Analysis of optical data by the conjugate Fourier-series approach

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(Received 3 January 1977)

A scheme based on conjugate Fourier series is proposed for the determination of the dissipative mode of an optical constant from the corresponding dispersive mode, and vice versa. The connection between the conjugate Fourier series and Fourier integral method is discussed. The advantages of the method in relation to the Kramers-Kronig approach are outlined.

INTRODUCTION

Until recently, the Kramers-Kronig relations have provided the only means for the inversion of optical data, that is, the extraction of the dispersive behavior from the absorption measurements and vice versa. In view of the enormous number of optical measurements being carried out, for many different properties and on a vast range of materials,[1] there is every reason to search for more effective means by which to achieve the inversion of experimental data in the most satisfactory manner possible.

For the purposes of this paper, we restrict our consideration to the dielectric constant. However, the method may be applied in a similar manner to *any* optical constant which is bounded. The well known Kramers-Kronig relations connecting the real $\epsilon_r(\omega)$, and imaginary $\epsilon_i(\omega)$, parts of the complex dielectric constant are[2]

$$\epsilon_r(\omega)-1=\frac{2}{\pi}\,P\int_0^\infty \frac{\omega'\epsilon_i(\omega')\,d\omega'}{\omega'^2-\omega^2}\;, \tag{1}$$

$$\epsilon_i(\omega)=-\frac{2\omega}{\pi}\,P\int_0^\infty \frac{[\epsilon_r(\omega')-1]\,d\omega'}{\omega'^2-\omega^2}\;. \tag{2}$$

Equation (2) as written applied to nonconductors. For a conducting medium, the right-hand side of Eq. (2) becomes modified by the addition of the term $4\pi\sigma/\omega$ where σ is the conductivity evaluated at $\omega=0$. One immediate observation from Eqs. (1) and (2) is the requirement that $\epsilon_r(\omega)$ or $\epsilon_i(\omega)$ be known over the complete frequency interval $(0,\infty)$, in order to determine the appropriate conjugate function. This infinite range is an indirect result of constructing the derivation on a minimum of assumptions. Finite frequency range Hilbert relations can in principle be obtained, but such relations will be directly dependent on various models for the material under investigation. In such cases, there will be no relation of comparable generality to those of Eqs. (1) and (2). This consideration will apply to all alternative equivalent forms of the Kramers-Kronig relations.

FOURIER TRANSFORM METHOD

In a recent paper, Peterson and Knight[3] propsed an alternative to the Kramers-Kronig approach for the inversion of optical data. Their result is well known in the mathematical theory of conjugate Fourier integrals[4,5] and is often referred to as the allied Fourier integral, which connects the real and imaginary parts of a function holomorphic in the appropriate domain. The Fourier transform relations for the dielectric constant take the form

$$\epsilon_i(\omega)=\frac{2}{\pi}\int_0^\infty dt\,\sin\omega t\int_0^\infty[\epsilon_r(\omega')-1]\cos\omega' t\,d\omega'\;, \tag{3}$$

$$\epsilon_r(\omega)-1=\frac{2}{\pi}\int_0^\infty dt\,\cos\omega t\int_0^\infty \epsilon_i(\omega')\sin\omega' t\,d\omega'\;. \tag{4}$$

Brot[6] has given a brief discussion of this form and its connection with the Kramers-Kronig relations. These results are implicit in the review of Scaife,[7] who has written the real and imaginary parts of the complex susceptibility as the Fourier cosine and Fourier sine transforms of the impulse response, respectively. Scaife also gives the inversion of each of these results, and Eqs. (3) and (4) follow immediately. The Fourier transform results are also implicit in the work of Cole and Cole,[8] in which expressions for the transient current are given in terms of the Fourier cosine and sine transforms of the real and imaginary parts of the dielectric constant. It is a simple matter to invert these relations to find expressions for $\epsilon_i(\omega)$ and $\epsilon_r(\omega)$, thereby obtaining Eqs. (3) and (4). An explicit derivation of Eqs. (3) and (4) appropriate for dielectric loss was given some time ago by Gross.[9] The results were then converted into the usual Kramers-Kronig form, which was considered by Gross at that time to be more suitable for numerical applications. Modern computing procedures have now reversed this situation. For a rigorous account of the equivalence of the Fourier integral approach and the conventional Hilbert transform method, the work of Titchmarsh[4,5] should be consulted.

