Temperature-dependent carrier transport: Low-complexity model for the infrared optical and radiative properties of nickel

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We propose a framework for modeling the temperature-dependent infrared optical and radiative properties of metals exhibiting nonideal free-carrier dynamics. In order to do so, we derive a parsimonious model that possesses both multivariate (in temperature and wavelength) and single variate (in wavelength) components. The model is realized as the complex-valued relative permittivity, and is applicable to optically smooth media. A procedure is outlined for regressing both components of the model under an appropriate set of physical constraints that preclude superfluous degrees of freedom. The procedure is demonstrated by applying the model to nickel, a transition metal of technical significance that possesses nontrivial valency. The resulting model yields practically accurate results for eight data sets spanning four separate studies, representing the approximate wavelength (\(\lambda\)) bandwidth between 1 and 16 \(\mu\)m, and the approximate temperature (\(T\)) range between 0 and 1400 K. The proposed model framework retains phase information and can therefore be directly interfaced with more complex Fresnel frameworks, such as those commonly used for modeling systematically or randomly roughened surfaces.

I. INTRODUCTION

The interaction between matter and electromagnetic radiation is a topic of great practical importance for both theory- and design-driven applications. Scientist and engineer alike benefit from models capable of reproducing the properties of the material response to electromagnetic forcing. Broadly speaking, these properties are divided into two categories: optical and radiative. Optical properties are typically defined by complex-valued quantities, such as the electric susceptibility or the refractive index, that describe the manner in which the phase, amplitude, and spectra of a given field are dispersed as it permeates through and between various media. Surface radiative properties, on the other hand, are typically realized in terms of real-valued quantities that correspond to energy balances at relevant interfaces. In either case, the properties generally vary both as a function of the radiative wavelength and as a function of the temperature of the medium.

Fresnel’s celebrated relations provide a theoretical coupling between the dispersive properties of a given optically smooth medium and the properties governing its radiative exchange with the surrounding environment. This makes it so that one possible approach to effectively modeling both sets of properties is to begin with a microscopic differential equation of motion and then move toward a continuous, complex-valued macroscopic Fourier description of the response. When the spectrum of interest is the infrared and the medium being modeled is metallic, the archetypical example of this methodology is the model proposed by Drude over a century ago.\(^1\) The Drude model pertains mainly to the infrared regime since the infrared optical and radiative properties of nickel

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\(\mu m, \) and the approximate temperature (\(T\)) range

\([7–11]\) are expected to represent “good” free-electron metals (e.g., the monovalent noble metals) have been shown to deviate from the Drude model results at very long wavelengths.\(^{10,12}\) The matter of modeling these materials is further complicated when one seeks to accurately describe thermophysical property variations. Since not all wavelength-dependent dynamics are also temperature-dependent, a practically useful thermophysical model must be capable of reproducing the independent effects of these contributions. Few models exist that are capable of meeting these needs while also observing the principle of parsimony. Those that can be found are, for the most part, defined over limited bandwidths and limited temperature ranges—in the infrared, a typical spectral-thermophysical response model will encompass a few microns and at most several hundred kelvins.

Consequently, it is desirable to obtain both a physically motivated structure for describing the temperature- and wavelength-dependent responses in these more complex settings, and a method for realizing this model from a consistent set of direct measurements. In this work, we derive a model to accomplish this goal and illustrate its
use by applying it to optical and radiative measurements taken from nickel, a transition metal whose infrared response exhibits complex dynamics. Nickel is also an appropriate candidate for such an endeavor due to its numerous and varied uses in relevant engineering contexts.

This work is organized as follows. In Sec. II, the microscopic Drude model is described under a Langevin description and the proposed thermophysical model is subsequently derived by generalizing this description. The properties of the anomalous model are investigated in detail in Sec. II B. The subject of Sec. III is the application to describe the general procedure for deriving the model parameters from experimental data and Sec. III B for the analysis of the results. In Sec. IV we provide a brief concluding discussion of the central elements of the study.

II. THEORY

Drude’s free-carrier transport model describes the response of a bulk metallic solid to incident electromagnetic radiation. It derives from a microscopic equation of motion governing the behavior of a single carrier and can be written as a Langevin equation:13,14

\[ m^* \frac{d\mathbf{v}(t)}{dt} + \zeta v(t) = e \mathbf{E}(t) + e \eta(t), \tag{1} \]

where \( v \) denotes the carrier velocity for a carrier with effective mass \( m^* \), \( \zeta = m^*/\tau_c \) is a phenomenological damping associated with velocity-randomizing scattering events occurring at an average rate \( 1/\tau_c \), and \( e \) denotes the elementary charge. Here, \( \mathbf{E} \) is the ordered local field and the noise force has been modeled in terms of a random field noise, \( \eta \), that is zero-mean and ergodic.

