Dispersion relations and sum rules for the normal reflectance of conductors and insulators

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A systematic derivation of sum rules satisfied by the normal reflectivity and phase of conductors and insulators is presented. The derivation of the dispersion relations for the generalized reflectivity is investigated, and some special features of these relationships are noted. The reflectivity at complex frequencies is examined, and this leads to a simple sum rule for testing theoretical models of reflectance data.

I. INTRODUCTION

Recently, there has been increasing interest in the derivation of rigorous sum rules for the optical properties of a general medium.[1–12] The motivation for much of this work has undoubtedly been the rapid growth in the determination of the optical properties of an extensive range of materials.[13] In the past, optical data measurements for most materials were subject to two major limitations. The most important being the effect of sample impurity on the measured optical constants. Surface impurities and the formation of oxidation products on clean surfaces have resulted in conflicting optical data from different laboratories for many materials. The second limitation is that the optical constant measurements were frequently limited to a narrow spectral range. The situation is now changing; for many materials, there are accurate optical constant measurements over wide spectral ranges on high purity samples.

The ideal role of theory is clearly the *a priori* calculation of the dispersion curve for any optical property. Unfortunately, this is not possible at the present time. However, theory can provide a useful guide as to the quality of measured optical data. The quantities of inestimable value for quality analysis of optical data are the finite moments of the optical property of interest. Some relations of this kind are known, but for the most part these results are not of great utility. The reason for this is simply that all such finite moment results are based on particular approximations for specific materials, and hence they have no generality. Frequently, the validity of the approximations are difficult to determine. The most general moment formulae and sum rules will involve the spectral range $(0, \infty)$.[12] It is also important to recognize that if general sum rules applicable to a wide range of materials are to be obtained, then very general assumptions on the nature of the medium must be employed.[5,14,15]

The optical constant that is the subject of this work is the normal reflectance. This is one of the most important optical properties, and it is also one that is easily accessible over a wide spectral range. Determination of the generalized (complex) reflectivity provides a route to other important optical properties such as the refractive index, dielectric constant, energy loss function, etc. Although a great deal of discussion of the dispersion relations for the reflectance has been published,[16–42] there has been very little attention directed at obtaining sum rules for this important optical property.[10] This situation can be attributed to the following two facts: The first is that the real and imaginary parts of the generalized reflectance depend upon *both* the phase $\theta(\omega)$ and the reflectivity $R(\omega)$. The generalized reflectivity $\tilde{r}(\omega)$ is defined as

$$\tilde{r}(\omega) = r(\omega)\, e^{i\theta(\omega)}\,, \tag{1}$$

where

$$r(\omega) = R(\omega)^{1/2}\,. \tag{2}$$

The nonseparable behavior for $\tilde{r}(\omega)$ contrasts the situation for most other generalized optical constants, for which the real and imaginary parts may be identified with the dispersive and dissipative modes, respectively. The obvious procedure by which the real and imaginary parts may be identified with $R(\omega)$ and $\theta(\omega)$ is to take the logarithm of Eq. (1). Thus, the appropriate function to consider is

$$\ln\tilde{r}(\omega) = \ln r(\omega) + i\theta(\omega)\,. \tag{3}$$

Equation (3) provides the necessary separability, but introduces a second complication. The problems that arise using the function $\ln\tilde{r}(\omega)$ are difficulties associated with the asymptotic behavior, and the more subtle question concerning the existence of zeros of $\tilde{r}(\omega)$ for complex frequencies. The asymptotic behavior of the reflectivity coefficient assuming the medium responds like a free electron gas is

$$R(\omega) = O(\omega^{-4})\,, \quad \omega \to \infty\,, \tag{4}$$

and hence $\ln R(\omega)$ displays a logarithm divergence as $\omega \to \infty$. This fact eliminates a number of simple and useful sum rules that could be obtained by analogy with other optical properties. The asymptotic problem also prevents application of the superconvergence technique[2] to the standard form of the dispersion relations for the reflectance. The above comments apply for incident light which is plane polarized. For the case of magnetoreflection, the asymptotic constraints are not as severe, and as a result, some useful sum rules have recently been derived for this quantity.[10,11,43]

II. DISPERSION RELATIONS

The dispersion relations (also known widely as the Kramers-Kronig relations) for the reflectance and phase have been discussed at length in the literature. They take the form[16–19]

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$$\theta(\omega')=\frac{-\omega' P}{\pi}\int_0^\infty \frac{\ln R(\omega)\,d\omega}{\omega^2-\omega'^2}, \tag{5}$$

$$\ln R(\omega')-\ln R(\omega'')=\frac{4P}{\pi}\int_0^\infty \omega\theta(\omega)\left(\frac{1}{\omega^2-\omega'^2}-\frac{1}{\omega^2-\omega''^2}\right)d\omega. \tag{6}$$

In Eqs. (5) and (6), P denotes the principal value of the integral. These relations are derived using the basic assumptions of the causal nature of the medium and the resulting analytical behavior of $\ln\tilde{r}(\omega)$ at complex frequencies. Application of the Cauchy integral theorem to the functions

$$\frac{\ln\tilde{r}(\omega)}{\omega-\omega'}$$

and

$$\frac{\ln\tilde{r}(\omega')-\ln\tilde{r}(\omega'')}{\omega'-\omega''}$$

leads to Eqs. (5) and (6).

