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Classical generalization of the Drude formula for the optical conductivity

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A simple classical generalization of the Drude formula is derived based on the impulse response approach and Poisson statistics. The new feature is a parameter *c*, which is a measure of persistence of velocity. With negative values of *c*, it is possible to mimic the infrared properties of poor metals that display a minimum in the optical conductivity at zero frequency. The electron current in these cases reverses direction before decaying to zero. Specific examples considered are Hg and its amalgams, liquid Te, and the quasicrystal $Al_{63.5}Cu_{24.5}Fe_{12}$. Discussion is offered on the connection with interband transitions, on the distinction between the electron lifetime and the transport relaxation time, and on other generalizations of the Drude formula.

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I. INTRODUCTION

For a good metal the frequency dependence of the optical conductivity is given by the well-known Drude formula

$$\sigma(\omega)=\sigma_0/(1+\omega^2\tau^2), \tag{1}$$

where the dc conductivity σ_0 is given by $n^*e^2\tau/m$, n^* is the effective density of electrons, and τ is a relaxation time. The formula is rather inflexible. It requires that the frequency dependence of the conductivity should have a maximum at zero frequency and then fall off with Lorentzian form. Departures from this behavior have been observed, and we shall be concerned in particular with those materials in which $\sigma(\omega)$ displays a minimum at zero frequency and a transfer of oscillator strength to higher frequencies in the form of an infrared peak. The intent of this paper is to elaborate an exceedingly simple classical generalization of the Drude formula based on the impulse response approach and Poisson statistics,[1] and to show that it can accommodate some of the observed departures.

The structure of the paper is as follows. The classical derivation is presented immediately in Sec. II. The principal feature is the introduction of a ''persistence of velocity'' parameter *c*. Some applications of the formula are presented in Sec. III. Finally, in Sec. IV, discussion is offered on the possible connection with interband transitions, on the distinction between the electron lifetime and the transport relaxation time, and on some of the other generalizations of the Drude formula to be found in the literature.

II. CLASSICAL DERIVATION

A. Impulse response approach

Let us adopt the conceptually simple impulse response approach[2] to the optical conductivity. The procedure is to imagine a unit impulse of electric field applied to the electron system at time $t=0$ and then to examine the resulting current response $j(t)$. The complex frequency-dependent conductivity is the Fourier transform of $j(t)$:

$$\tilde{\sigma}(\omega)=\int_0^\infty j(t)\exp(i\omega t)\,dt. \tag{2}$$

A δ-function impulse of field is greater than any of the other forces acting on the system, and so each electron behaves initially as if it were perfectly free, giving $j(0)=n^*e^2/m$. Since $j(t)$ and $\tilde{\sigma}(\omega)$ are Fourier transforms of each other, the oscillator-strength sum rule on $\sigma(\omega)$, the real part of $\tilde{\sigma}(\omega)$, immediately drops out:

$$\int_0^\infty \sigma(\omega)\,d\omega=\left(\frac{\pi}{2}\right)j(0)=\frac{\omega_p^2}{8}, \tag{3}$$

where we have introduced the plasma frequency ω_p given by $\omega_p^2=4\pi n^*e^2/m$. Since causality has been invoked at the outset, the Kramers-Krönig relations must inevitably be satisfied by the real and imaginary parts of any expressions for $\tilde{\sigma}(\omega)$ that are obtained. Thus, not only is the impulse response approach conceptually simple, it also has some built-in consistency safeguards.

If the initial current decays exponentially to its equilibrium value of zero with a relaxation time τ, we have

$$j(t)/j(0)=\exp(-t/\tau) \tag{4}$$

and

$$\tilde{\sigma}(\omega)=(n^*e^2\tau/m)/(1-i\omega\tau). \tag{5}$$

This is the standard Drude formula which we now generalize.