The macroscopic equation of motion is then obtained by taking the ensemble average \( \langle \cdot \rangle \) of (1), leading to

\[ \tau_c \frac{dj(t)}{dt} + j(t) = \frac{n_d e^2 \tau_c}{m^*} E(t), \tag{2} \]

where the current density \( j = n_d e \langle \mathbf{v} \rangle \) describes the average charge carrier motion in a material having a carrier number density \( n_d \), \( E = \langle \mathbf{E} \rangle \), and \( \langle e \eta \rangle = 0 \). The conductivity is obtained under a Fourier transform of (2) and may be written in wavelength-dependent form by noting that \( \omega = 2\pi c_0/\lambda \). This leads to the unbound harmonic response

\[ \sigma_d(\lambda) = \frac{\sigma_y \lambda}{\lambda - i\lambda_c}, \tag{3} \]

where we have defined the characteristic wavelength \( \lambda_c = 2\pi c_0 \tau_c \), with \( c_0 \) being the speed of light in a vacuum. The DC conductivity is then \( \lim_{\omega \to 0} \sigma_d(\omega) = \sigma_y = n_d e^2 \tau_c/m^* \).

The Drude susceptibility follows from the usual transform,15 leading to

\[ \chi_d(\lambda) = -\frac{\lambda^2}{2\pi c_0 \varepsilon_0} \left( \frac{\sigma_y}{i\lambda + \lambda_c} \right), \tag{4} \]

where \( \varepsilon_0 \) is the vacuum permittivity.

The temperature-dependent model expands upon our previous study for the description of anomalous carrier dynamics over broad infrared bandwidths.12 Here the term “anomalous” refers to intraband dynamics that systematically depart from the ideal free electron profile. The anomalous model interprets such departures as the addition of a structured component to the otherwise random perturbations in (1):

\[ \tilde{\eta}(t) = F \left( \mathcal{E}(t), \tau_f \frac{d\mathcal{E}(t)}{dt} \right) + \eta(t), \tag{5} \]

where the parameter \( \tau_f \) defines a characteristic field relaxation period. A zero-order field effect is already accounted for in Drude’s model, so that the most basic modification to the local field fluctuation is one that considers the Markovian relaxation \( F = \tau_f \frac{d\mathcal{E}}{dt} \). This modification can be generalized, however, to one that accounts for a field damping memory:

\[ \tilde{\eta}(t) \equiv \lim_{t_0 \to -\infty} \int_{t_0}^{t} K(t - s) \frac{d\mathcal{E}(s)}{ds} ds + \eta(t), \tag{6} \]

which assumes that a long enough time has passed since the introduction of the field so that the distribution has completely decorrelated from its initial state. Here \( K \) is a dimensionless function known as the memory kernel.

The choice of \( K \) is dictated by the requirement that the model remain amenable to physically meaningful interpretation while also accurately describing the experimental observations. These needs are balanced, however, by the desire for a low-dimensional description of the anomalous behaviors. An appropriate choice for the memory kernel is therefore

\[ K(t) = \frac{(\tau_f/t)^{\mu}}{\Gamma(1 - \mu)}, \tag{7} \]

where \( \Gamma(\cdot) \) is the gamma (generalized factorial) function and \( \mu \in [0, 1) \). The kernel (7) imparts a power-law memory decay. When \( \mu = 0 \), the memory is said to be perfect (this is analogous to the Drude model). For \( \mu > 0 \), memory of field perturbations decays asymptotically with a decay strength dependent on the value of \( \mu \). As \( \mu \to 1 \), the limiting behavior of (7) in (6) is such that memory kernel behaves as the IID distribution \( \delta(t) \), which implies the previously noted Markovian relaxation.

The memory kernel given by (7) is such that in the stationary limit of (6), one arrives at the causal convolution:

\[ \lim_{t_0 \to -\infty} K(t) \ast \frac{d\mathcal{E}(t)}{dt} = \lim_{t_0 \to -\infty} \tau_f \frac{d^{\mu} \mathcal{E}(t)}{dt^{\mu}}. \tag{8} \]
where the notation on the right hand side implies either of the Riemann-Liouville or Caputo fractional derivative definitions. In Appendix A, we show that a more general approach can be taken with the memory kernel that nevertheless leads to (8).

By combining (6), (7), and (8), and then inserting the result into (1), a temporally nonlocal macroscopic transport model is obtained:

\[
\tau_c \frac{dj(t)}{dt} + j(t) = \left( \frac{n_d e^2 \tau_c}{m^*} \right) \left( E(t) + \tau_f \frac{d\mu}{dt} E(t) \right).
\]

The result is a simplified analog to the hydrodynamic equation of motion governing the momentum of a small particle within harmonic Stokes flow. This scenario leads to the Basset memory drag, which is a force term that arises as the half derivative of the disturbance flow.