An important feature of the derivation of these two dispersion relations seems to have passed unnoticed. Equations (5) and (6) are obviously not conjugate relations in the sense of Hilbert transform theory.[44] The dispersion relations for most other optical properties are skew reciprocal when written as integrals over the domain $(-\infty,\infty)$, i.e., if

$$f(\omega)=\frac{P}{\pi}\int_{-\infty}^\infty \frac{g(\omega')\,d\omega'}{\omega'-\omega} \tag{7}$$

is one of the dispersion relations, then the replacement $f(\omega)\to g(\omega)$, $g(\omega)\to -f(\omega)$ generates the other

$$g(\omega)=-\frac{P}{\pi}\int_{-\infty}^\infty \frac{f(\omega')\,d\omega'}{\omega'-\omega}. \tag{8}$$

Here, $f(\omega)$ and $g(\omega)$ denote the real and imaginary parts of an analytic function with appropriate asymptotic behavior, respectively. This is of course a well known result for Hilbert transform pairs.[44]

Although Eqs. (5) and (6) are both correct, they have been derived from separate analytic functions.[19] Smith[40] has recently given a clear and concise derivation of Eqs. (5) and (6) from a single analytic function. It is possible to provide a straightforward derivation of dispersion relations for the reflectance and phase which exhibit the skew reciprocal behavior of Eqs. (7) and (8). We choose the following function:

$$F(\omega)=\frac{\ln\tilde{r}(\omega)}{\omega+i\omega'} \tag{9}$$

and consider two cases: (i) ω' is real and >0, and (ii) ω' is imaginary ($\omega'=i\omega''$, $\omega''>0$). For convenience, we shall denote real and complex frequencies by ω and Ω, respectively. The function $\tilde{r}(\Omega)$ is analytic in the upper half complex frequency plane and has no zeros there.[19] The function $F(\omega)$ is bounded in $[0,\infty)$ and the pole at ω' is located in the lower half plane for case (i) and on the real frequency axis for case (ii). We now consider the contour integral

$$\oint_\Gamma \frac{F(\Omega)\,d\Omega}{\Omega-\omega_0},$$

where $\omega_0>0$. For case (i), the contour Γ includes the real axis indented into the upper half-plane at the frequency ω_0, and a semicircular arc in the upper half-plane (whose radius is allowed to $\to\infty$). Evaluation of the contour integral leads to

$$\frac{\omega'\ln r(\omega_0)-\omega_0\theta(\omega_0)}{\omega_0^2+\omega'^2}=\frac{P}{\pi}\int_{-\infty}^\infty \frac{[\omega\ln r(\omega)+\omega'\theta(\omega)]\,d\omega}{(\omega^2+\omega'^2)(\omega-\omega_0)}, \tag{10}$$

$$\frac{\omega_0\ln r(\omega_0)+\omega'\theta(\omega_0)}{\omega_0^2+\omega'^2}=-\frac{P}{\pi}\int_{-\infty}^\infty \frac{[\omega'\ln r(\omega)-\omega\theta(\omega)]\,d\omega}{(\omega^2+\omega'^2)(\omega-\omega_0)}. \tag{11}$$

Written in this form, it is apparent that these dispersion relations are skew reciprocal. The functions $f(\omega)$ and $g(\omega)$ can be identified by comparison of Eqs. (7) and (8) with (10) and (11), and these are, of course, just the real and imaginary parts of $F(\omega)$, respectively. If the crossing conditions for plane polarized light

$$r(-\omega)=r(\omega), \tag{12}$$

$$\theta(-\omega)=-\theta(\omega) \tag{13}$$

are employed, Eqs. (10) and (11) simplify to

$$\frac{\omega'\ln r(\omega_0)-\omega_0\theta(\omega_0)}{\omega_0^2+\omega'^2}=\frac{2P}{\pi}\int_0^\infty \frac{[\omega^2\ln r(\omega)+\omega'\omega\theta(\omega)]\,d\omega}{(\omega^2+\omega'^2)(\omega^2-\omega_0^2)}, \tag{14}$$

$$\frac{\omega_0\ln r(\omega_0)+\omega'\theta(\omega_0)}{\omega_0^2+\omega'^2}=\frac{-2\omega_0P}{\pi}\int_0^\infty \frac{[\omega'\ln r(\omega)-\omega\theta(\omega)]\,d\omega}{(\omega^2+\omega'^2)(\omega^2-\omega_0^2)}, \tag{15}$$

respectively. The most interesting feature of the skew reciprocal dispersion relations is that the real and imaginary parts of $\ln\tilde{r}(\omega)$ are nonseparable.

For case (ii), the contour Γ is the same for case (i), except that the singularity at ω'' is bypassed with a semicircular arc whose radius $\to 0$. Evaluation of the contour integral for case (ii) gives

$$\theta(\omega_0)-\theta(\omega'')=2(\omega''-\omega_0)\frac{P}{\pi}\int_0^\infty \frac{\ln r(\omega)(\omega^2+\omega''\omega_0)\,d\omega}{(\omega^2-\omega''^2)(\omega^2-\omega_0^2)}, \tag{16}$$

$$\ln r(\omega_0)-\ln r(\omega'')=2(\omega_0^2-\omega''^2)\frac{P}{\pi}\int_0^\infty \frac{\omega\theta(\omega)\,d\omega}{(\omega^2-\omega_0^2)(\omega^2-\omega''^2)}. \tag{17}$$

Equations (16) and (17) represent *subtracted* dispersion relations for the phase and reflectivity. The advantage of this form is the faster convergence of the integrals. However, this is offset by the requirement that the function to be evaluated must be known *a priori* at one particular frequency in advance. The convergence properties can be further improved, but this is at the expense of knowing the function *a priori* at a number of different frequencies (equal to the number of subtractions). For this reason, the subtracted dispersion relations are usually less useful than the unsubtracted dispersion relations. The unsubtracted dispersion relation for the phase [Eq. (1)] can be obtained either by solving Eqs. (14) and (15) for $\theta(\omega_0)$, or by examining the limit $\omega'\to 0$ in Eq. (14) or $\omega''\to 0$ in Eq. (16).