B. Poisson statistics

Let us suppose that an electron experiences collisions that are randomly distributed in time but with an average time interval τ between collision events. The probability $p_n(0,t)$ of *n* events in the time interval $(0,t)$ is given by the Poisson distribution

$$p_n(0,t)=(t/\tau)^n\exp(-t/\tau)/n!. \tag{6}$$

The probability of zero collisions is $\exp(-t/\tau)$. So Eq. (4) can be seen as merely the first term in a series. Taking account of what happens after the first and subsequent collisions we write

$$j(t)/j(0)=\exp(-t/\tau)\left[1+\sum_{n=1}^{\infty}c_n(t/\tau)^n/n!\right]. \tag{7}$$

The coefficient c_n represents that fraction of the electron's original velocity that is retained after the nth collision. It is a memory or persistence of velocity effect. Taking the Fourier transform yields

$$\tilde{\sigma}(\omega)=\frac{n^*e^2\tau/m}{(1-i\omega\tau)}\left[1+\sum_{n=1}^{\infty}\frac{c_n}{(1-i\omega\tau)^n}\right]. \tag{8}$$

This generalized Drude formula is the principal result of this paper. There are now three possible directions in which to proceed. First, we could consider inclusion of only the first new term, the one whose coefficient is c_1. Second, there is a circumstance, whose discussion is deferred until Sec. IVB, in which the series of Eqs. (7) and (8) can be summed to infinity. Third, the series of Eq. (8) could be used as an empirical fitting scheme using as disposable parameters as many of the coefficients c_n that one is willing to tolerate. Note that the sum rule and the Kramers-Krönig relations are automatically satisfied for any set of real c_n values. We shall proceed in the first direction.

C. Single-scattering approximation

The key assumption upon which we now proceed is that persistence of velocity is retained for only one collision ($c_n=0$ for $n>1$). With this truncation of the series, we have (dropping the subscript and writing $c_1=c$)

$$j(0)/j(t)=(1+ct/\tau)\exp(-t/\tau). \tag{9}$$

Separating real and imaginary parts, we have for the conductivity

$$\sigma(\omega)=\frac{n^*e^2\tau/m}{(1+\omega^2\tau^2)}\left[1+\frac{c(1-\omega^2\tau^2)}{(1+\omega^2\tau^2)}\right] \tag{10}$$

and

$$1-\epsilon_1(\omega)=\frac{\omega_p^2\tau^2}{(1+\omega^2\tau^2)}\left[1+\frac{2c}{(1+\omega^2\tau^2)}\right], \tag{11}$$

where, following common custom, we have expressed the imaginary part of the conductivity as $\epsilon_1(\omega)$, the real part of a dielectric function.

These generalized Drude formulas have interesting and versatile properties, particularly for negative values of c. Figure 1 shows the behavior of $j(t)$, $\sigma(\omega)$, and $\epsilon_1(\omega)$ for values of $c=0$, -0.5, and -1.0. For elastic collisions, c would be $\langle\cos\theta\rangle$, the expectation value of $\cos\theta$ where θ is the scattering angle. Negative values of c therefore imply a predominance of backscattering, and it is seen that the net current $j(t)$ carried by the electron system actually reverses direction before relaxing to its equilibrium value of zero. The effect on $\sigma(\omega)$ is to depress the dc conductivity and to shift oscillator strength to higher frequencies. For values of $c<-2/3$, $\sigma(\omega)$ displays a minimum at zero frequency followed by a maximum at $(\omega\tau)^2=(3c+1)/(c-1)$. This behavior first manifests itself as a shoulder, and then develops into a well-defined maximum. For the case $c=-1$, the dc conductivity is completely suppressed and the maximum occurs at $\omega\tau=1$.