Memory operators like the one employed in (9) are useful for the description of certain high-order semi-stochastic systems due to their intrinsic infinite dimensionality. In such systems, they provide a linear differential description of dynamics that may otherwise represent non-differentiable processes. It has also been demonstrated that operators of this type are consistent with a Hamiltonian description of emergent damping effects, whereas this is not generally the case for the more conventional Markov approximation. These behaviors are commonly found in systems that are subject to anomalous diffusion. Accordingly, the generalized fluctuating field of (6) with the kernel (7) may be understood as modeling a non-Markovian temporal diffusion profile induced by elements of system disorder.

In this work, we extend the carrier transport model of (9) to account for temperature effects by considering a temperature-dependent conductivity informed, e.g., by the solution to the Boltzmann equation in the Relaxation Time Approximation (BRTA):

\[
\sigma(T) = \frac{n_d e^2}{m^*} \tau_c(T),
\]

where the temperature-dependence of the relaxation time derives from the collision integral in the BRTA equation. In an ideal lattice, the theory predicts \( \tau_c \propto T^{-3} \) in the low temperature regime, \( T/\Theta_T << 1 \) (\( \Theta_T \) is the Debye temperature at \( T \)). When \( T/\Theta_T >> 1 \), an asymptotic dependence of \( \tau_c \propto T^{-1} \) is expected. Since we are interested in a model yielding a general empirical fidelity over a regime that includes intermediate temperatures, we obtain the dependence in (10) for our model directly from suitable experimental data.

In this work, we refer to (10) as the photonic conductivity and to its inverse as the photonic resistivity. This is done since the DC conductivity one normally associates with this value may not be equivalent to the regressed parameter in the Drude model (3) when the metal is not well described by the free-electron model at longer wavelengths. Nickel—which forms the objective of the modeling study undertaken in Sec. III—is a particularly strong example of this anomaly, and this has been frequently noted in the historical and recent literature.

We account for the possibility of macroscopic anomalous carrier dynamics that behave independently from the bulk Drude behavior with a single effective carrier and an associated relaxation time that is altered in the independent regimes. This is achieved by introducing the dimensionless linear scaling \( \alpha(T) \) such that \( \tau_\alpha = \alpha \tau_c \). This leads to

\[
\tau_c(T) \frac{dj_c(t)}{dt} + j_c(t) = \frac{n_d e^2}{m^*} \tau_c(T) E(t),
\]

\[
\tau_\alpha(T) \frac{dj_\alpha(t)}{dt} + j_\alpha(t) = \frac{n_d e^2}{m^*} \tau_\alpha(T) \alpha \frac{d\mu}{dt} E(t),
\]

where the total current density is taken to be the stationary sum of the Drude component and the anomalous component. The model described in (9) and its generalization to distinct regimes in (11) may be interpreted as a type of “two-carrier” model, although with the exception that the model actually accounts for a single carrier whose dynamics are modified in the presence of a disordered local field.

The concept of a two-carrier model was first introduced by Drude in 1900 before establishing his more well-known model four years later in response to the predominant theoretical doctrine at the time. Five decades subsequent, Roberts reassessed Drude’s original formula for the purposes of modeling more complex dynamics typically observed in metals that are not well described by the free-electron model. Since that time, the concept of a multi-carrier model has been leveraged in a number of contexts to accurately capture the complex optical and radiative responses for a wide range of media.

One notable realization of the two-carrier model that bears relevance to the present study is that described by Nagel and Schnatterly for modeling the effects of highly disordered regimes of electron dynamics. In that study, the authors describe a single effective carrier type having a time constant that becomes modified in regions of high disorder. In our model, we further allow for this disorder to be driven by field oscillations (i.e., when \( \mu > 0 \)), in which case the anomalous response vanishes in the long-wavelength limit where the Drude component is expected to dominate (this is substantiated in the model analysis to follow). A similar behavior is observed in the previously noted hydrodynamic analog, where the Basset force gives way to a pure Stokes drag in the low-frequency limit. Setting \( E(t) = E_0 = \text{constant} \), this behavior is recovered from (9) and (11b) in the stationary setting. Furthermore, Nagel and Schnatterly have conjectured that the disordered component of their model should be independent of temperature. In advance of the results presented further on, we note that this is precisely the behavior we have observed empirically in our study.