To derive the skew symmetric dispersion relations, we have employed a very simple modification of the function $\ln\tilde{r}(\omega)$ [see Eq. (9)]. This form is taken so that the logarithmic divergence as $\omega\to\infty$ is avoided. Also,

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the domain for which $F(\Omega)$ is analytic, the entire upper half-plane, is unchanged with respect to $\ln\tilde{r}(\Omega)$, except for an additional pole on the real axis when ω' is complex [case (ii)]. The skew symmetric dispersion relations are mainly of academic interest, since neither Eq. (14) or (15) provides a means to determine the phase from the reflectivity, or *vice versa*. There is, however, one important point that emerges from the above derivation. An unsubtracted dispersion relation for the reflectivity in terms of the phase does not exist, i.e., the reflectivity is *not* determined from a knowledge of the phase alone. To obtain an unsubtracted dispersion relation for the reflectivity, the logarithm of the generalized reflectance must be multiplied by a weight function which satisfies the following two conditions: (i) the integral of the weight function multiplied by $\ln\tilde{r}(\omega)$ must converge for the integration domain $(-\infty, \infty)$; (ii) the weight function must not introduce any poles on the real axis or in the *entire* complex frequency plane. It is not difficult to see that conditions (i) and (ii) are mutually exclusive. This may be best understood by the following mathematically nonrigorous argument. Weight functions can be divided into two basic groups. In the first class, the weight function contains a denominator factor which might be constructed from a polynomial in the frequency (more complex functions can of course be present in the denominator of the weight function, but this does not alter the argument). Such denominator factors can always be constructed such that the integral of $\ln\tilde{r}(\omega)$ times the weight function is convergent. However, condition (ii) cannot be satisfied, for the polynomial in the denominator must have roots that lie somewhere in the *entire* complex plane. Any zero in the denominator of the weight function (at either real or imaginary frequency) leads directly to a subtracted dispersion relation for the reflectance at *real* frequencies. It is possible, however, to construct, with appropriately chosen weight functions, unsubtracted dispersion relations for the reflectivity evaluated at imaginary frequencies. The second class of possible weight functions are those that have no poles in the entire complex plane; thus, condition (ii) is satisfied. It is a simple matter to construct a suitable weight function satisfying condition (ii) and also satisfy condition (i) on a restricted domain of the complex frequency plane. For example, a Gaussian function of frequency would be appropriate on the real frequency axis, but *not* in all parts of the complex plane. The contour integral must be convergent for all ω in the upper half-plane. It is therefore suggested that all weight functions which have no poles do not satisfy the convergence condition, and that all weight functions that satisfy the convergence constraint have poles somewhere in the entire complex plane.

III. DIRECT TREATMENT OF THE GENERALIZED REFLECTANCE

The majority of sum rules now known to be satisfied by various optical properties involve not a single optical constant, but a combination of the dispersive and dissipative modes of any given generalized optical property. The sum rules that are most useful for practical data analysis are those that depend on only one optical property. However, those sum rules that depend on *both* the dispersive and dissipative modes still have utility for providing additional checks on experimental data. For those optical constants for which no single mode sum rules can be derived, the latter category provide the only means to check experimental data.

There are two basic ways by which to overcome the divergent asymptotic behavior of $\ln\tilde{r}(\omega)$. The first approach involves discussion of $\tilde{r}(\omega)$ directly, instead of $\ln\tilde{r}(\omega)$, and that is the subject of this section. The next method entails the introduction of a weighting factor, which removes the asymptotic divergence of $\ln R(\omega)$ as $\omega\to\infty$.

Direct treatment of the complex reflectance $\tilde{r}(\omega)$ does not yield dispersion relations for the practical computation of the phase from the measured reflectivity. It can however lead to some simple sum rules involving both $\theta(\omega)$ and $r(\omega)$. If we consider the integral

$$I(\omega_0)=\oint_\Gamma \frac{\tilde{r}(\Omega)\,d\Omega}{\Omega-\omega_0}\ , \tag{18}$$

where the contour Γ includes the real axis, indented into the upper half-plane at the real positive frequency ω_0, and completed by a semicircular arc whose radius is allowed to become infinite. Evaluation of the integral yields the following dispersion relations:

$$r(\omega_0)\cos\theta(\omega_0)=\frac{2P}{\pi}\int_0^\infty \frac{\omega r(\omega)\sin\theta(\omega)\,d\omega}{\omega^2-\omega_0^2}\ , \tag{19}$$

$$r(\omega_0)\sin\theta(\omega_0)=\frac{-2\omega_0 P}{\pi}\int_0^\infty \frac{r(\omega)\cos\theta(\omega)\,d\omega}{\omega^2-\omega_0^2}\ . \tag{20}$$