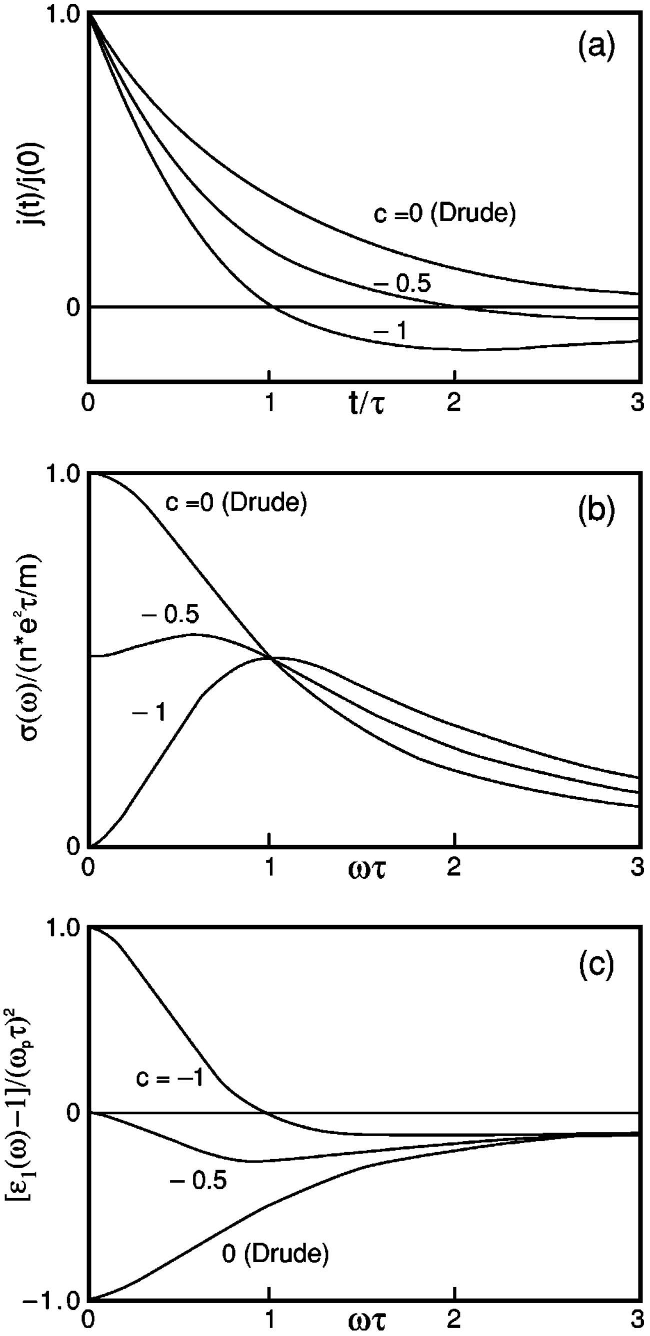

FIG. 1. Persistence of velocity effects. Dependence on c of (a) the impulse response function $j(t)$, (b) the real part of the conductivity $\sigma(\omega)$, and (c) the dielectric function $\epsilon_1(\omega)$. For negative values of c, $j(t)$ reverses sign before decaying to zero. With increasingly negative c, the dc conductivity is depressed, $\sigma(\omega)$ develops a peak at nonzero frequency, and $\epsilon_1(\omega)$ becomes positive at low frequencies.

The predicted behavior of $\epsilon_1(\omega)$ is also interesting. For a good metal, $\epsilon_1(\omega)$ at low frequencies is large and negative. For values of $c<-1/2$, $\epsilon_1(\omega)-1$ switches sign and, for values of c closer to -1, becomes large and positive. These dramatic behaviors for $\sigma(\omega)$ and $\epsilon_1(\omega)$ are of course mutually consistent with each other as required by the Kramers-Krönig relations. The generalized formulas therefore have,

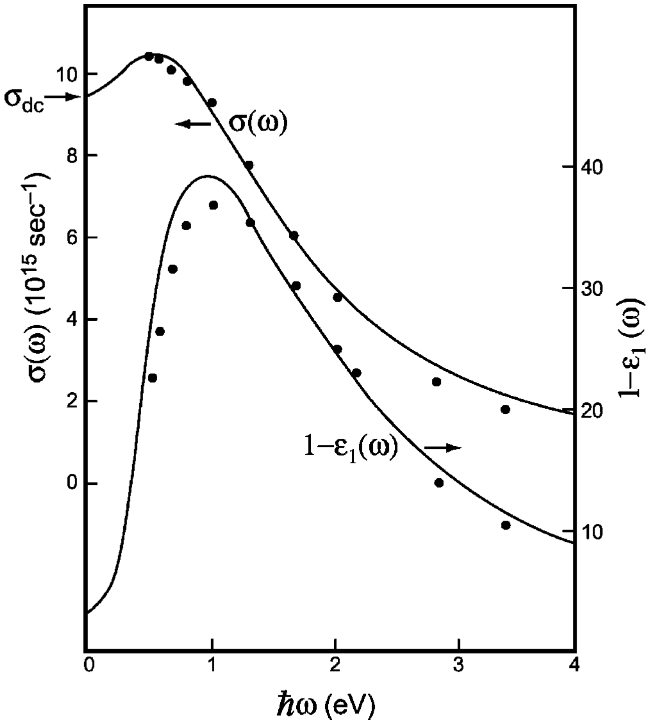

FIG. 2. Frequency dependence of the real and imaginary parts of the optical conductivity of liquid mercury. The solid circles represent the experimental measurements of Hodgson (Ref. 5). The curves are the predictions of the classical generalized Drude formulas [Eqs. (10) and (11)] with a value $c=-0.49$ for the persistence of velocity parameter.

with inclusion of only a single additional parameter, a versatility not present in the standard Drude formulas.