The transport model of (11) leads to the wavelength-dependent susceptibility model

\[
\chi_\phi(\lambda, T) = \chi_d(\lambda, T) + \chi_\alpha(\lambda),
\]

where $\phi$ denotes free-carrier dynamics and we have preemptively applied the previously noted temperature-independence of the disordered carrier dynamics, which arises under the empirical observation that $\alpha(T) \tau_c(T) = \text{constant}$. The anomalous susceptibility is

$$\chi_a(\lambda) = (-i)^\mu \frac{\lambda^2}{2 \pi c_0 \varepsilon_0} \left( \frac{\lambda_f}{\lambda} \right)^\mu \left( \frac{\sigma_a}{i \lambda + \lambda_a} \right),$$  

(13a)

$$= -\frac{\lambda^2 \sigma_a}{2 \pi c_0 \varepsilon_0} \left( \frac{\lambda_f}{\lambda} \right)^\mu \left( \frac{f_r(\mu) - i f_i(\mu)}{i \lambda + \lambda_a} \right),$$  

(13b)

where we recall that the time constant in anomalous regimes is $\tau_a = \alpha \tau_c$, so that $\lambda_a = 2 \pi c_0 \tau_a$ and $\sigma_a = n_d e^2 \tau_a / m^*$ define the anomalous relaxation wavelength and anomalous conductivity contribution, respectively. Here we have defined $f_r(\mu) = \cos(\mu \pi/2)$ and $f_i(\mu) = \sin(\mu \pi/2)$, so that

$$\sqrt{f_r(\mu)^2 + f_i(\mu)^2} = 1.$$  

(14)

The numerator in the second set of parentheses in (13b) demonstrates that one of the effects of the parameter $\mu$ is the bifurcation of the anomalous term. The result in (14) shows that the bifurcation produces a complimentary partition of the strengths of the two resulting terms. This is to say that at any fixed frequency, the ratio of the amplitude of these two terms as a function of $\mu$ is $|f_r(\mu)/f_i(\mu)|$, with the total contribution constrained by (14). The energy partitioning property of nonlocal operators in a stationary frequency domain setting has been rigorously investigated in our recent study.29

Decomposing the proposed model (12) into its real and imaginary components $\chi_{\phi} = \chi_{\phi}' + i \chi_{\phi}''$ and appealing to the relation $\varepsilon = 1 + \chi = 1 + \chi_{\phi} + \sum \chi_{\beta}$,30 where the $\chi_{\beta}$ are the contributions from bound states, one has for the temperature-dependent relative permittivity

$$\varepsilon'(\lambda, T) = \varepsilon_{\beta}'(\lambda, T) - \frac{\lambda^2 \lambda_c(\mu)}{2 \pi c_0 \varepsilon_0} \left( \frac{\lambda_f(T)}{\lambda^2 + \lambda_c(T)^2} \right)^\mu + \frac{\lambda^2 \lambda_a(\mu)}{2 \pi c_0 \varepsilon_0} \left( \frac{f_r(\mu)}{\lambda^2 + \lambda_a^2} \right)^\mu,$$

$$\varepsilon''(\lambda, T) = \varepsilon_{\beta}''(\lambda, T) + \frac{\lambda^3 \sigma_a(\mu)}{2 \pi c_0 \varepsilon_0} \left( \frac{\lambda_f(T)}{\lambda^2 + \lambda_c(T)^2} \right)^\mu + \frac{\lambda^3 \sigma_a(\mu)}{2 \pi c_0 \varepsilon_0} \left( \frac{f_r(\mu)}{\lambda^2 + \lambda_a^2} \right)^\mu,$$

(15a)

(15b)

where $\sigma_f / \lambda_c = \sigma_a / \lambda_a = \text{constant}$, which are physical constraints that we observe in order to avoid overfitting experimental data during model development. Though this constraint was not directly enforced in Roberts’ re-visititation of Drude’s two-carrier model,7 he did note its presence in the empirical fits of his subsequent thermo-physical study31 and leveraged it there for the purposes of extrapolating parameter regression to higher temperature data.

The bound state contribution to expressions (15) is

$$\varepsilon_{\beta}(\lambda, T) = 1 + \sum_{\beta} \chi_{\beta}(\lambda, T).$$  

(16)

Generally, one models the interband dynamics with an appropriately motivated bound harmonic oscillator definition.11 When there is a sufficient decoupling of the intraband dynamics from the interband dynamics—typically, when the latter have resonances at smaller-than-visible wavelengths—the bound oscillations remain approximately in phase with the incident field. In this case, one may take the long-wavelength approximation

$$\varepsilon_c = \lim_{\lambda \to \infty} \varepsilon_{\beta}(\lambda, T),$$  

(17)

where the core contribution $\varepsilon_c$ is a real constant in the limit due to negligible absorption. The approximation (17) also assumes that the medium surface is free of dielectric layers (e.g., oxidation), since, in addition to imparting a characteristic surface roughness, such layers admit temperature- and wavelength-dependent phononic absorption that must then be separately modeled as in (16).