From Eq. (20), we have

$$\int_0^\infty \frac{r(\omega_0)\sin\theta(\omega_0)\,d\omega_0}{\omega_0}=\frac{-2}{\pi}\int_0^\infty d\omega_0 P\int_0^\infty \frac{r(\omega)\cos\theta(\omega)\,d\omega}{\omega^2-\omega_0^2}$$
$$=\frac{-2}{\pi}\int_0^\infty d\omega\, r(\omega)\cos\theta(\omega) P\int_0^\infty \frac{d\omega_0}{\omega^2-\omega_0^2}\ . \tag{21}$$

On noting the relation

$$P\int_0^\infty \frac{d\omega'}{\omega^2-\omega'^2}=\frac{-\pi^2}{4}\,\delta(\omega)\ , \tag{22}$$

Eq. (21) simplifies to

$$\int_0^\infty \frac{r(\omega)\sin\theta(\omega)\,d\omega}{\omega_0}=\frac{\pi}{2}\int_0^\infty r(\omega)\cos\theta(\omega)\,\delta(\omega)\,d\omega$$
$$=\tfrac{1}{2}\pi r(0)\cos\theta(0)\ . \tag{23}$$

The integral on the right hand side of Eq. (23) converges for both conductors as well as insulators, since, for conductors, $\omega^{-1}r(\omega)\sin\theta(\omega)\sim\omega^{-1/2}$ as $\omega\to 0$. Recalling the fact that

$$\theta(0)=0 \tag{24}$$

for both conductors and insulators leads to the following result:

$$\int_0^\infty \omega^{-1}R(\omega)^{1/2}\sin\theta(\omega)\,d\omega=\tfrac{1}{2}\pi R(0)^{1/2}\ . \tag{25}$$

For insulators, the quantity $R(0)$ must be determined

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experimentally, whereas for metals, $R(0)=1$. From Eq. (19), we have in a similar manner

$$\int_0^\infty r(\omega)\cos\theta(\omega)\,d\omega=\frac{2}{\pi}\int_0^\infty d\omega'\int_0^\infty \frac{\omega r(\omega)\sin\theta(\omega)\,d\omega}{\omega^2-\omega'^2}$$

$$=\frac{2}{\pi}\int_0^\infty \omega r(\omega)\sin\theta(\omega)\,d\omega P\int_0^\infty \frac{d\omega'}{\omega^2-\omega'^2}$$

$$=-\tfrac{1}{2}\pi\int_0^\infty r(\omega)\sin\theta(\omega)\omega\delta(\omega)\,d\omega\ ,$$

and hence

$$\int_0^\infty R(\omega)^{1/2}\cos\theta(\omega)\,d\omega=0\,. \tag{26}$$

If we now consider the square of Eq. (19), and then multiply both sides by ω^2, we obtain

$$\int_0^\infty \omega^2[r(\omega)\cos\theta(\omega)]^2\,d\omega=\frac{4}{\pi^2}\int_0^\infty \omega^2\,d\omega P\int_0^\infty \frac{\omega' r(\omega')\sin\theta(\omega')\,d\omega'}{\omega'^2-\omega^2}\,P\int_0^\infty \frac{\omega'' r(\omega'')\sin\theta(\omega'')\,d\omega''}{\omega''^2-\omega^2}$$

$$=\frac{4}{\pi^2}\int_0^\infty \omega' r(\omega')\sin\theta(\omega')\,d\omega'\int_0^\infty \omega'' r(\omega'')\sin\theta(\omega'')\,d\omega'' P\int_0^\infty \frac{\omega^2\,d\omega}{(\omega^2-\omega'^2)(\omega^2-\omega''^2)}\,. \tag{27}$$

Noting the relation

$$P\int_0^\infty \frac{\omega^2\,d\omega}{(\omega^2-\omega'^2)(\omega^2-\omega''^2)}=\tfrac{1}{4}\pi^2[\delta(\omega'-\omega'')+\delta(\omega'+\omega'')] \tag{28}$$

allows Eq. (27) to be simplified to

$$\int_0^\infty [\omega r(\omega)\cos\theta(\omega)]^2\,d\omega=\int_0^\infty \omega' r(\omega')\sin\theta(\omega')\,d\omega'\int_0^\infty \omega'' r(\omega'')\sin\theta(\omega'')[\delta(\omega'+\omega'')+\delta(\omega'-\omega'')]\,d\omega''$$

$$=\int_0^\infty [\omega r(\omega)\sin\theta(\omega)]^2\,d\omega\ , \tag{29}$$

and hence

$$\int_0^\infty \omega^2 R(\omega)\cos 2\theta(\omega)\,d\omega=0\,. \tag{30}$$

From Eq. (20), we obtain in a similar manner

$$\int_0^\infty r(\omega)^2\sin^2\theta(\omega)\,d\omega=\int_0^\infty r(\omega)^2\cos^2\theta(\omega)\,d\omega\,, \tag{31}$$

which can be written more compactly as

$$\int_0^\infty R(\omega)\cos 2\theta(\omega)\,d\omega=0\,. \tag{32}$$

Equation (31) also follows directly from Eqs. (19) and (20), using a well known theorem in Hilbert transform theory.[44] The same procedure just discussed may be applied to the product of Eqs. (19) and (20); the final result is