III. APPLICATIONS

A. Liquid metals

The generalized Drude formula described above was proposed originally to account for the unusual behavior of the optical properties of mercury. The optical properties of liquid metals generally display standard Drude-like behavior with with a reasonable value of the effective valency n^*/n_a, where n_a is the atomic density.[3] Exceptions are mercury and liquid tellurium.

In the case of Hg, the early infrared data of Hodgson[4,5] indicated the possibility of a weak peak in $\sigma(\omega)$ at low frequencies, a possibility strongly reinforced by a complementary dramatic variation in $\epsilon_1(\omega)$. Figure 2 shows the attempt made by the author[1] to reproduce the experimental behavior using the generalized Drude formulas. The procedure was to to adjust n^*, τ, and c but with the constraint that $n^*e^2\tau(1+c)/m$ must reproduce the measured dc conductivity. A reasonable representation was found with $c=-0.49$ and $n^*/n_a=2.7$. Comins[3] has subsequently pushed the measurements further into the infrared and has confirmed the peak in $\sigma(\omega)$ and the unusual low-frequency behavior of $\epsilon_1(\omega)$.

Izeki *et al.*[6] and Hefner *et al.*[7] have reported experimental results on the optical properties of expanded fluid Hg. They find that, as they decrease the density from its normal value (13.6 g cm^{-3}), $\sigma(\omega)$ undergoes a depression of the dc conductivity and a transfer of oscillator strength to higher frequencies. Their results bear a strong resemblance to the behavior shown in Fig. 1(b) for increasingly negative values of c. Complete suppression of the dc conductivity occurs at a density of 8 g cm^{-3}. For even lower densities, $\sigma(\omega)$ displays a form more characteristic of a semiconductor with the eventual opening up of a real gap in the electron density of states.

The infrared measurements on Hg have been further extended by Guggenheim[8] with the study of its amalgams with In, Sn, Bi, Zn, and Cd. Of these, the results on In are the most extensive since concentrations of In as high as 65% were investigated. Detailed fits of Eqs. (10) and (11) were made to the data. The parameter which shows the strongest variation with In concentration is c, the persistence of velocity parameter. Starting at $c=-0.5$ for pure Hg, c rises and levels off at zero for large In concentrations. Apparently, whatever agency is responsible for the strong backscattering implied by negative c is disrupted by the addition of impurity atoms leading to removal of the depression of the dc conductivity and reversion to standard Drude behavior.

In the case of liquid Te, the infrared data of Hodgson[9] show departures from Drude behavior that are even stronger than those for Hg. The conductivity $\sigma(\omega)$ shows a pronounced minimum at $\omega=0$ followed by a maximum ($\approx 2\sigma_0$) at higher frequencies. These results (not shown) are well reproduced by Eq. (10) with a value of $c=-0.74$. The associated results for ϵ_1 are of positive sign, in agreement with the model and with the Kramers-Krönig relations. As an historical aside, it is worth noting that both Hg and liquid Te were proposed at one time by Mott[10,11] as candidates for a metal on the borderline of nonconducting behavior.

B. Quasicrystal $Al_{63.5}Cu_{24.5}Fe_{12}$

The elemental constituents of the quasicrystal compound $Al_{63.5}Cu_{24.5}Fe_{12}$ are all individually good metals. Yet the compound is a poor metal and its infrared conductivity, as reported by Homes *et al.*,[12] is very interesting. Starting with a very low dc conductivity $\sigma_0=351\,\Omega^{-1}\,\mathrm{cm}^{-1}, \sigma(\omega)$ increases nearly linearly with frequency well into the near infrared and then displays a maximum with $\sigma_{\max}=6500\,\Omega^{-1}\,\mathrm{cm}^{-1}$ as shown in Fig. 3.

