This uncertainty regarding the use of K-K data analysis has to be clearly pointed out in the software packages of commercial spectrophotometers (Lichvar *et al*. 2002). However, the success of data inversion can be improved using additional information on the complex refractive index at anchor points. Such information is relatively easily available, for example, through the ATR spectroscopy of liquids (Goplen *et al* 1980). For reflectance data, the concept of multiple anchor points is essential to improve the accuracy of the data obtained by K-K relations (Ahrenkiel 1979, Palmer *et al* 1998). Although Palmer considered only one pair of the so-called multiply subtractive K-K relations, *Paper IV* generalized his concept to hold for a pair of multiply subtractive K-K relations. *Paper V* introduced a novel way of utilizing singly subtractive K-K relations by simultaneously coupling anchor point data at a real and imaginary circular frequency. A review on the utilization of the K-K relations in nonlinear and terahertz spectroscopy was published in (Peiponen & Saarinen 2009).

4.2 Hamaker's constant

Surface chemistry plays an important role in adsorption and adhesion phenomena at the solid-liquid interface. Understanding how ink sets on paper during the

printing process has consequences for the quality of print, in which poor quality may appear as gloss and color mottling (Juuti *et al.* 2007). One feature that is important for gloss inspection is the complex refractive index of the ink. Recent studies, including *Paper VI*, have estimated the complex refractive index of offset inks in a liquid (Niskanen *et al.* 2007a) and in a dry solid ink film (Niskanen *et al.* 2007b).

To understand how ink behaves on a paper surface requires considering attractive energy. The attractive energy of a macroscopic body, such as a particle or a plate in a liquid, may be characterized by the Hamaker constant, which is important for the prediction of cohesion between solid and liquid objects (Hunter 1989). Hamaker's constant for the case of parallel half spaces of material 1 and 2, separated by fluid 3, is given by the following expression:

$$H_{123} = \frac{3kT}{2} \sum_{n=0}^{*} \sum_{s=1} \left[\frac{\varepsilon_1(i\xi_n) - \varepsilon_3(i\xi_n)}{\varepsilon_1(i\xi_n) + \varepsilon_3(i\xi_n)} \right]^s \left[\frac{\varepsilon_2(i\xi_n) - \varepsilon_3(i\xi_n)}{\varepsilon_2(i\xi_n) + \varepsilon_3(i\xi_n)} \right]^s / s^3 \quad (49)$$

where k is Boltzmann's constant, T absolute temperature and permittivity ε_j , j = 1, 2 or 3, has an imaginary variable. The star on the summation indicates that the n = 0 term is given half weight. Permittivity with an imaginary frequency variable can be calculated using an appropriate K-K relation, which has been briefly dealt with in (Peiponen *et al.* 1999). Replacing a real frequency variable by an imaginary one results in a real susceptibility function. In the present case, we can write

$$\varepsilon(i\xi) = \varepsilon_o \left(1 + \frac{2}{\pi} \int_0^\infty \frac{\omega \operatorname{Im} \varepsilon(\omega) d\omega}{\omega^2 + \xi^2}\right). \quad (50)$$

This expression is analogous to a K-K relation except of the imaginary variable. Furthermore, there is no longer a need to take a principal value, because the integral converges. The imaginary part of relevant permittivity can be obtained either from the transmission or reflection spectrum of a medium.

Hough and White [28] derived an expression for contact angle

$$\cos \Theta_{SL} = \frac{\sum_{n=0}^{*} \ln \left[\left(\frac{\varepsilon_S(i\xi_n) + 1}{\varepsilon_S(i\xi_n) + \varepsilon_L(i\xi_n)} \right)^2 \varepsilon_L(i\xi_n) \right]}{\sum_{n=0}^{*} \ln \left\{ \frac{[\varepsilon_L(i\xi_n) + 1]^2}{4\varepsilon_L(i\xi_n)} \right\}}, \quad (51)$$

where S denotes solid and L liquid. In the expression of Eq. (51), as in the case of (49), the permittivity of the medium at an imaginary frequency has crucial importance.

