# On prediction of optical properties of two- and multiphase nanocomposites for nanomedicine

Kai-Erik Peiponen
Evgeny Gornov

Department of Physics and Mathematics, University of Joensuu, Joensuu, Finland

**Abstract:** The theory of optical properties of nanoparticles is considered with the aid of dispersion relations, which are based on the Kramers-Kronig analysis. It is shown that one can utilize rather general dispersion relations, which hold for liquid matrices that contain nanoparticles. Wiener bounds incorporating the Kramers-Kronig analysis are utilized in assessment of the complex permittivity of a nanoparticle.

**Keywords:** nanoparticle, nanocomposite, optical properties, dispersion theory

## Introduction

Nanoparticles have drawn much attention in science due to their extraordinary properties. There are applications of nanoparticles both in engineering and medicine (Holdridge 1999). Biodegrable nanoparticles can be used for controlled drug delivery (Ravi Kumar 2000), whereas semi-conducting and metallic nanoparticles have applications in genomics and proteomics (Jain 2006). In the monitoring of disease or in drug delivery by nanoparticles there is an interest to sense the molecular processes involved. For example, in the case of quantum dots one makes use of the optical properties of a two-phase nanocomposite, ie, a liquid containing nanoparticles (Haes and Van Duyne 2004). The point is that the spectral properties of nanostructures are sensitive to their size, shape, material properties and the environments. The trend is to make use of the optical properties of such nanocomposites both in enhancement and detection of a signal due to a molecular process. It is possible to monitor changes of a nanocomposite using the concept of linear or nonlinear optical process. The most typical is a linear optical process, ie, the intensity of the probe light is weak. In the case of nonlinear optical process the intensity of the light beam/beams is high. This means that in the latter case one is using a laser as a light source. The class of different nonlinear optical process is large (Shen 1984). The common thing for linear and nonlinear optical spectroscopy is the desire to gain signal strength and to enhance sensitivity to changes in the system, such as the nanocomposite. In order to optimize the light interaction with a nanocomposite, or any other medium, one has to know the spectral properties of the nanocomposite. The critical quantity for this purpose is the complex permittivity of the composite. The interaction of radiation with electrons of a medium in the spectral range of visible light is related to the polarization of electrons (Peiponen et al 1999). The strength of the polarization, ie, the response of the nanocomposite system to an external electric field, is proportional to the complex permittivity of the medium.

In this paper we consider wavelength-dependent optical properties of two- and multiphase nanocomposites by treating them as effective media (Maxwell Garnett 1904, Bruggeman 1935). The idea is to provide, without any prior knowledge of the shape and size of the nanoparticles, rather general methods to extract the effective complex permittivity of the nanocomposite, and also the complex permittivity of

Correspondence: Kai-Erik Peiponen, Department of Physics and Mathematics, University of Joensuu, PO Box 111, FI-80101 Joensuu, Finland
Email peiponen@cc.joensuu.fi

the nanoparticle itself. This is accomplished with the aid of dispersion relations for the permittivity (Peiponen et al 1999). We deal with the transmission and reflection of light in nanostructured media.

## Dispersion relations for nanocomposites

If nanoparticles are put into water one observes different colours of the two-phase nanocomposite depending on the size and fill fraction of the nanoparticles. Transmission spectra can be recorded for further analysis (Haes and Van Duyne 2004). Unfortunately, the transmission spectrum will not provide the full picture of the optical properties of the two-phase nanocomposite, which may contain insulating, metallic or semi-conducting nanoparticles. In addition to light absorption there will always appear dispersion of the light in the medium. The coupling of the absorption and the dispersion is described by the complex effective permittivity defined by the expression:

$$\varepsilon_{eff} = \varepsilon_{eff}(\omega, f, d) = \mathrm{Re}\,\varepsilon_{eff}(\omega, f, d) + i\,\mathrm{Im}\,\varepsilon_{eff}(\omega, f, d), \tag{1}$$