A. Optical and Radiative Properties of Metals in the Infrared

The radiative properties of an optically smooth absorbing medium in response to an incident homogeneous electromagnetic plane wave may be computed if the complex index of refraction is known:32

$$\tilde{n} = n + i k,$$  

(18)

where $n$ is the dispersive index and $k$ is the absorptive index. The complex index is related to the relative permittivity by $\tilde{n} = \sqrt{\varepsilon}$, so that

$$n = \sqrt[2]{\frac{1}{2}(|\varepsilon| + \varepsilon')},$$  

(19a)

$$k = \sqrt[2]{\frac{1}{2}(|\varepsilon| - \varepsilon')},$$  

(19b)

with $|\cdot|$ being the complex modulus of $(\cdot)$. The reflectivity is the ratio of the reflected radiant energy to the
incoming radiant energy. It can therefore be expressed in terms of the incident field \( E^{(i)} \) as
\[
\rho = \frac{|E_p^{(i)}|^2 \rho_p + |E_s^{(i)}|^2 \rho_s}{|E_p^{(i)}|^2 + |E_s^{(i)}|^2},
\]
where \( (\cdot)_p \) and \( (\cdot)_s \) denote components that are parallel and perpendicular to the plane of incidence, respectively. The polar reflectivity components represent the squared amplitudes of the corresponding complex Fresnel reflection coefficients:
\[
\rho_p = |r_p|^2, \quad (21a) \quad \rho_s = |r_s|^2. \quad (21b)
\]
The transmitted energy can then be obtained from an energy balance at the interface: \( \tau = 1 - \rho, \tau_s = 1 - \rho_s, \) and \( \tau_p = 1 - \rho_p. \) For radiation emitted from a non-absorbing medium with \( \tilde{n}_1 = n_1 \) onto an absorbing medium with \( \tilde{n}_2 = n_2 + i k_2, \) the reflection coefficients are determined by the geometric relations governing the magnitudes of the incoming and outgoing fields. The relations are a result of applying the phase-matching requirement to the boundary conditions at the interface.

If the absorbing medium is a metallic conductor and the spectrum of interest is the infrared, then above some characteristic length of field disorder approaches zero \( \lambda_f \to 0 \) and one recovers the Drude model from (15). The second important feature is that in the DC limit (\( \lambda \to \infty \)) where the contribution from the anomalous term vanishes, the conductivity model associated with (13) returns \( \sigma_\gamma, \) which is also in agreement with the Drude model.

In order to provide a basis for the analysis and interpretation of non-integer order differential dynamics in a stationary frequency domain setting, we have recently described a generalized spectroscopic analysis framework. The framework is derived under the formalism of variable order calculus. It allows one to express the linear response of a given system as a variable order transfer function. Within the context of the present discussion, this leads to the frequency-dependent expression
\[
\chi_\phi(\omega) = \frac{\omega_p^2}{\gamma(\omega)(-\omega + \gamma(\omega))}, \quad (26)
\]
with \( \omega = 2\pi c_0 \lambda^{-1} \) and where \( \omega_p = \sqrt{\sigma_\gamma/\varepsilon_0 \tau_c} = \sqrt{n_e e^2/m^* \varepsilon_0} \) is the plasma frequency. We refer to the parameters
\[
q(\omega) = \frac{2}{\pi} \text{atan}(-Z''(\omega), Z'(\omega)), \quad (27a) \\
\gamma(\omega) = \omega^{-q(\omega)} |Z(\omega)|, \quad (27b)
\]
as the variable order coordinates (VOCs). They are expressed in terms of \( Z = Z' + i Z'' , \) where \( Z = \omega_p^2/\chi_\phi. \) Here \( \text{atan}2 \) is the quadrant-preserving arctangent function. The parameter \( q \) is called the generalized derivative order (GDO). The GDO is, in particular, useful for characterizing the dynamical order of the system in response to a given wavelength of radiative forcing.

In this work, we find the GDO useful for analyzing the influence of the anomalous susceptibility component (13). Specifically, we note that there exist two distinct regimes of behavior depending on the value of \( \mu. \) The first regime is that corresponding to \( \mu = 0 \) and may be deduced directly from (13): the model reduces to a simple Drude term. The second regime is that defined by \( \mu \in (0,1], \) for which the anomalous term exhibits a quasi-bound state behavior—that is, it interpolates free and bound particle dynamics. These points are further illustrated by the plots in Fig. 1, which demonstrate the separate and combined (superposed) effects of the model components. The model represented in the plots is that obtained from (13) for nickel. In each plot, the model is evaluated over the infrared band \( \lambda \in [1,16] \mu m \) for \( T = 4 K \) and presented alongside experimental data ob-
tained at the same temperature. Plot 1(a) shows the susceptibility and plot 1(c) shows the corresponding GDO. The memory decay parameter associated with the model in the plots is $\mu = 0.593$.