A successful estimation of the Hamaker constant usually requires data in a rather wide spectral range. A novel way to estimate the Hamaker constant is to apply Eq. (4) to permittivity and to subtract it from (15). The result is

$$\varepsilon_r'(i\xi) - \varepsilon_r'(\xi_1) = \frac{2(-\xi^2 - \xi_1^2)}{\pi} P\int_0^\infty \frac{\omega \varepsilon_r''(\omega) d\omega}{(\omega^2 + \xi^2)(\omega^2 - \xi_1^2)}. \qquad (52)$$

To provide an example of how to utilize the formalism above, *Paper V* applies it to the assessment of interaction forces between paper and printing ink, which also has a technical importance for the printing process in terms of optimizing the absorption of ink by paper.

4.3 Maximum entropy method in phase retrieval from reflectance

In optical power spectrum measurements, the intensity distribution of light $I(\omega)$ is proportional to the squared modulus $|f(\omega)|^2$ of a complex valued function $f(\omega)$ with a real variable ω. Reflectance spectroscopic studies, for example, measure the intensity reflectance $R(\omega)=|r(\omega)|^2$. Typically, only the modulus of $f(\omega)$ can be measured, although it is necessary to know the complex function $f(\omega)=|f(\omega)|\exp\{i\delta(\omega)\}$ itself, including also the phase $\delta(\omega)$. A new phase retrieval approach was proposed in (Vartiainen *et al*. 1992). Known as the maximum entropy model, MEM, it is based on Burg's study (Burg 1968) on the calculation of power spectra, data for which consisted of signal measurements taken over a period of time. Although the MEM model is based purely on informatics, it has an analogy with dispersion relations, as shown in (Feng & Lee 2001).

The usage and applicability of MEM as a phase retrieval procedure has been verified for linear reflectance by various publications (Peiponen *et al.* 1999, Lucarini *et al.* 2005). Experiments conducted using liquids from the process industry and subsequent comparisons with other spectral devices and data analysis methods also demonstrated the correct functioning of MEM analysis using data obtained using the reflectometer presented in *Paper I*.

One significant merit of MEM is that it does not require reflectance determination over the entire electromagnetic spectrum, but only within the region of interest, $\omega_1 \leq \omega \leq \omega_2$. As well as reflectance data, additional information about a

given sample is required in order to determine its optical constants. Such information, known as anchor points, commonly comprises the real and/or imaginary parts of the complex refractive index of the sample determined at a frequency within the range $\omega_1 \leq \omega \leq \omega_2$. In practice, the MEM phase retrieval procedure includes the experimental reflectance R given by the following formula (a somewhat lengthy mathematical derivation can be found in (Peiponen *et al.* 1999)):

$$R(v) = \frac{|\beta|^2}{\left|1 + \sum_{m=1}^{M} a_m \exp(-i2\pi mv)\right|^2} \quad , \tag{53}$$

where the normalized angular frequency v is defined by

$$v = \frac{\omega - \omega_1}{\omega_2 - \omega_1} \quad . \tag{54}$$

The unknown MEM coefficients a_m and $|\beta|$ can be obtained from a set of linear Yule-Walker equations

$$\sum_{m=0}^{M} a_m C(n-m) = \begin{cases} |\beta|^2 & \text{n} = 0 \\ 0 & \text{n} = 1,...,\text{M} \end{cases} \quad , \tag{55}$$

where the auto-correlation $C(t)$ is computed by a Fourier transform of $R(v)$ as

$$C(t) = \int_0^1 R(v) \exp(i2\pi tv) dv \quad . \tag{56}$$

Phase retrieval can now be based on MEM for reflectivity

$$r(v) = \frac{|\beta| \exp[-i\phi(v)]}{1 + \sum_{m=1}^{M} a_m \exp(-i2\pi mv)} \quad . \tag{57}$$

In (57), the error phase $\phi(v)$ is the only quantity that cannot be obtained by a measurement of $R(v)$. The idea of using MEM in phase retrieval is that the problem of finding the phase $\delta(v)$ is reduced to a problem of finding the error phase $\phi(v)$ (typically, ϕ is a much simpler function than δ). Additional information

on $r(\nu)$, determined at L+1 discrete frequencies ν_l, is used to find an estimate for $\phi(\nu)$

$$\begin{pmatrix} 1 & \nu_0 & \cdots & \nu_0^{\,L} \\ 1 & \nu_1 & \cdots & \nu_1^{\,L} \\ \vdots & \vdots & & \vdots \\ 1 & \nu_L & \cdots & \nu_{\mathrm{L}}^{\,L} \end{pmatrix} \begin{pmatrix} B_0 \\ B_1 \\ \vdots \\ B_L \end{pmatrix} = \begin{pmatrix} \phi(\nu_0) \\ \phi(\nu_1) \\ \vdots \\ \phi(\nu_L) \end{pmatrix} , \tag{58}$$

where B_l is obtainable from a Vandermonde system.