The integrals appearing in Eqs. (3) and (4) have been written in terms of sine and cosine functions. Noting the symmetry properties of the real and imaginary parts of the dielectric constant

$$\epsilon_r(-\omega)=\epsilon_r(\omega)\;, \tag{5}$$

$$\epsilon_i(-\omega)=-\epsilon_i(\omega)\;, \tag{6}$$

allows Eqs. (3) and (4) to be cast into an alternative form containing exponential frequency factors. Since fairly sophisticated methods for rapid numerical computation of Fourier integrals are available, it is not surprising that Eqs. (3) and (4) should provide a somewhat more economical alternative to the Kramers-Kronig relations Eqs. (1) and (2). This numerical convenience has been fully stressed by Peterson and Knight.

A very direct argument can be presented for obtaining the conjugate relations, Eqs. (3) and (4). Let $f(\omega)$ denote either the real or imaginary part of the generalized dielectric constant $\epsilon(\omega)$; actually it is necessary to choose the function $\epsilon(\omega)-1$, which is square integrable over the

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real frequency axis. Now the Fourier integral formula is

$$f(\omega)=\frac{1}{\pi}\int_0^{\infty} du \int_{-\infty}^{\infty} \cos[u(\omega-t)]f(t)\,dt\ . \tag{7}$$

From the causality condition and Titchmarsh's theorem,[5] it can be readily established by considering the contour integral $\oint e^{i\omega t}[\epsilon(\omega)-1]d\omega$ around a half-circle contour in the upper half-frequency plane, that

$$\int_0^{\infty} [\epsilon_r(\omega)-1]\cos\omega t\,d\omega=\int_0^{\infty} \epsilon_i(\omega)\sin\omega t\,d\omega \quad \text{for } t>0 \tag{8}$$

by Jordan's lemma. Combining Eqs. (7) and (8) with $f(\omega)$ taken as either $\epsilon_i(\omega)$ or $\epsilon_r(\omega)-1$ and noting the symmetry conditions, Eqs. (5) and (6), gives the desired results directly.

CONJUGATE FOURIER SERIES METHOD

The purpose of this paper is to suggest an alternative form to the Kramers-Kronig relations, which is complementary with the Peterson-Knight approach. The method is based on the theory of conjugate functions, but instead of considering integral forms, we choose the Fourier conjugate series as a starting point. The mathematical methods presented are all very well known,[4,10–13] but do not appear to have been previously employed as an approach for the analysis of optical data.

The conjugate Fourier series are defined in the following manner: given the Fourier series

$$\sum_{m=1}^{\infty} (a_m \cos mx + b_m \sin mx)\ ,$$

then the conjugate series is given in the form

$$\sum_{m=1}^{\infty} (b_m \cos mx - a_m \sin mx)\ .$$

It will become clear below how this connection arises.

The fundamental hypothesis required to derive Eqs. (1)–(4) is the causality condition, from which it can be deduced that the complex dielectric constant is an analytic function in the upper half of the complex frequency plane.[14] The first step to obtain a series formulation is to convert the upper half-frequency plane into a more suitable domain. A conformal mapping of the upper half plane into the interior of the unit circle centered at the origin is carried out. This is accomplished by the transformation

$$Z=(\omega-i)/(\omega+i)\ . \tag{9}$$

It is then possible to write

$$\begin{aligned}\epsilon(\omega)-1 \to \epsilon[-i(Z+1)(Z-1)^{-1}]-1 \\ =\sum_{m=0}^{\infty} c_m Z^m\ , \quad |Z|\le 1\end{aligned} \tag{10}$$

and the expansion follows from the fact that $\epsilon(\omega)-1$ is analytic in the interior of the unit circle in the complex Z plane. In the analysis carried out in this paper, we are interested in the dielectric constant defined on the real frequency axis and its extension into the upper half complex ω plane. The real axis in ω space maps into the boundary of the unit circle [using Eq. (9)], and hence the radius of convergence in Eq. (10) includes $|Z|=1$. Writing Eq. (10) in its present form assumes a restriction to insulators. The discussion for metals follows in exactly the same manner, if we first make a subtraction to account for the singularity at $\omega=0$ ($Z=-1$), i.e., in place of $\epsilon(\omega)-1$, it is necessary to employ $\epsilon(\omega)-1-4\pi i\sigma/\omega$.