where $i$ is the imaginary unit, "Re" stands for the real and "Im" for the imaginary part. The circular frequency of light is denoted by $\omega$, $f$ is the fill fraction and $d$ is the size of the nanoparticles. In the case of non-spherical particles the effective permittivity depends on the shape and size distribution of the particles (Spanoudaki and Pelster 2001). The effective permittivity depends also on the temperature and pressure of the nanocomposite. Transmittance and reflectance, even in the case of close packing of regular shape nanoparticles, can be calculated using analytic formulas (Fedotov et al 2004). Unfortunately, it may happen that the nanoparticles depart from a regular shape such as spherical, due for example to fabrication problems. Then one cannot find a comprehensive analytic theory for the optical properties of the nanocomposite that would link the theory with the measured data of the transmittance and/or reflectance. Fortunately, we can utilize rather general dispersion relations that are valid also for complicated cases of nanostructured media. Here we use Kramers–Kronig (K–K) relations (Lucarini et al 2005) in the description of the optical properties of the two- or multiphase nanocomposites. By a multi-phase composite we mean a matrix where nanoparticles made from different materials have been embedded.

### Transmission data

In the case of light transmission measurement we get information on the effective absorption coefficient via the Beer-Lambert intensity law:

$$I = I_o \exp(-l\alpha_{eff}(\omega)), \tag{2}$$

where $l$ is the thickness of the nanocomposite and $\alpha_{eff}$ is the effective absorption coefficient. In Equation (2) the only explicit variable is the circular frequency, which is obtained with the aid of the wavelength of the light. Hence, we have no precise information on the fill fraction, or the size and shape of the nanoparticles. Yet, we have a chance to find out more information on the optical properties of such a system. The effective complex permittivity is related to the effective complex refractive index of the nanocomposite as follows:

$$\varepsilon_{eff}(\omega) = N_{eff}^2(\omega) = [n_{eff}(\omega) + ik_{eff}(\omega)]^2, \tag{3}$$

where $n_{eff}$ is the effective real refractive index and $k_{eff}$ the extinction coefficient of the nanocomposite. Note that we have preserved the only explicit variable namely the circular frequency. The effective extinction coefficient obeys the formula (Peiponen et al 1999)

$$k_{eff}(\omega) = \frac{c\alpha_{eff}(\omega)}{2\omega}, \tag{4}$$

where $c$ is the light velocity in vacuum. If we wish to optimize the strength of light interaction with the electrons of a nanoparticle, whether insulator or metal, the crucial factor is the $\mathrm{Re}\varepsilon_{eff}$. We do not have information on the real part of the effective permittivity via light transmission measurement but it can be estimated with the aid of the K–K relation:

$$n_{eff}(\omega') - n_{eff}(\infty) = \frac{2}{\pi} P\int_0^\infty \frac{\omega k_{eff}(\omega)}{\omega^2 - \omega'^2} d\omega, \tag{5}$$

where $P$ stands for the Cauchy principal value (Lucarini et al 2005) and $n_{eff}(\infty)$ is the high frequency refractive index of the nanocomposite. Using Equations (2–5) one can construct the real part of the effective permittivity. In the case of a well-known liquid matrix, such as water, we may know that it is not absorbing much light at the spectral range of visible light. Thus in the case of a coloured nanocomposite we may conclude that the refractive index change, Equation (5), and hence the spectral features of the real part of the effective permittivity stem dominantly from the optical properties of the nanoparticles. The value of the real part of the effective permittivity and also its change as a function of the circular frequency give information on the strength of the polarization of the electrons, which are confined inside a small volume of a nanoparticle.

It is well known that the Kramers–Kronig relation (Equation 5) is susceptible to extrapolation errors in the data inversion. The reliability of the extraction of the correct real refractive index of the nanocomposite can be improved in the case when additional optical data at so-called anchor points are available. In such a case one can make use of multiply subtractive K–K relations (Lucarini et al 2005). As far as we know, multiply subtractive K–K relations for the complex effective refractive index of nanocomposites have not been treated in the literature until now. First we write a singly subtractive K–K relation for the calculation of the real refractive index of the nanocomposite as follows:

$$n_{eff}(\omega') - n_{eff}(\omega_1) = \frac{2(\omega'^2 - \omega_1^2)}{\pi} P\int_0^\infty \frac{\omega k_{eff}(\omega)}{(\omega^2 - \omega'^2)(\omega^2 - \omega_1^2)} d\omega, \tag{6}$$