The error phase is usually a slowly varying function, and in favourable cases only one or two anchor points are necessary; in other words, the optimum degree of the polynomial is low. Brun (Brun *et al.* 2001) has presented an optimization method designed to improve the error phase smoothening of reflection spectra. Important applications of the MEM method include the use of coherent anti-Stokes Raman scattering spectroscopy, or CARS, for the study of biological and medical objects (Vartiainen *et al.* 2006, Rinia *et al.* 2006).

5 Measurement devices

5.1 Reflectometer

Estimates of the complex refractive index of opaque media, such as slurries, can be obtained over a wide spectral range by the use of a reflectometer and relevant spectra analysis methods (Räty *et al.* 2004). An alternative apparatus is an ellipsometer, which provides information on the complex refractive index of solid samples, but usually over a relatively narrow spectral range. In the process industry, the principle of ellipsometry is utilized for monitoring purposes, but these applications tend to use a laser light source. Fig. 4 shows a multifunction reflectometer, which was developed for process water analysis in pulp and paper mills. This prism reflectometer has different measurement modes, including scanning of the angle of incidence or the wavelength. It also permits selecting linear polarization, such as *s*- and *p*-polarizations, of the incident light. In the case of strongly light absorbing liquid the attenuated total reflection mode (ATR) is often utilized for the determination of the optical properties of the liquid. However, the concept of the critical angle is no more as clear as in the case of clear liquids. A small angle shift of incident light beam around the critical angle can cause dramatic change in the recorded internal reflection spectrum (see e.g. Mirabella 1993, p. 331). In (Räty & Peiponen 2000) the error of optical constants was simulated. Best accuracy was obtained when the angle of incidence was slightly below the critical angle. Anyhow in most of the cases regarding industrial optical inspection the precise accuracy of the optical constants is not usually a big issue. The accuracy, stability and repeatability of the reflectometer are described in the dissertation of Räty (Räty 1999)

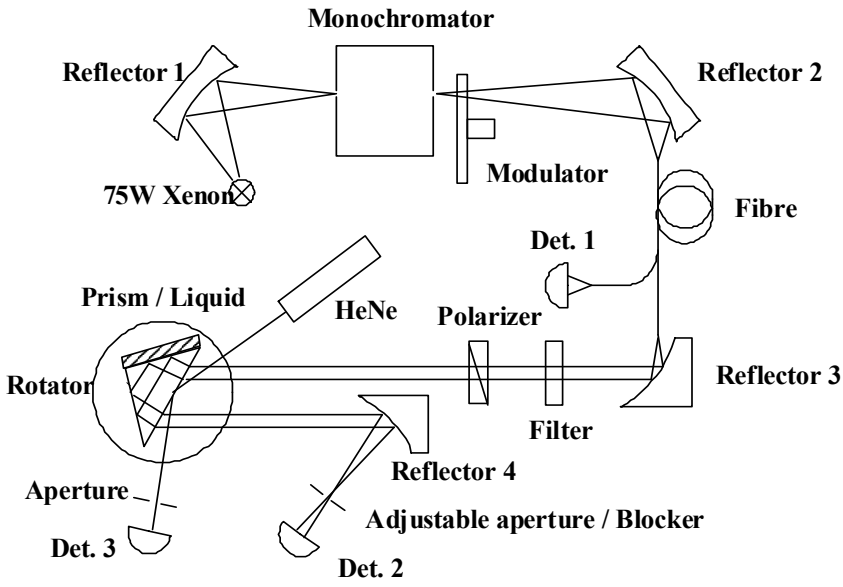

Fig. 4. Schematic diagram of a reflectometer.

Fig. 5 presents reflectance for the 12 red wines that were considered previously. The data were recorded as a function of wavelength for a fixed angle of incidence using *s*- polarized light. Assuming a relatively low extinction coefficient enables us to solve the refractive index of the wines from (20), since there is only one unknown quantity, namely, the real refractive index n. Fig. 6 displays the dispersion curves of the 12 red wines, based on the data shown in Fig. 5.