Introducing the substitution

$$Z=e^{i\theta} \tag{11}$$

leads to the following expansion for Eq. (10):

$$\begin{aligned}\epsilon[-i(Z+1)(Z-1)^{-1}]-1=\sum_{m=0}^{\infty} c_m \cos m\theta \\ +i\sum_{m=1}^{\infty} c_m \sin m\theta\ .\end{aligned} \tag{12}$$

If we define the quantities

$$\epsilon'(\theta)=\epsilon_r(\cot\tfrac{1}{2}\theta)-1\ , \tag{13}$$

$$\epsilon''(\theta)=\epsilon_i(\cot\tfrac{1}{2}\theta)\ , \tag{14}$$

then Eq. (10) becomes

$$\epsilon(\omega)-1 \to \epsilon(-\cot\tfrac{1}{2}\theta)-1=\epsilon'(\theta)-i\epsilon''(\theta) \tag{15}$$

and the symmetry properties, Eqs. (5) and (6), have been employed. Now the functions $\epsilon'(\theta)$ and $\epsilon''(\theta)$ can be expanded in a Fourier series in $(-\pi,\pi)$, which leads to (noting the symmetry properties of ϵ' and ϵ'')

$$\epsilon'(\theta)=\frac{a_0}{2}+\sum_{m=1}^{\infty} a_m \cos m\theta\ , \tag{16}$$

$$\epsilon''(\theta)=\sum_{m=1}^{\infty} b_m \sin m\theta\ . \tag{17}$$

Substituting Eqs. (16) and (17) into (15) leads to

$$\begin{aligned}\epsilon(-\cot\tfrac{1}{2}\theta)-1=\frac{a_0}{2}+\sum_{m=1}^{\infty} a_m \cos m\theta \\ -i\sum_{m=1}^{\infty} b_m \sin m\theta\ .\end{aligned} \tag{18}$$

Comparing Eqs. (18) and (12) leads to

$$a_0=2c_0\ , \quad a_m=c_m\ ; \quad b_m=-c_m\ , \quad m\ne 0\ , \tag{19}$$

and, therefore,

$$a_m=-b_m\ , \quad m\ne 0\ . \tag{20}$$

Hence, the series for $\epsilon'(\theta)$ and $\epsilon''(\theta)$ are

$$\epsilon'(\theta)=\frac{a_0}{2}+\sum_{m=1}^{\infty} a_m \cos m\theta\ , \tag{21}$$

$$\epsilon''(\theta)=-\sum_{m=1}^{\infty} a_m \sin m\theta\ , \tag{22}$$

which can now be recognized as conjugate Fourier series for functions with the appropriate symmetry properties.

The results (21) and (22) can be employed in the following manner. The experimental results for the dispersive mode of the dielectric constant are used to construct $\epsilon'(\theta)$ [Eq. (13)], which is then fitted to a Fourier cosine series, Eq. (21). In practical calculations, the series will be truncated, that is $a_m = 0$ for m greater than some specified m. The dissipative mode ϵ'' is then *determined directly* from the conjugate expression (22), and hence the imaginary part of the dielectric constant follows from Eq. (14), i.e.,

$$\epsilon_i(\cot\tfrac{1}{2}\theta) = -\sum_{m=1}^{\infty} a_m \sin m\theta \ . \tag{23}$$

There is now no need to make any integral transformation to invert the data. The Fourier series coefficients are most conveniently determined by fitting a finite number of data points by the fast Fourier transformation procedure (e.g., the Cooley-Tukey algorithm), which involves summation over a finite number of points.