These results are very well reproduced by Eq. (10) using a value for $c=-0.973$ as also shown in Fig. 3. This value of c is immediately obtainable from the data by noting that the ratio $\sigma_{\max}/\sigma_0=-(c-1)2/8c(c+1)$. The value of τ is then adjusted to obtain good alignment for the overall frequency dependence. The excellent quality of the fit in Fig. 3 is essentially identical to that obtained by Burkov, Timusk, and Ashcroft[13] using a theoretical model based on conventional interband transitions that will be discussed immediately below.

IV. DISCUSSION

A. Interband transitions

We have seen that our generalized Drude formula can generate an infrared peak within the *intraband* contribu-

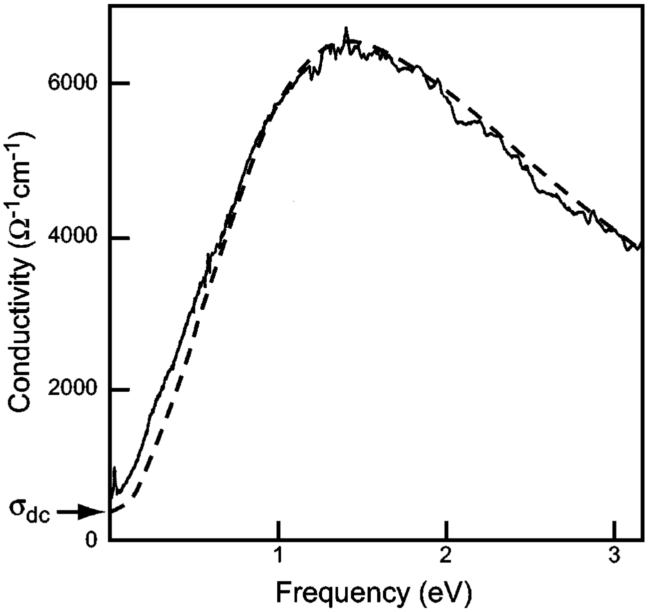

FIG. 3. Optical conductivity of the quasicrystal $Al_{63.5}Cu_{24.5}Fe_{12}$. The experimental measurements of Homes *et al.* (Ref. 12). are compared with the classical generalized Drude formula (dashed curve) with a value $c=-0.973$ for the persistence of velocity parameter.

tion to $\sigma(\omega)$. In the quasicrystal example considered above there is therefore no need to invoke an *interband* contribution. Nevertheless, there is an intriguing similarity with the results of the nearly free electron (NFE) treatment of interband transitions in a quasicrystal by Burkov *et al.*[13] It is instructive to discuss the physics behind this similarity.

A key ingredient in the approach of Burkov *et al.* is the large number of reciprocal lattice vectors G in a quasicrystal that have $G\approx 2k_F$ where k_F is the Fermi wave number. Within the NFE model, an interband transition is an umklapp process in which an electron with wave vector k simultaneously absorbs a photon and undergoes Bragg diffraction through a reciprocal lattice vector G. After summation over the multiplicity of reciprocal lattice vectors and introduction of a phenomenological damping time τ, the expression for the interband absorption contribution to the optical conductivity reduces to

$$\sigma_i(\omega)=\sigma_G\omega^2\tau^2/(1+\omega^2\tau^2)^2, \tag{12}$$

where σ_G is a coefficient involving the average value of G and the band gap energy.

We observe immediately a remarkable similarity. Equation (12) has precisely the same frequency dependence as the $c=-1$ limit of Eq. (10). On reflection, however, this similarity is not too surprising. Because of the multiplicity of reciprocal lattice vectors having $G\approx 2k_F$, a typical electron with wave vector k will, on diffraction to $k-G$, reverse its direction of motion. We may think of Bragg diffraction in this circumstance as an intense form of backscattering, thereby providing a physical mechanism for large negative values of c. In our generalized Drude formula, however, the strong backscattering is subsumed into the classical *intraband* contribution to $\sigma(\omega)$ without need to separate it out into an *interband* contribution.