A number of important conclusions can be drawn from the plots. First, it should be noted that free-carrier dynamics are those taking place independent of any 0-order (Hooke’s law) binding forces, so that we expect the infrared dynamics to be defined on the viscoinertial regime $q \in [1, 2]$ in plot 1(b). This is precisely the behavior of the data and the model. The Drude component is also necessarily restricted to this regime, since it derives explicitly from a differential force balance expressed in this domain. The anomalous component, on the other hand, exits the viscoinertial regime at $\lambda \approx 1.78 \mu m$ and enters the viscoelastic regime $q \in [0,1]$. This is indicative of the previously noted quasi-bound state behavior. It is also made evident by inspection of the GDO plot that a global characteristic of the anomalous term is to apply a dissipative correction—that is, away from the conservative inertial boundary toward the dissipative viscous boundary—to the pure Drude component.

In the susceptibility plot 1(a), the Drude component is observed to play the dominant role at longer wavelengths, while the anomalous component contributes more substantially at shorter wavelengths (i.e., the disorder-based component is driven by higher frequency field oscillations). In the viscoelastic regime, the real part of the anomalous susceptibility acquires a sign inversion which reduces the amplitude of the real Drude susceptibility to arrive at the total in-phase modeled response. The appropriate interpretation for this behavior is that of a disorder-based screening applied to the in-phase component of the ideal free-electron dynamics, the effect of which is primarily evident at intermediate wavelengths. With respect to nickel, one may also interpret this as characterizing the activation of the lower lying d-orbital valencies at smaller wavelengths. Plots 1(b) and 1(d) depict the complex refractive index and the spectral normal emissivity, respectively. The temperature- and wavelength-dependent model used to generate the profiles is the same that we describe in detail in Sec. III. The model accurately reproduces emissivity profiles at eight temperatures spanning four distinct studies, so that its capacity for explaining the experimental data is not limited to the results portrayed in Fig. 1.

The significance of the tunable field memory decay is more completely characterized in Fig. 2, where we have once more plotted the susceptibility and GDO of the total model (12) at $T = 4K$ for the values $\mu \in \{0, 0.2, 0.4, 0.6, 0.8, 1\}$. The wavelength range in this plot has been extended to the far infrared. In the model, the characteristic wavelengths of the two terms are related by $\lambda_1 = \alpha \lambda_2$, with $\alpha = 0.0588$ indicating over an order of magnitude separation between the time constants of the differing terms.

When $\mu = 0$, the model is comprised of two superposed, dynamically similar Drude terms. In this case, the GDO has a qualitative character similar to that of a single Drude term: in the long-wavelength limit, the effective mass has an infinitely long time to equilibrate to the field, so that only the damping effects are important and $q \rightarrow 1$ (in the case of an interband oscillator, this low-frequency asymptotic would instead be $q \rightarrow 0$ due to the Hooke’s law term). At smaller wavelengths, Newton’s law inertial effects dominate the high-frequency particle-field interactions, so that $q \rightarrow 2$. As $\mu$ is increased, indicating that the memory of the anomalous term acquires a decaying character due to increased field disorder, a secondary dissipative minimum develops in the GDO at $\lambda \approx 1 \mu m$. This induces an inflection in the profile of the absorptive susceptibility component. Due to the relatively large separation in the timescales of the model components, variation in $\mu$ has little effect on the long-wavelength performance of the model, which is primarily determined by the more well-ordered and temperature-dependent Drude response, as discussed further on.

### III. APPLICATION TO NICKEL

We demonstrate the utility of the proposed model by applying it to nickel, a metal that is encountered in a wide variety of common applications. Nickel is an appropriate choice for the present study due its multivalent electron configuration $[\text{Ar}]3d^{8}4s^{1}$, which gives rise to an augmented absorption profile—that is, with respect to the predictions of the free electron model—in the small-wavelength portion of the intraband regime. In this regime, band theory predicts activation of valencies in the lower lying $d$ subshell.