In order to determine the dispersion mode from the dissipative mode, there is one obvious problem to circumvent. The dissipative spectrum determines all the coefficients a_m except a_0. This is not however a serious problem since there is a simple relation by which a_0 can be determined. Combining Eqs. (13) and (21), and looking at the asymptotic behavior gives

$$\lim_{\omega\to\infty}[\epsilon_r(\omega) - 1] = \lim_{\theta\to 0}[\epsilon_r(\cot\tfrac{1}{2}\theta) - 1] = \frac{a_0}{2} + \sum_{m=1}^{\infty} a_m = 0 \tag{24}$$

and hence,

$$a_0 = -2\sum_{m=1}^{\infty} a_m \ . \tag{25}$$

It has been assumed thus far that $\epsilon_r(\infty) = 1$; if for some particular model it does not, then $\epsilon_r(\omega) - 1$ must be replaced by $\epsilon_r(\omega) - \epsilon_r(\infty)$.

A very simple example will illustrate the method. Consider the dispersion curve for $\epsilon_r(\omega) - 1$ to be given by

$$\epsilon_r(\omega) - 1 = 1/(1+\omega^2) \ ,$$

then

$$\epsilon'(\theta) = \sin^2\tfrac{1}{2}\theta \ .$$

The Fourier series coefficients in Eq. (21) can be determined by inspection; they are

$$a_0 = 1 \ ; \quad a_m = -\tfrac{1}{2}\delta_{m1} \ , \quad m \neq 0 \ .$$

Employing Eq. (22) yields

$$\epsilon''(\theta) = \tfrac{1}{2}\sin\theta$$

and hence,

$$\epsilon_i(\omega) = \omega/(\omega^2 + 1) \ .$$

The above choice for $\epsilon_r(\omega) - 1$ was made for reasons of simplicity only, because it allows an analytic solution for $\epsilon_i(\omega)$ to be found very easily. It is to be noted, however, that the above example does not satisfy a number of fundamental constraints which the true dielectric constant must satisfy [for example, Eq. (30) is not obeyed]. The above results for $\epsilon_r(\omega) - 1$ and $\epsilon_i(\omega)$, which are the Debye equations (with the introduction of the appropriate constant factors) are nevertheless widely discussed.

DISCUSSION

The approach employed in this work is equivalent to the standard Kramers-Kronig relations connecting the conjugate variables, it is only the form of presentation which is different. Equations (21) and (22) are both exact. The three schemes for analysis of optical data which have been mentioned in this paper: the Kramers-Kronig relations, the Fourier integral procedure, and the conjugate Fourier series method represent the three well known (to mathematicians at least) approaches to the theory of Hilbert transforms, which are the underlying basis for the connection between the dissipative and dispersive modes.

The method of derivation employed by Peterson and Knight is by appeal to the connection between the correspondence of a physical output with a physical input. This approach becomes slightly awkward for those functions which cannot, on physical grounds, be expressed in this form. An example of such a function is the generalized refractive index.[14,15] The allied Fourier integral is still perfectly valid for this function, since the derivation of this formula can be carried out from the known analytic properties of the generalized refractive index. A point unspecified by Peterson and Knight in their derivation is the necessity for the functions under consideration to have an appropriate asymptotic behavior. A convenient restriction is to require the functions to be square integrable on $(-\infty, \infty)$. This point has caused some confusion, since some authors[16] have employed the result of Peterson and Knight for $\epsilon_r(\omega)$, rather than $\epsilon_r(\omega) - \epsilon_r(\infty)$. The integrals in terms of $\epsilon_r(\omega)$ alone are not convergent. This can be seen from the asymptotic behavior at large frequencies, which is most conveniently determined from the free-electron gas model, for which

$$\epsilon_r(\omega) - 1 = -\omega_p^2/\omega^2 \quad \text{as} \quad \omega\to\infty \tag{26}$$

and ω_p is the plasma frequency.