B. Lifetime and the transport relaxation time

A basic assumption of simple kinetic models is that the duration of a collision is negligible in comparison with the interval between collisions. If we further assume that the collisions are independent of each other, we may write $c_n=c^n$. It is then very easy to sum the series in Eqs. (7) and (8) to infinity to obtain

$$j(t)/j(0)=\exp(-t/\tau_c) \tag{13}$$

and

$$\tilde{\sigma}(\omega)=(n^*e^2\tau_c/m)/(1-i\omega\tau_c), \tag{14}$$

with a transport scattering rate

$$\frac{1}{\tau_c}=\frac{1}{\tau}(1-c). \tag{15}$$

In other words, we retrieve the standard (and inflexible) Drude equation but with a transport relaxation time τ_c that is different from the average lifetime between collisions τ. For elastic collisions, c can be identified with $\langle\cos\theta\rangle$, the average value of $\cos\theta$, where θ is the scattering angle. Collisions with large scattering angles contribute more strongly to the resistivity. We have therefore arrived in an extremely simple way at the intuitively obvious $(1-\cos\theta)$ weighting factor that enters into the scattering rate in expressions for the resistivity based on Boltzmann-type theories. In quantum-mechanical theories based on the Kubo formalism, incorporation of the $(1-\cos\theta)$ weighting factor is nontrivial. Mahan, for example, in his classic textbook on many particle theory,[14] devotes a substantial part of a chapter in getting from a conductivity expression involving only the lifetime to an expression incorporating the $(1-\cos\theta)$ factor. Even in a simpler one-particle approach, Faber[15,16] has shown that meticulous attention to subtle phase coherence within a certain set of multiple scattering processes is essential to extract the $(1-\cos\theta)$ factor. As he points out, "it is curious how elaborate the proof of this result becomes once the traditional kinetic approach to conduction is abandoned."

So if the summation to infinity is so easy and the $(1-\cos\theta)$ factor is so easy to derive in our simple kinetic model, why bother to truncate after a single scattering? The honest answer is based on empirical performance and versatility. Equation (14) has the standard Drude form whose inflexibility we are trying to escape.

C. Other generalized Drude formulas

There have been other attempts to enhance flexibility of the Drude formula. The following is a sampling of some of the approaches to found in the literature.

Recent measurements of the optical conductivity of semiconductors in the THz frequency region have exposed inadequacies of the Lorentzian form of the simple Drude formula. Better fits are obtained with modified Lorentzians of the form

$$\tilde{\sigma}(\omega)=\sigma_0/[1-(i\omega\tau)^{1-\alpha}]^{\beta}, \tag{16}$$

where the exponents $1-\alpha$ and β are treated as disposable parameters. This formula is imported from the community that studies dielectric relaxation in fluids and polymers where there is a formal similarity between the Debye theory of dielectric relaxation and the Drude theory of metallic conduction. With $\alpha=0$ and $\beta=1$, we retrieve the standard Drude (Debye) result. Setting $\beta=1$ and varying only α is called the Cole-Cole (CC) model.[17] Setting $\alpha=0$ and varying only β is called the Cole-Davidson (CD) model.[18] In THz experiments on doped Si, Jeon and Grischkowsky[19] report success with the CD model. In transient photoconductivity measurements on GaAs, on the other hand, Beard, Turner, and Schmuttenmaer[20] prefer to keep both α and β in play. They refer to this as a generalized Drude (GD) model, although in the dielectrics community it is sometimes called the Havriliak-Negami (HN) expression.[21]

Another approach is to replace the simple exponential of Eq. (4) with a Kohlrausch stretched exponential $\exp[-(t/\tau)^{\beta}]$. In the dielectrics community, this is called the Williams-Watts (WW) model.[22] These various formulas (CC, CD, GD, HN, and WW) imply a distribution of relaxation times, and there is an extensive literature on what this might mean.[23–27] The formulas themselves, however, are essentially empirical.

Mayou[28] has recently derived a generalized Drude formula of the CD form by considering the time evolution of an electron wave packet in a quasicrystal. At early times the electron propagation is ballistic, and at later times it becomes diffusive. Herein lies a possible rationalization for the basic assumption of the model presented here, that persistence of velocity is lost after only a single scattering.

Yet another approach is to assume the validity of the standard form of the Drude expression but to treat the relaxation time as frequency dependent. In order to preserve causality, the scattering rate $1/\tau(\omega)$ must be treated as both frequency dependent and complex, and there is a relationship with the complex electron self-energy. Puchkov, Basov, and Timusk,[29] for example, have applied this approach in the analysis of infrared data on high-temperature superconductors.