$$\int_0^\infty \omega R(\omega)\sin 2\theta(\omega)\,d\omega=0\,. \tag{33}$$

Many important sum rule constraints have been derived by examining the asymptotic expansion of the kernel of the dispersion relations.[2,5,9,45] The basic requirement is that the numerator of Eq. (7) approach zero as $\omega\to\infty$ faster than ω^{-1}. We can exploit the asymptotic expansion technique for the direct treatment of the complex reflectance. The functions $r(\omega)$ and $\theta(\omega)$ satisfy the following asymptotic conditions:

$$r(\omega)=\frac{1}{4}\frac{\omega_p^2}{\omega^2}\,,\qquad \omega\to\infty\,, \tag{34}$$

$$\theta(\omega)=\pi\,,\qquad \omega\to\infty\,, \tag{35}$$

where ω_p is the plasma frequency. Using Eqs. (34) and (35), the left hand side of Eq. (19) satisfies

$$\lim_{\omega_0\to\infty} r(\omega_0)\cos\theta(\omega_0)\to-\frac{1}{4}\frac{\omega_p^2}{\omega_0^2}\,, \tag{36}$$

and the right side yields

$$\lim_{\omega_0\to\infty}\frac{2P}{\pi}\int_0^\infty \frac{\omega r(\omega)\sin\theta(\omega)\,d\omega}{\omega^2-\omega_0^2}$$

$$=\frac{-2}{\pi\omega_0^2}\int_0^\infty \omega r(\omega)\sin\theta(\omega)\,d\omega+O(\omega_0^{-2-\alpha})\ , \tag{37}$$

where $\alpha>0$. Comparison of Eqs. (36) and (37) leads to the sum rule

$$\int_0^\infty \omega R(\omega)^{1/2}\sin\theta(\omega)\,d\omega=\tfrac{1}{8}\pi\omega_p^2\,. \tag{38}$$

The asymptotic expansion method may also be applied to Eq. (20). From the definition of the generalized reflectivity in terms of the complex refractive index $N(\omega)$, i.e.,

$$\tilde{r}(\omega)=\frac{N(\omega)-1}{N(\omega)+1}$$

$$=\frac{n(\omega)+i\kappa(\omega)-1}{n(\omega)+i\kappa(\omega)+1}\,, \tag{39}$$

we have that

$$\lim_{\omega\to\infty} r(\omega)\sin\theta(\omega)=2\lim_{\omega\to\infty}\kappa(\omega) \tag{40}$$

and hence

$$r(\omega_0)\sin\theta(\omega_0)=o(\omega_0^{-2})\ ,\qquad \omega_0\to\infty\,. \tag{41}$$

The right hand side of Eq. (20) yields

$$\lim_{\omega_0\to\infty}\frac{-2\omega_0 P}{\pi}\int_0^\infty \frac{r(\omega)\cos\theta(\omega)\,d\omega}{\omega^2-\omega_0^2}$$

$$\to\frac{2}{\pi\omega_0}\int_0^\infty r(\omega)\cos\theta(\omega)\,d\omega+O(\omega_0^{-2})\,. \tag{42}$$

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Comparison of the asymptotic expansions given by Eqs. (41) and (42) yields

$$\int_0^\infty R(\omega)^{1/2}\cos\theta(\omega)\,d\omega=0\,, \qquad (43)$$

which is in agreement with the result obtained by direct integration of Eq. (20). Although a number of additional sum rules involving $R(\omega)$ and $\theta(\omega)$ can be obtained by the direct treatment of the reflectivity, the simplest results have been derived in this section.

IV. WEIGHTING FACTOR APPROACH

To the author's knowledge, the general mathematical problem of identifying weight functions for which the Hilbert transform is bounded has not yet been solved, although recent progress on this problem has been made.[46] A general solution to this problem would be of considerable interest, as it would provide a route to sum rule equalities and inequalitites that are likely to be very useful, especially for damping the high frequency spectral region. An example of this approach has been given by the author for the refractive index.[6]

The generalized reflectivity possesses an asymptotic behavior that is sufficiently suitable that no weighting factors are required in the contour integral in Eq. (18), other than the standard factor $(\omega-\omega_0)^{-1}$. There is, however, one advantage in introducing weight factors, even though they may not be essential (for reasons of convergence) for the function of interest, e.g., $\tilde{r}(\omega)$. The convergence properties of sum rules may be greatly enhanced by the appropriate choice of weight factors. The drawback to this procedure is that the dispersion relations become increasingly complicated as convergence properties are improved. The simplest example of this procedure can be illustrated by a slight modification of Eq. (18). If we take $\tilde{r}(\omega)(\omega+i\omega')^{-1}$ (where $\omega'>0$) in place of $\tilde{r}(\omega)$, and employ the same contour Γ, the resulting dispersion relations are

$$r(\omega_0)[\omega_0\cos\theta(\omega_0)+\omega'\sin\theta(\omega_0)] = 2\omega_0(\omega_0^2+\omega'^2)\frac{P}{\pi}\int_0^\infty \frac{r(\omega)[\omega\sin\theta(\omega)-\omega'\cos\theta(\omega)]d\omega}{(\omega^2+\omega'^2)(\omega^2-\omega_0^2)}\,, \qquad (44)$$

$$r(\omega_0)[\omega'\cos\theta(\omega_0)-\omega_0\sin\theta(\omega_0)] = 2(\omega_0^2+\omega'^2)\frac{P}{\pi}\int_0^\infty \frac{r(\omega)[\omega\cos\theta(\omega)+\omega'\sin\theta(\omega)]\omega\,d\omega}{(\omega^2+\omega'^2)(\omega^2-\omega_0^2)}\,. \qquad (45)$$