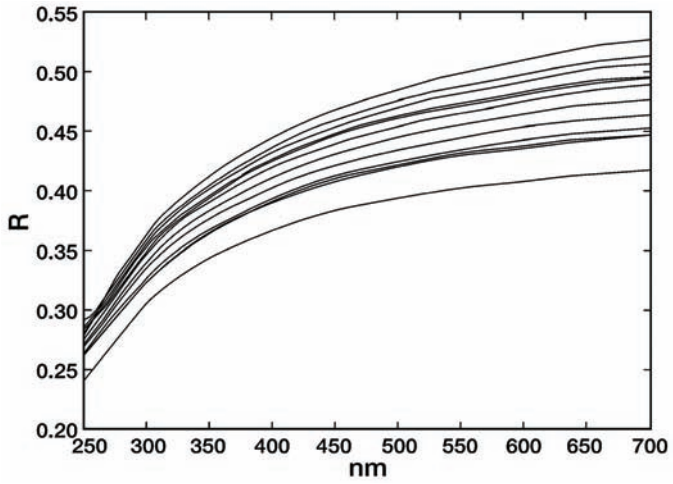

Fig. 5. Reflectance from 12 red wine samples as a function of wavelength. The curves were recorded by a reflectometer using *s*-polarized light. The samples present products of various grapes.

By inspecting Fig. 6, we observe that a relatively good way of monitoring the concentration of the red wines involves integrating the refractive index curves. Using the sodium D-line (589.3nm) to distinguish between the wine samples results in somewhat poorer sensitivity.

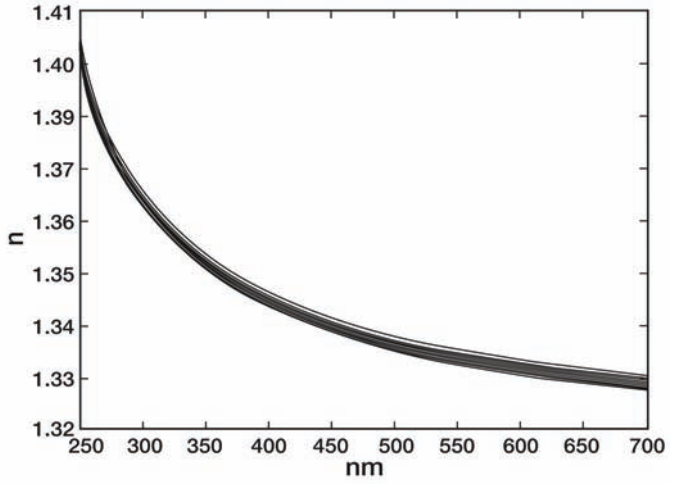

Fig. 6. Real refractive index of 12 red wines based on data shown in Fig. 5.

In the case of scanning the angle of incidence for a fixed wavelength, an estimate for the complex refractive index can be obtained using an optimization method presented in (Räty & Peiponen 1999a). This method minimizes the least square sum of the difference between the reflectance obtained from the theory by inserting candidates for the complex refractive index N as follows:

$$S = Min \sum_{\theta} \left[R_m(\theta) - R_t(\theta) \right]^2 , \tag{59}$$

where R_m and R_t are the measured and theoretical reflectance, respectively.

An advanced version of the reflectometer which is coined the name multifunction spectrophotometer (MFS) has been successfully used in estimation of effective refractive index of birefringent (Niskanen *et al.* 2008) and novel nanostructured paper fillers (Koivunen *et al.* 2009) by incorporating MFS and liquid immersion method.

5.2 Surface plasmon resonance sensor

Plasma oscillation in the surface mode can be generated by a prism with one face coated by a thin metal film and a laser as a light source. If the complex permittivities of the metal film and the liquid sample are chosen properly, surface plasmon resonance (SPR) can be excited for a fixed wavelength at an angle that is larger than the critical angle of reflection. SPR occurs when the wave number of the incident field parallel to the surface matches the complex wave number of the surface plasmon.