where $\omega_l$ is an anchor point where the effective real refractive index of the nanocomposite is known. The point with this formula is much stronger convergence of the integral than in the case of Equation (5). In many cases the measured data without extrapolations beyond the measured range is sufficient for the data inversion by Equation (6). The refractive index of the nanocomposite at the anchor point may have been measured, e.g. using the ATR-technique (attenuated total reflection) (Räty et al 2004). If information on the refractive index of the nanocomposite is available at many anchor points then we can utilize a multiply subtractive K–K relation (MSKK) which can be given by the expression:

$$\begin{aligned} n_{eff}(\omega') = {} & \left[ \frac{(\omega'^2 - \omega_2^2(\omega'^2 - \omega_3^2)\cdots(\omega'^2 - \omega_Q^2)}{(\omega_1^2 - \omega_2^2)(\omega_1^2 - \omega_3^2)\cdots(\omega_1^2 - \omega_Q^2)} \right] n_{eff}(\omega_1) \\ & + \ldots \left[ \frac{(\omega'^2 - \omega_1^2)\cdots(\omega'^2 - \omega_{j-1}^2)}{(\omega_j^2 - \omega_1^2)\cdots(\omega_j^2 - \omega_{j-1}^2)} \right. \\ & \left. \frac{(\omega'^2 - \omega_{j+1}^2)\cdots(\omega'^2 - \omega_Q^2)}{(\omega_j^2 - \omega_{j+1}^2)\cdots(\omega_j^2 - \omega_Q^2)} \right] n_{eff}(\omega_j) \\ & + \cdots + \left[ \frac{(\omega'^2 - \omega_1^2)(\omega'^2 - \omega_2^2)}{(\omega_Q^2 - \omega_1^2)(\omega_Q^2 - \omega_2^2)} \right. \\ & \left. \frac{\cdots(\omega'^2 - \omega_{Q-1}^2)}{\cdots(\omega_Q^2 - \omega_{Q-1}^2)} \right] n_{eff}(\omega_Q) \\ & + \frac{2}{\pi}\Big[ (\omega'^2 - \omega_1^2)(\omega'^2 - \omega_2^2) \\ & \cdots(\omega'^2 - \omega_Q^2) \Big] P \\ & \int_0^\infty \frac{\omega k_{eff}(\omega) d\omega}{(\omega^2 - \omega'_2)(\omega^2 - \omega_1^2)\cdots(\omega^2 - \omega_Q^2)} \end{aligned} \tag{7}$$

where the number of the anchor points is $Q$.

## Reflection data

If the optical density of the nanocomposite is very high, eg, due to close packing of the nanoparticles, we may not be able to measure the light transmission. Then we usually are forced to detect light reflection, ie, to measure the reflectance from the interface of the nanocomposite and a measurement window. For the sake of simplicity we deal here only with the case of normal light incidence. The theory below can be generalized to hold also for oblique light incidence. The reflectance from a nanocomposite, in the frame of the effective medium assumption, obeys the Fresnel's law:

$$R_{eff}(\omega) = \left| \frac{1 - N_{eff}(\omega)}{1 - N_{eff}(\omega)} \right|^2 = \left| r_{eff}(\omega) \exp i\left[ \varphi_{eff}(\omega) \right] \right|^2 \tag{8}$$

where φ is the phase of the reflected light wave. Now the complex effective refractive index, and hence the complex effective permittivity of the nanocomposite, can be obtained by a phase retrieval procedure. This phase retrieval can be based on the Kramers–Kronig analysis or on the maximum entropy method (MEM) (Lucarini et al 2005). We write the phase function for the case of MSKK:

$$\begin{aligned} \varphi_{eff}(\omega') = {} & \left[ \frac{(\omega'^2 - \omega_2^2(\omega'^2 - \omega_3^2)\cdots(\omega'^2 - \omega_Q^2)}{(\omega_1^2 - \omega_2^2)(\omega_1^2 - \omega_3^2)\cdots(\omega_1^2 - \omega_Q^2)} \right] \ln\left| r_{eff}(\omega_1) \right| \\ & + \ldots \left[ \frac{(\omega'^2 - \omega_1^2)\cdots(\omega'^2 - \omega_{j-1}^2)}{(\omega_j^2 - \omega_1^2)\cdots(\omega_j^2 - \omega_{j-1}^2)} \right. \\ & \left. \frac{(\omega'^2 - \omega_{j+1}^2)\cdots(\omega'^2 - \omega_Q^2)}{(\omega_j^2 - \omega_{j+1}^2)\cdots(\omega_j^2 - \omega_Q^2)} \right] \ln\left| r_{eff}(\omega_j) \right| \\ & + \cdots + \left[ \frac{(\omega'^2 - \omega_1^2)(\omega'^2 - \omega_2^2)}{(\omega_Q^2 - \omega_1^2)(\omega_Q^2 - \omega_2^2)} \right. \\ & \left. \frac{\cdots(\omega'^2 - \omega_{Q-1}^2)}{\cdots(\omega_Q^2 - \omega_{Q-1}^2)} \right] \ln\left| r(\omega_Q) \right| \\ & + \frac{2}{\pi}\Big[ (\omega'^2 - \omega_1^2)(\omega'^2 - \omega_2^2) \\ & \cdots(\omega'^2 - \omega_Q^2) \Big] P \\ & \int_0^\infty \frac{\omega \ln\left| r_{eff}(\omega) \right| d\omega}{(\omega^2 - \omega'_2)(\omega^2 - \omega_1^2)\cdots(\omega^2 - \omega_Q^2)} \end{aligned} \tag{9}$$

In the case of no a priori information on the phase at anchor points the MSSK reduces to a more familiar K–K expression that reads:

$$\varphi_{eff}(\omega') = \frac{2}{\pi} P \int_0^\infty \frac{\omega \ln |r_{eff}(\omega)|}{\omega^2 - \omega'^2} d\omega \qquad (10)$$

Once the phase function has been calculated we get both the real and imaginary parts of the complex effective refractive index from the first equality in Equation (8).

So far, we have shown that it is possible to extract the complex effective refractive index as well as the complex effective permittivity of the system consisting of irregular shaped nanoparticles with unknown fill fractions. The next issue is how can we estimate the optical properties of the nanoparticles? We wish to address this question in the next section.

## Wiener bounds for nanocomposite

Let us first consider a two-phase nanocomposite. We assume that the nanocomposite can be treated as an effective medium. However, we permit fluctuation in the shape and size of the nanoparticles, but assume that they are made from the same material. The only way to estimate effective complex permittivity of irregular-shaped nanoparticles is to use the Wiener bounds (Wiener 1912). In our case these bounds can be given by the expressions:

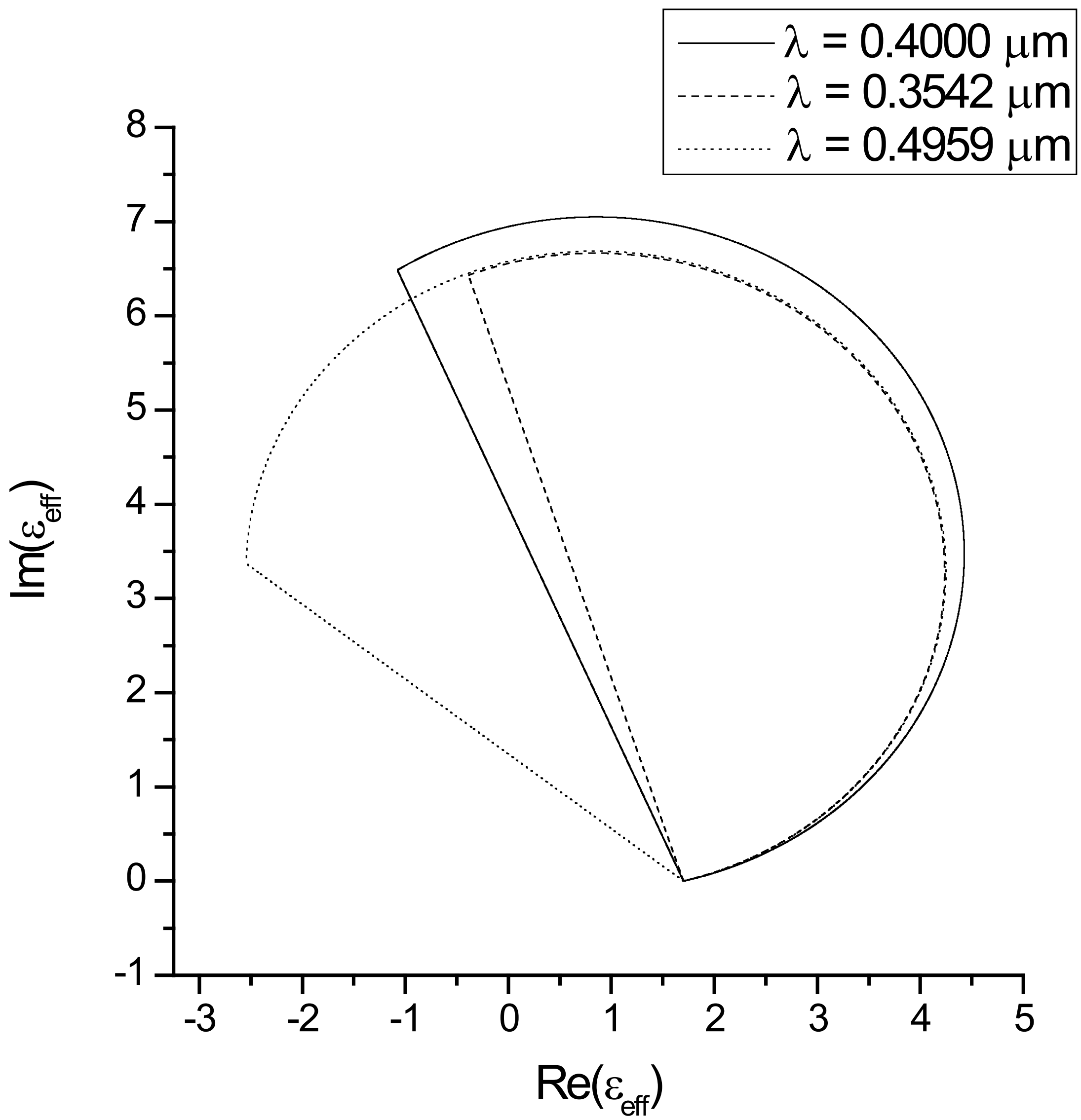


**Figure 1** The Wiener bounds for effective permittivity of water with gold inclusions. The permittivity is inside closed curve. The fill fraction of inclusions is between 0 and 1.

$$\varepsilon_{eff}(\omega) \le f\varepsilon_{nano,eff}(\omega) + (1-f)\varepsilon_{liq}(\omega)$$
$$\frac{1}{\varepsilon_{eff}(\omega)} \le \frac{f}{\varepsilon_{nano,eff}(\omega)} + \frac{1-f}{\varepsilon_{liq}(\omega)}, \quad (11)$$

where $f$ is the fill fraction, $\varepsilon_{nano,eff}$ is the complex effective permittivity of the nanoparticle and $\varepsilon_{liq}$ is the complex permittivity of the liquid (in the case of water it can be taken as a real quantity at the spectral range of visible light). In the case of nanoparticles their shape affects how they are screened, which will affect the polarization of the charges, and hence the permittivity of the nanocomposite. The equalities of the Wiener bounds present two extreme cases namely no screening and maximum screening (Aspnes 1982). Here we assume that the fill fraction of nanoparticles is known, but not fixed. Now because we have the information of the complex effective permittivity of the nanocomposite, obtained using the K–K analysis presented in section 2, and also we usually have a priori knowledge of the complex permittivity of the liquid matrix, we get bounds for the complex permittivity of an "effective nanoparticle" by solving from Equation (11) the following expressions:

$$\varepsilon_{nano,eff}(\omega) \ge \frac{\varepsilon_{eff}(\omega) - (1-f)\varepsilon_{liq}}{f}$$
$$\varepsilon_{nano,eff}(\omega) \le \frac{f}{\dfrac{1}{\varepsilon_{eff}(\omega)} - \dfrac{1-f}{\varepsilon_{liq}(\omega)}} \quad (12)$$

In the event that a multiphase nanocomposite has to be treated, we always get the complex effective refractive index using the methods in section 2. It is possible to generalize the Wiener bounds to hold for such a system too. However, then one has to know the fill fractions of all components except one. We have described such a system with the aid of barycentric coordinates (Peiponen and Gornov 2006). In Figure 1 we show an example about Wiener bounds for the effective permittivity of a two-phase nanocomposite. In the simulation the gold nanoparticle is assumed to obey the optical properties given in (Palik 1998) and the liquid is water. As we can observe the domain of the allowed complex permittivity depends on the wavelength of the incident light.