D. Closing remarks

It is hoped that the classical expressions presented here will be useful to experimentalists as an alternative to the other generalizations of the Drude formula that have appeared in the literature. A midinfrared peak has been observed in a variety of materials.[30–32] Indeed, it has been pointed out[33] that a peak in the conductivity at nonzero frequency is a generic feature of disordered conductors at the verge of the metal-insulator transition. As we have seen, the Fourier transform of $\tilde{\sigma}(\omega)$ in such cases implies an impulse response function or, in the language of the Kubo formalism, a current-current autocorrelation function that reverses sign before relaxing to its equilibrium value. This is perhaps the principal finding of this work. The strength of the generalized Drude formula presented here lies in its ability to accommodate this sign reversal.

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[1] N. V. Smith, Phys. Lett. **26A**, 126 (1968).

[2] A. B. Pippard, in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abeles (North-Holland, Amsterdam, 1966), p. 622.

[3] N. R. Comins, Philos. Mag. **25**, 817 (1972).

[4] J. N. Hodgson, Philos. Mag. **4**, 183 (1959).

[5] J. N. Hodgson, Philos. Mag. **7**, 229 (1962).

[6] H. Ikezi *et al.*, Phys. Rev. B **18**, 2494 (1978).

[7] W. Hefner, R. W. Schmutzler, and F. Hensel, J. Phys. (Paris), Colloq. **8**, C-62 (1980).

[8] J. Guggenheim, Philos. Mag. **22**, 833 (1970).

[9] J. N. Hodgson, Philos. Mag. **8**, 343 (1963).

[10] N. F. Mott, Philos. Mag. **13**, 989 (1966).

[11] N. F. Mott, Adv. Phys. **16**, 49 (1967).

[12] C. C. Homes *et al.*, Phys. Rev. Lett. **67**, 2694 (1991).

[13] S. E. Burkov, T. Timusk, and N. W. Ashcroft, J. Phys.: Condens. Matter **4**, 9447 (1992).

[14] G. D. Mahan, *Many-Particle Physics*, 2nd ed. (Plenum, New York, 1990), pp. 610–630.

[15] T. E. Faber, *Introduction to the Theory of Liquid Metals* (Cambridge University Press, Cambridge, England 1972), pp. 415–420.

[16] T. E. Faber, Adv. Phys. **15**, 547 (1966).

[17] K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).

[18] D. W. Davidson and R. H. Cole, J. Chem. Phys. **19**, 1484 (1951).

[19] T. I. Jeon and D. Grischkowsky, Phys. Rev. Lett. **78**, 1106 (1997).

[20] M. C. Beard, G. M. Turner, and C. A. Schmuttenmaer, Phys. Rev. B **62**, 15 764 (2000).

[21] S. Havriliak and S. Negami, Polymer **8**, 161 (1967).

[22] G. Williams and D. C. Watts, Trans. Faraday Soc. **66**, 80 (1970).

[23] C. P. Lindsey and G. D. Patterson, J. Chem. Phys. **73**, 3348 (1980).

[24] T. C. Guo and W. W. Guo, J. Phys. C **16**, 1955 (1982).

[25] R. M. Hill and L. A. Dissado, J. Phys. C **18**, 3829 (1985).

[26] G. A. Niklasson, J. Phys.: Condens. Matter **5**, 4233 (1993).

[27] G. Williams and J. Fournier, J. Chem. Phys. **104**, 5690 (1995).

[28] D. Mayou, Phys. Rev. Lett. **85**, 1290 (2000).

[29] A. V. Puchkov, D. N. Basov, and T. Timusk, J. Phys.: Condens. Matter **8**, 10 049 (1996).

[30] L. Degiorgi, E. J. Nicol, O. Klein, G. Grüner, P. Wachter, S.-M. Huang, J. Wiley, and R. B. Kaner, Phys. Rev. B **49**, 7012 (1994).

[31] F. Bommeli, L. Degiorgi, P. Wachter, F. B. Anders, and A. V. Mitin, Phys. Rev. B **56**, R10 001 (1997).

[32] H. Okamura, M. Matsunami, T. Inaoka, T. Nanba, S. Kimura, F. Iga, S. Hiura, J. Klijn, and T. Takabatake, Phys. Rev. B **62**, R13 265 (2000).

[33] D. N. Basov, B. Dabrowski, and T. Timusk, Phys. Rev. Lett. **81**, 2132 (1998).