On following the procedure set out at the start of Sec. III, we obtain from Eq. (45)

$$\int_0^\infty \frac{R(\omega)^{1/2}[\omega'\cos\theta(\omega)-\omega\sin\theta(\omega)]d\omega}{(\omega^2+\omega'^2)}=0\,, \qquad (46)$$

and from Eq. (44)

$$\int_0^\infty \frac{R(\omega)^{1/2}[\cos\theta(\omega)+(\omega'/\omega)\sin\theta(\omega)]d\omega}{(\omega^2+\omega'^2)}=\frac{1}{2}\,\frac{\pi}{\omega'}\,R(0)^{1/2}. \qquad (47)$$

Equations (46) and (47) have enhanced convergence properties relative to the simple sum rules (26) and (25), and the computational advantage becomes evident when the experimental results at high energies are either of poor quality or nonexistent. Equation (25) can be derived from Eqs. (46) and (47) by elimination of the cosine contribution.

When the particular function under consideration does not display a suitable asymptotic behavior as $\omega\to\infty$, the weighting factor approach is the only method to obtain sum rules and dispersion relations. This is the situation for the function $\ln\tilde{r}(\omega)$. The methods discussed in Sec. III cannot be applied to the simplest dispersion relations for $\ln R(\omega)$ and $\theta(\omega)$ [Eqs. (5) and (6), respectively] because of the unfavorable asymptotic properties of these functions as $\omega\to\infty$. The introduction of a simple weight factor as has been done to obtain the dispersion relations Eqs. (14) and (15) is also insufficient. Sum rules cannot be obtained by direct integration of Eqs. (14) and (15) because the resulting integrals are divergent. In order to obtain sum rules for $\ln r(\omega)$ and $\theta(\omega)$, more involved weighting factors are necessary. The introduction of simple weighting factors couples the two functions $\ln r(\omega)$ and $\theta(\omega)$, so the resulting sum rules will depend upon both of these quantities. If we multiply $\ln\tilde{r}(\omega)$ by the simple weight factor $(\omega+i\omega_a)(\omega+i\omega_b)^{-1}$, with $\omega_a>0$ $\omega_b>0$, and consider the integral

$$I=\oint \frac{\ln\tilde{r}(\Omega)\,d\Omega}{(\Omega+i\omega_a)(\Omega+i\omega_b)(\Omega-\omega_0)}\,, \qquad (48)$$

we obtain the dispersion relations

$$\pi[\omega_0(\omega_a+\omega_b)\ln r(\omega_0)+(\omega_a\omega_b-\omega_0^2)\theta(\omega_0)]=2\omega_0(\omega_0^2+\omega_a^2)(\omega_0^2+\omega_b^2)P\int_0^\infty \frac{[(\omega^2-\omega_a\omega_b)\ln r(\omega)+(\omega_a+\omega_b)\omega\theta(\omega)]d\omega}{(\omega^2+\omega_a^2)(\omega^2+\omega_b^2)(\omega^2-\omega_0^2)}\,, \qquad (49)$$

$$\pi[(\omega_0^2-\omega_a\omega_b)\ln r(\omega_0)+\omega_0(\omega_a+\omega_b)\theta(\omega_0)]=2(\omega_0^2+\omega_a^2)(\omega_0^2+\omega_b^2)P\int_0^\infty \frac{\omega[(\omega^2-\omega_a\omega_b)\theta(\omega)-\omega(\omega_a+\omega_b)\ln r(\omega)]d\omega}{(\omega^2+\omega_a^2)(\omega^2+\omega_b^2)(\omega^2-\omega_0^2)}\,. \qquad (50)$$

If we restrict to the case $\omega_a=\omega_b$, then the methods of Sec. III applied to Eq. (50) yields

$$\int_0^\infty \frac{(\omega^2-\omega_a^2)\ln R(\omega)\,d\omega}{(\omega^2+\omega_a^2)^2}=4\omega_a\int_0^\infty \frac{\omega\theta(\omega)\,d\omega}{(\omega^2+\omega_a^2)^2}\,, \qquad (51)$$

and from Eq. (49) for $\omega_a=\omega_b$,

$$\int_0^\infty \frac{[\omega_a\omega\ln R(\omega)+(\omega_a^2-\omega^2)\theta(\omega)]d\omega}{\omega(\omega^2+\omega_a^2)^2}=\frac{1}{4}\,\frac{\pi}{\omega_a^2}\ln R(0)\,. \qquad (52)$$

It should be apparent from this section that deriving sum rules for the function $\ln\tilde{r}(\omega)$ in place of $\tilde{r}(\omega)$ leads to additional complexity. The original motivation for examining $\ln\tilde{r}(\omega)$ was to obtain dispersion relations that were separable functions of $\ln r(\omega)$ and $\theta(\omega)$. To obtain sum rules using the function $\ln\tilde{r}(\omega)$, weight factors must be introduced, and such factors lead to nonseparable dispersion relations. For the purposes of deriving

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sum rules, it is therefore simpler to examine $\tilde{r}(\omega)$ directly rather than $\ln\tilde{r}(\omega)$.