The data, analysis, and results presented here expand considerably on those presented in our earlier preliminary investigation. Data for the emissivity of nickel is compiled from three separate studies. The data are defined over the approximate spectrum $\lambda \in [1, 16] \mu m$ and consist of measurements taken at seven temperatures, $T = \{4, 305, 583, 722, 1083, 1238, 1403\} K$. The high purity, polished samples represent an ideal Fresnel surface in the sense that models derived from a set of physically meaningful constraint equations should be capable of a smooth, continuous description of the data. Such models can then be directly interfaced with more elaborate Fresnel frameworks one typically uses when modeling, for example, rough surfaces (e.g., statistical optics).

#### A. Implementation

Development of a mid-infrared wavelength- and temperature-dependent emissivity model for nickel is achieved principally in two steps: (i) the permittivity model of (15) is fit independently to the relevant data under the established physical constraints, and (ii) a functional form for the temperature-dependent parameters is established from the independent fits. Replacing the
FIG. 1. Model component analysis at \( T = 4 \) K. In (a) and (c): complete model (solid lines), Drude component (long-dashed lines), anomalous component (short-dashed lines), and data (markers).\(^{33,34}\) In (a): \( | - \chi' | \) (dark, blue) and \( \chi'' \) (light, orange). In (b): \( n \) (dark, blue) and \( k \) (light, orange). The overall effect of the anomalous component in (c) is to apply a dissipative correction to the pure Drude response. The anomalous term leaves the viscoinertial (\( i.e., \) free-carrier) regime defined by \( q \in [1, 2] \) (light region) and enters the viscoelastic regime \( q \in [0, 1] \) (dark region). This indicates the existence of a quasi-bound state character and explains the attenuated amplitudes of both the real and imaginary parts of the anomalous term at longer wavelengths, where the Drude term dominates. In the viscoelastic regime, the anomalous susceptibility applies a positive correction to the negative real Drude susceptibility. This represents a disorder-based screening of the overall in-phase response. For nickel, the augmentation at lower energies characterizes the contribution due to activation of lower lying d-orbital valencies. As demonstrated in the results section of this work, the model used to produce the \( T = 4 \) K profiles in these plots accurately reproduces the nickel emissivity data for eight temperatures spanning four distinct studies using only temperature and wavelength as inputs, so that the results implied here generalize beyond the \( T = 4 \) K measurements.

dependently fit components with the functional material parameters then constitutes a decoupling of the model from the data. Ideally, the parameters for our model would be obtained by purely systematic means. To do so, however, would mean disregarding certain implicit and rather obvious modifications to the procedure that are made evident by heuristic analyses. We describe these modifications presently.

Within a fixed model structure, the task of reproducing emissivity data taken at higher temperatures is more robust to variation in the temperature-independent components—that is, those characterizing the field perturbations as well as the fixed-ratio constraints we have previous established. In order to reduce parametric uncertainty, we therefore include the requirement that the data used to obtain these quantities should sufficiently exercise the full complexity of the model. For this reason, we have obtained these values using the data at the lowest two temperatures (which also have the greatest bandwidth). Physically, this is tantamount to the idea that the temperature-independent parameters can be more accurately determined in the absence of phononic lattice distortion imposed at higher temperatures.

Throughout the procedure, we fix the core contribution to \( \varepsilon_c = 4.396 \). This was obtained from a model in our previous study,\(^{11}\) where the interband dynamics were realized in terms of our previously derived bound oscillator model.\(^{39}\) Application of (17) to that model yields the constant contribution, which represents contributions from bound states having resonant wavelengths much smaller than the smallest wavelength of the modeled band, \( \lambda = 1 \) \( \mu \)m. The temperature-dependent parameters are determined independently from the respective data sets at each temperature. This is done after first
determining and then fixing the resulting temperature-independent model constraints. Subsequent to these steps, it was discovered that

$$\alpha(T) \sigma_\gamma(T) = \frac{n_d e^2}{m^*} \alpha(T) \tau_c(T) \approx \text{constant.} \quad (28)$$

That is, by permitting thermal-dependence of the time constant scaling law, optimal values for this parameter regressed over seven independent data sets suggest the temperature-independent anomalous time constant, $\tau_n = \alpha \tau_c$.

It’s remarkable that Roberts observed similar behaviors in his five-term (three unbound terms, two bound terms) model despite the fact that his model was obtained by “manual fitting” methods over the more restricted NIR range $\lambda \in [0.365, 2.65] \mu$m included in his measurements.\(^\text{31}\) In his study, Roberts was unable to uniquely determine the parameters in the constant ratio $\sigma_\gamma/\lambda$, and was therefore forced to assume theoretical predictions for the DC electrical conductivity. Fortunately, we have at our disposal several resources that allow us to more fully characterize this behavior entirely in terms of the optical response. These include data obtained at helium temperatures ($T = 4$ K), data that exhaust the full range of mid-infrared wavelengths, and modern nonlinear programming techniques that make it possible to ensure the optimality of our fits (inclusive of any desired physical constraints). Enforcing the constraint implied by (28) and then once more optimizing the independent fits yields the temperature-conductivity pairings at each experimental temperature. The determination of these pairings represents the completion of step (i) in the model application procedure.