Typically, the thickness of the metal film is ca. 50 nm. In laboratory experiments, silver film is usually used due to the relatively strong SPR signal, whereas commercial sensors favor gold film. Commercial SPR sensors make use of Kretchmann's configuration (Homola *et al.* 1999) and a focused light beam that is incident on the interface between the sample and the prism (Matsubara *et al.* 1988). The focused beam automatically provides a range of incidence angles of the light rays, thus eliminating the need to rotate the probing prism. Obviously, the range of variation of the refractive index is limited by the magnitude of the cone of the incident light and the refractive index of the probe prism. For a particular liquid, this range of variation (variation of concentration) can usually be estimated and taken into account in the construction of the SPR sensor. A photodetector, an array of detectors or a CCD camera is used for detecting the spatial variation of the

dip in the intensity of the reflected light. Fig. 7 shows a schematic diagram of an SPR sensor.

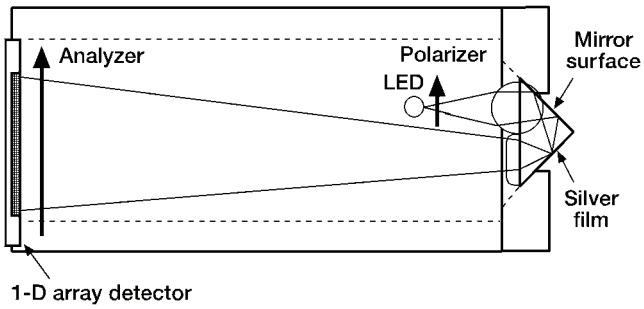

Fig. 7. Schematic diagram of the SPR sensor.

The list of different types of applications based on SPR sensors is long, including measurement of optical properties and thickness of metal films, adsorption (or desorption) of gas molecules, drug discovery, food stuff applications, loading of pigments used in paper, paint and other sectors of industry where liquids and pigments play an important role. In some applications, the metal surface has a special feature such that the surface texture of the metal film is modified by introducing a lipid bilayer, adsorbed co-polymers, etc. This is particularly important in the monitoring of dynamic biological interactions, where the liquid to be measured is under a flowing process in a flow cell coupled into the SPR measurement head. Such a scheme is useful, for example, for monitoring the kinetics of protein adsorption into biomaterials. The reflectometer presented in *Paper I* has been modified and can, therefore, also be used in the SPR measurement mode (Räty *et al.* 2002).

6 Summary

Measuring and analyzing optical spectra obtained from turbid liquids is an issue that has much practical importance for quality analysis in industrial environments and medicine, but also for pollution monitoring in natural water bodies. There are different types of commercial gauges on the market designed to monitor the optical properties of turbid liquids. Most often such sensors provide information on the refractive index, transmission or turbidity of a liquid sample. In many cases, such as the Abbe refractometer, the sensor only gives data at a fixed standardized wavelength, which makes the measurement easier and faster than scanning over a spectrum. However, a spectrum provides a better means of identifying different species and their sizes.

Nowadays, the role of nanoparticles has become crucial for many applications in nanomedicine and the food industry, where they are used in beverages to obtain an optimal color. Although nanoparticles have many advantages, there is the problem that very small particles may be harmful for the human body. Due to this nanotoxicological aspect, it is very important to develop new imaging and sensing devices for the detection of nanoparticles both in liquid and solid matrices. Fortunately, measuring the optical response of nanoparticles in a liquid matrix is a fairly simple procedure. Such features as nanoparticle size, shape, complex permittivity and the optical properties of the host medium rule the optical spectra of two- or multicomponent nanocomposites.

In this thesis, I have developed spectral analysis methods for turbid liquids, such as inks and liquids containing nanoparticles. Two different methods, namely, Kramers-Kronig relations and the maximum entropy method form the main body of this thesis. In addition, Azzam's method was applied for the study of dry ink. I have shown that the spectral methods presented in this thesis allow us to obtain a better picture of turbid liquids than the measured spectrum alone. These spectral analysis methods can be implemented into spectrometer software. Especially the implementation of MEM increases the possibilities for spectral analysis, while also providing a straightforward instrument for comparison with data analysis based on K-K relations.

In terms of the printing industry, this thesis also includes new dispersion relations that have a fundamental significance for basic studies, including the Hamaker constant of inks. The final goal is to couple the optical properties of ink with the setting of ink on paper. Knowledge of the optical properties of inks plays a great role in gloss and gloss mottling. This thesis provides partial solutions for improving print quality.

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ISBN 978-951-42-9167-8 (Paperback)
ISBN 978-951-42-9168-5 (PDF)
ISSN 0355-3213 (Print)
ISSN 1796-2226 (Online)

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