V. REFLECTIVITY AT COMPLEX FREQUENCIES

The crossing relation for complex frequencies is

$$r(\Omega)^* = r(-\Omega^*) . \tag{53}$$

From this relation, it follows that the phase is zero at imaginary frequencies, i.e., for ω real,

$$\theta(i\omega) = 0 . \tag{54}$$

The simplest approach to obtain sum rules is to consider the function $\tilde{r}(\omega)$ directly, and choose an appropriate contour. We now consider the contour integral

$$I = \oint_\Gamma \tilde{r}(\Omega)\, d\Omega , \tag{55}$$

where the contour Γ includes the real axis $[0, \gamma]$, the imaginary axis $[0, \gamma]$, and a circular arc, radius γ, which is allowed to $\to \infty$. Since there are no poles in the first quadrant, we obtain very simply

$$\int_0^\infty R(\omega)^{1/2} \cos\theta(\omega)\, d\omega = 0 , \tag{56}$$

$$\int_0^\infty R(\omega)^{1/2} \sin\theta(\omega)\, d\omega = \int_0^\infty R(i\omega)^{1/2}\, d\omega . \tag{57}$$

If we employ $\tilde{r}(\omega)^2$ in place of $\tilde{r}(\omega)$, then we obtain

$$\int_0^\infty R(\omega) \cos 2\theta(\omega)\, d\omega = 0 , \tag{58}$$

$$\int_0^\infty R(\omega) \sin 2\theta(\omega)\, d\omega = \int_0^\infty R(i\omega)\, d\omega . \tag{59}$$

To obtain Eqs. (56)–(59), we have made use of Eq. (54). Equations (56) and (58) have been derived in a slightly more complicated manner in Sec. III.

If we consider the following contour integral:

$$I(\omega_0) = \oint_\Gamma \frac{\ln\tilde{r}(\Omega)\, d\Omega}{\Omega^2 + \omega_0^2} , \tag{60}$$

where $\omega_0 > 0$, and the contour Γ includes the real axis and a semicircular arc in the upper half plane whose radius $\to \infty$. Since only a single pole is enclosed, we obtain the following connection for the reflectivity at complex frequencies with that at real frequencies:

$$\ln R(i\omega_0) = \frac{2\omega_0}{\pi} \int_0^\infty \frac{\ln R(\omega)\, d\omega}{(\omega^2 + \omega_0^2)} . \tag{61}$$

If $\ln\tilde{r}(\Omega)$ is replaced by $\tilde{r}(\Omega)^2$, then the alternative form

$$R(i\omega_0) = \frac{2\omega_0}{\pi} \int_0^\infty \frac{R(\omega) \cos 2\theta(\omega)\, d\omega}{(\omega^2 + \omega_0^2)} \tag{62}$$

is obtained. Since reflectivities cannot be measured at complex frequencies, Eqs. (61) and (62) cannot be employed directly to test experimental data. However, these relations can serve a useful purpose, particularly Eq. (61), which depends on a *single* optical constant. Equations (61) and (62) can be employed directly to test theoretical models. If experimental reflectivity is assumed to fit some model functional form, whose frequency dependence is explicitly known, then the model must satisfy Eq. (61).

The standard dispersion relation for the reflectivity at complex frequency takes the form

$$\ln r(\omega_0) - \ln r(i\omega') = 2(\omega_0^2 + \omega'^2) \frac{P}{\pi} \int_0^\infty \frac{\omega\theta(\omega)\, d\omega}{(\omega^2 + \omega'^2)(\omega^2 - \omega_0^2)} . \tag{63}$$

This is the simplest dispersion relation involving $\ln\tilde{r}(\omega)$ at complex frequencies. Cardona[47] has proposed the following result:

$$\ln r(\omega_0) - \ln r(i) = \frac{2P}{\pi} \int_0^\infty \frac{\omega\theta(\omega)\, d\omega}{\omega^2 - \omega_0^2} . \tag{64}$$

Equation (64) is clearly incorrect; because of the asymptotic condition on $\theta(\omega)$ [Eq. (35)], the integral in Eq. (64) has a logarithmic divergence as $\omega \to \infty$. There is also a sign error in Cardona's expression.

VI. FOURIER ALLIED INTEGRAL REPRESENTATION

There are two alternative ways to express the connection between the real and imaginary parts of an analytic function satisfying certain conditions. Both of these approaches are mathematically equivalent to the Hilbert transforms. The first alternative is the Fourier allied integral representation, which can be written in the form[48–50]

$$f_i(\omega) = \frac{2}{\pi} \int_0^\infty dt \sin\omega t \int_0^\infty f_r(\omega') \cos\omega' t\, d\omega' , \tag{65}$$

$$f_r(\omega) = \frac{2}{\pi} \int_0^\infty dt \cos\omega t \int_0^\infty f_i(\omega') \sin\omega' t\, d\omega' , \tag{66}$$

where f_r and f_i denote the real and imaginary parts of an analytic function f, respectively. The second alternative involves the Fourier series expansion of the functions $f_r(\omega)$ and $f_i(\omega)$ over a suitable interval. If the expansion coefficients of one of the Fourier series are known, then analytic function theory provides a means to determine the Fourier series of the conjugate function.[50–52]