Some simple relations can be provided to check the value of the expansion coefficient a_0. For a nonconducting media, the following result can be deduced from Eq. (1):

$$\epsilon_r(0) - 1 = \frac{2}{\pi}\int_0^{\infty} \frac{\epsilon_i(\omega)\, d\omega}{\omega} \ . \tag{27}$$

Employing Eqs. (14) and (21) leads to the expression

$$\frac{a_0}{2} = \frac{2}{\pi}\int_0^{\infty} \frac{\epsilon_i(\omega)}{\omega}\, d\omega - \sum_{m=1}^{\infty}(-1)^m a_m \ , \tag{28}$$

or using the Fourier integral formula, we have

$$\frac{a_0}{2} = \frac{2}{\pi}\int_0^{\infty} dt \int_0^{\infty} \epsilon_i(\omega)\sin\omega t\, d\omega - \sum_{m=1}^{\infty}(-1)^m a_m \ . \tag{29}$$

Conducting media are excluded because of the singularity at $\omega = 0$. A third method for obtaining the coefficient a_0, which is valid for both conductors and nonconductors, is based on a knowledge of the zero(s) of $\epsilon_r(\omega) - 1$. That there must exist one such value of ω for which $\epsilon_r(\omega) - 1 = 0$ may be understood from the following argument.[17] The analytic and asymptotic properties of $\epsilon(\omega) - 1$ are sufficient to establish for nonconductors, the relation

(see, for example, Ref. 7, p. 17)

$$\int_0^\infty [\epsilon_r(\omega) - 1]\, d\omega = 0 \,, \tag{30}$$

from which it is apparent that the function $\epsilon_r(\omega) - 1$ cannot be everywhere positive, i.e., there must exist at least one frequency which we shall denote as ω_0, for which $\epsilon_r(\omega_0) - 1 = 0$. For conductors, the right-hand side of Eq. (30) is modified by the addition of the term $-2\pi^2\sigma$.[18] The argument used for nonconductors therefore does not carry over to conductors. For those conductors for which an ω_0 can be determined (experimentally or otherwise), we then have the following result valid for both conductors and nonconductors

$$\frac{a_0}{2} = -\sum_{m=1}^{\infty} a_m \cos m\theta_0 \,, \tag{31}$$

where the angle θ_0 is given by

$$\theta_0 = -2\cot^{-1}\omega_0 \,. \tag{32}$$

Equations (28), (29), and (31) can all be used to check the result determined by the simple relationship, Eq. (25).

A recent paper by Johnson[19] appeared while this work was in progress, discussing a series approach to the Kramers-Kronig relations, which is complementary to the present work. The approach taken by Johnson is to expand $\epsilon_r(\omega) - 1$ and $\epsilon_i(\omega)$, which are assumed to be band limited to the interval $-\omega_1 < \omega < \omega_1$, in the following series:

$$\epsilon_r(\omega) - 1 = \sum_{k=-\infty}^{\infty} p_k \exp\left(\frac{ik\pi\omega}{\omega_1}\right) \,, \tag{33}$$

$$\epsilon_i(\omega) = -i \sum_{k=-\infty}^{\infty} q_k \exp\left(\frac{ik\pi\omega}{\omega_1}\right) \,. \tag{34}$$

The symmetry conditions on the coefficients p_k and q_k, and the connection between p_k and q_k $[p_k = \mathrm{sgn}(k) q_k]$ being determined indirectly from the Fourier transforms over the finite range $-\omega_1 < \omega < \omega_1$. The approach taken in this work of carrying out a conformal mapping to obtain a suitable range, seems to be a somewhat more useful procedure, since it has not been necessary to introduce the assumption that the optical property is band limited over a finite interval. The method employed in this work is exact, irrespective of whether the function is band limited over a finite interval or not, provided the optical property has an appropriate asymptotic behavior. The asymptotic requirement is not a serious limitation, since it is frequently possible to substract a constant or introduce a weighting factor such as $(\omega^2 + \omega_\alpha^2)^{-1}$ to ensure the appropriate asymptotic behavior.

In order to implement the Fourier integral or Kramers-Kronig approaches, part of the energy spectrum must be fitted to some assumed analytic form, in order to extrapolate to both the high and low energy regions. A frequently employed procedure is to fit data to various models, e.g., Drude, and then carry out the Kramers-Kronig analysis. With the series approach, a single data fit to a Fourier series is sufficient, since the coefficients of one Fourier series determine the coefficients of the conjugate series.

Experimental profiles for optical data are always band limited, so suitably trucated series expansions will provide a suitable basis for data analysis. The main features of the conjugate series method are its simplicity and its avoidance of principal value integrals. Computation speed should prove to be an added feature.

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