If the fill fraction of the nanoparticles is fixed then more stringent limits for the effective permittivity can be established as shown in (Milton 1980). Naturally such limits help to get better approximation for the permittivity of the nanoparticle with aid of the K–K analysis presented in this study.

## Discussion

In this paper we have addressed the problem of getting the complex effective refractive index and complex effective permittivity of nanoparticles, which have applications in nanomedicine. We did not assume any particular size or shape of the nanoparticle nor its material properties, but assumed that the nanoparticles are in a liquid matrix, and the system can be treated as an effective medium. By utilizing Kramers–Kronig analysis we obtained the complex effective refractive index. We believe that the multiply subtractive Kramers–Kronig relations are given for the first time in this paper for nanocomposites of a rather general nature. We limited the study to the field of linear optical spectroscopy, but the dispersion relations of this paper hold also in the detection of nanoparticles using nonlinear optical processes such as harmonic wave generation. In such a case the dispersion relations are written for the nonlinear effective susceptibility of the nanocomposite.

The Wiener bounds incorporated with the Kramers–Kronig analysis related to measured transmission or reflection spectra from nanocomposites provide a way to gain information on the optical properties of the nanoparticles. In the case of metallic nanoparticles in water one may have a priori knowledge of their optical properties. However, if the shape of metallic nanoparticles is not regular, or if one makes use of insulating nanoparticles that may change they shape and size as a function of time, we face a problem in the description of the optical properties of the nanocomposite. The method of this paper provides a partial solution for such a problem.

## References

Aspnes DE. 1982. Local-field effects and effective-medium theory: A microscopic perspective. *Am J Phys*, 50:704–9.

Bruggeman DAG. 1935. Berechnung verschidener physikalischer konstanten von heterogenen substanzen I. Dielektrisitätkonstanten und leitfähigkeiten der mischkörper aus isotropen substanzen. *Ann Phys (Leipzig),* 24:636–79.

Fedotov VA, Emel'yanov VI, MacDonald KF, et al. 2004. Optical properties of closely packed nanoparticle films: spheroids and nanoshells. *J Opt A: Pure Appl Opt*, 6:155–60.

Haes J, Van Duyne RP. 2004. Preliminary studies and potential applications of localized surface plasmon resonance spectroscopy in medical diagnostics. *Expert Rev Mol Diagn*, 4:527–37.

Holdridge GM. 1999. Nanostructure science and technology R and D status and trends in nanoparticles, nanostructured materials, and nanodevices. Dordrecht: Kluwer.

Jain KK. 2006. Nanobiotech in genomics and proteomics. *Gen Eng News*, 32:6, April 1st.

Lucarini V, Saarinen JJ, Peiponen K-E, et al. 2005. Kramers-Kronig relations in optical materials research. Berlin: Springer.

Maxwell Garnett JC. 1904. Colours in metal glasses, in metallic films, and in metallic solutions. *Phil Trans A*, 203:385–420.

Milton GW. 1980. Bounds on the complex dielectric constant of a composite material. *Appl Phys Lett*, 37:300–2.

Palik ED. 1998. Handbook of optical constants of solids. New York: Academic Press.

Peiponen K-E, Gornov E. 2006. Description of Wiener bounds of multicomponent composites by barycentric coordinates. *Opt Lett*, 31:2202–4.

Peiponen K-E, Vartiainen EM, Asakura T. 1999. Dispersion, complex analysis and optical spectroscopy. Heidelberg: Springer.

Räty K, Peiponen K-E, Asakura T. 2004. UV-visible reflection spectroscopy of liquids. Berlin: Springer.

Ravi Kumar MNV. 2000. Nano and microparticles as controlled drug delivery devices. *J Pharm Pharmaceut Sci*, 3:234–58.

Shen YR. 1984. The principles of nonlinear optics. New York: Academic Press.

Spanoudaki A, Pelster R. 2001. Effective dielectric properties of composite materials: the dependence on the particle size distribution. *Phys Rev B*, 64:642051–6.

Wiener O. 1912. Die theorie des mischkörpes fur das feld der stationären strömung. *Abh Math Phys Kl Königl Ges*, 32:509–604.