Since Eqs. (65) and (66) offer certain computational advantages, these relations should be of some interest for analysis of reflectance data. One condition that must be satisfied in order to write down Eqs. (65) and (66) is that $f_i(\omega)$ and $f_r(\omega)$ must have some suitable asymptotic behavior as $\omega \to \infty$ and $\omega \to 0$. Clearly, the identification of $f_i(\omega)$ with $\theta(\omega)$ and $f_r(\omega)$ with $\ln r(\omega)$ leads to divergent integrals. If the function f is chosen to be

$$f(\omega) = \frac{\ln\tilde{r}(\omega) - \ln\tilde{r}(\omega'')}{\omega^2 - \omega'^2} , \tag{67}$$

then the allied integral formulas are

$$\ln R(\omega) - \ln R(\omega') = \frac{4}{\pi} (\omega^2 - \omega'^2) \int_0^\infty dt \cos\omega t \times \int_0^\infty d\omega'' \frac{[\theta(\omega'') - \theta(\omega')] \sin\omega'' t}{\omega''^2 - \omega'^2} , \tag{68}$$

$$\theta(\omega) - \theta(\omega') = \frac{(\omega^2 - \omega'^2)}{\pi} \int_0^\infty dt \sin\omega t \times \int_0^\infty d\omega'' \frac{[\ln R(\omega'') - \ln R(\omega')] \cos\omega'' t}{\omega''^2 - \omega'^2} . \tag{69}$$

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Since $\tilde{r}(\omega)$ is square integrable, the allied integral formulas can be written directly for this function; they are

$$r(\omega)\sin\theta(\omega)=\frac{2}{\pi}\int_0^\infty dt\sin\omega t\int_0^\infty r(\omega')\cos\theta(\omega')\cos\omega' t\,d\omega', \tag{70}$$

$$r(\omega)\cos\theta(\omega)=\frac{2}{\pi}\int_0^\infty dt\cos\omega t\int_0^\infty r(\omega')\sin\theta(\omega')\sin\omega' t\,d\omega'. \tag{71}$$

The disadvantage of the latter two dispersion relations is that $r(\omega)$ and $\theta(\omega)$ are nonseparable. Equations (70) and (71) can serve as a starting point for the derivation of sum rules. For example, direct integration of Eq. (71) yields

$$\begin{aligned}\int_0^\infty r(\omega)\cos\theta(\omega)\,d\omega &= \frac{2}{\pi}\int_0^\infty d\omega\int_0^\infty dt\cos\omega t \\ &\quad\times\int_0^\infty r(\omega')\sin\theta(\omega')\sin\omega' t\,d\omega' \\ &= \frac{1}{\pi}\int_0^\infty dt\left[\int_0^\infty d\omega' r(\omega')\sin\theta(\omega')\sin\omega' t\right]\delta(t) \\ &= 0.\end{aligned} \tag{72}$$

VII. SUMMARY

The main goal of this work has been to derive a number of simple sum rules for a general medium that the normal reflectivity $R(\omega)$ and phase $\theta(\omega)$ must obey. The most useful and interesting results are

$$\int_0^\infty \omega^{-1}R(\omega)^{1/2}\sin\theta(\omega)\,d\omega=\tfrac{1}{2}\pi R(0)^{1/2}, \tag{73}$$

$$\int_0^\infty R(\omega)^{1/2}\cos\theta(\omega)\,d\omega=0, \tag{74}$$

$$\int_0^\infty \omega^2 R(\omega)\cos 2\theta(\omega)\,d\omega=0, \tag{75}$$

$$\int_0^\infty R(\omega)\cos 2\theta(\omega)\,d\omega=0, \tag{76}$$

$$\int_0^\infty \omega R(\omega)\sin 2\theta(\omega)\,d\omega=0, \tag{77}$$

$$\int_0^\infty \omega R(\omega)^{1/2}\sin\theta(\omega)\,d\omega=\tfrac{1}{8}\pi\omega_p^2, \tag{78}$$

$$\int_0^\infty \frac{R(\omega)^{1/2}[\omega'\cos\theta(\omega)-\omega\sin\theta(\omega)]}{\omega^2+\omega'^2}\,d\omega=0 \quad (\omega'>0), \tag{79}$$

$$\int_0^\infty \frac{(\omega^2-\omega'^2)\ln R(\omega)\,d\omega}{(\omega^2+\omega'^2)^2}=4\omega'\int_0^\infty\frac{\theta(\omega)\omega\,d\omega}{(\omega^2+\omega'^2)^2} \quad (\omega'>0), \tag{80}$$

$$\int_0^\infty \frac{\ln R(\omega)\,d\omega}{\omega^2+\omega'^2}=\frac{1}{2}\frac{\pi}{\omega'}\ln R(i\omega'), \tag{81}$$

$$\int_0^\infty R(\omega)^{1/2}\sin\theta(\omega)\,d\omega=\int_0^\infty R(i\omega)^{1/2}\,d\omega, \tag{82}$$

$$\int_0^\infty R(\omega)\sin 2\theta(\omega)\,d\omega=\int_0^\infty R(i\omega)\,d\omega. \tag{83}$$

All the above relationships, except Eq. (81), involve both $R(\omega)$ and $\theta(\omega)$ coupled together. In order to test experimental data, it is necessary to determine $\theta(\omega)$ from experimental reflectivity data using Eq. (5), and then employ the above sum rules. Equation (81) is the only result which depends on the reflectivity alone. Since the reflectivity at complex frequencies is not an experimental quantity, Eq. (81) cannot be employed directly to test experimental data. However, if reflectivity data are fitted to various theoretical models, then the validity of these theoretical models can be directly tested using Eq. (81).

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