Step (ii) involves regressing the temperature-dependent parameters in order to arrive at a sensible form of the corresponding material function(s). The only remaining temperature-dependent parameter is the photonic conductivity, which has been expressed as the photonic resistivity $\rho_\gamma = 1/\sigma_\gamma$ since the latter can be more concisely formulated in terms of the underlying physics:

$$\rho_\gamma(T) = \rho_r + \rho_T(T). \quad (29)$$

The appropriateness of this form derives from the fact that the relaxation time is inversely proportional to the linearized collision integral in the BRTA, so that this proportionality extends to a linear superposition of independent scattering processes.\(^\text{14}\) This approximation is commonly known as Matthiessen’s rule. In real materials having lattice defects and impurities, one has a residual resistivity $\rho_r > 0$ that is independent of temperature. The temperature-dependent contribution $\rho_T$ arises due to electron-phonon coupling, with the phononic lattice response being directly dependent on temperature. The temperature-dependent resistivity is often expressed by combining Matthiessen’s rule with the Bloch-Grueneisen integral. For the data used in this study, we have found it useful to express the power-law dependence

$$\rho_T(T) = \rho_{\text{ref}} (T/T_{\text{ref}})^k, \quad (30)$$

where $\rho_{\text{ref}} = 0.092 \mu$ohm-m is the resistivity returned at the reference temperature $T_{\text{ref}} = 293$ K, and $k = 1.601$. The corresponding residual resistivity is $\rho_r = 0.099$. The power law (30), realized in terms of the foregoing values, grants closure to the application procedure and to the model since it is in good agreement with correlations reported in the literature for nickel.\(^\text{40}\)

B. Analysis of Results

The main result of this work is the seven-degrees-of-freedom model obtained by combining (15), (29), and (30) with the temperature-independent parameters from Tbl. I. Coupling this result with the relevant theory from Sec.IIA then yields a suite of closed-form expressions
that provide a full characterization of the temperature-dependent radiative and optical responses of nickel over the infrared band \( \lambda \in [1, 16] \) \( \mu \text{m} \) and for temperatures over the approximate range \( T \in [0, 1400] \) K.

Examples of closed-form, temperature-dependent spectral emissivity models for nickel are sparsely represented in the literature. Models that accomplish this task over the ranges of temperatures and wavelengths investigated here appear to be virtually nonexistent. One model that attempts to achieve this goal is the spectral normal emissivity correlation provided by Edwards and Bayard de Volo, which we abbreviate as the EBdV model. The EBdV model was derived by asymptotic analysis of the Drude-Roberts two-carrier model and applied directly to emissivity measurements taken at \( T = \{305, 583, 722\} \) K. Since these measurements constitute three of the data sets used in the present study, we expect their model to yield a competitive fidelity for at least these three sets. The performance of each model is investigated graphically in Fig. 3. The corresponding error associated with each model is quantified in Tbl. II for the respective data sets.

### TABLE II. Comparison of modeling error for the temperature-dependent emissivity models in the plots of Fig. 3.

<table>
<thead>
<tr>
<th>( \varepsilon )</th>
<th>( \rho )</th>
<th>( \rho_\text{ref} )</th>
<th>( k )</th>
<th>( \rho_\text{ref} )</th>
<th>( \lambda_f )</th>
<th>( \mu )</th>
<th>( \kappa )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 4.396 )</td>
<td>0.099</td>
<td>0.092</td>
<td>1.601</td>
<td>1.684</td>
<td>2.808</td>
<td>0.593</td>
<td>0.248</td>
</tr>
</tbody>
</table>

The EBdV model performs approximately as expected, yielding meaningful results only for the data from which the model parameters were originally regressed. Regardless, the bulk error metrics in Tbl. II—as well as the point-by-point relative residuals in Fig. 3—indicate that the proposed model yields a substantial improvement for six of the seven data sets. With respect to each of the helium temperature data, the fidelity of the proposed model yields roughly an order of magnitude improvement over the EBdV model.

It is possible that the performance of the EBdV model might be somewhat improved by regressing the model structure over all of the data sets included here. However, the relative residuals accumulated at very low (very high) temperatures and long (short) wavelengths will remain mostly unaffected. At higher temperatures, this is due to the artificial imposition of a cross point (or X-point), which causes large residuals at small wavelengths where the model is unnaturally forced toward an intersecting value. An X-point is the wavelength-emissivity pairing \( \epsilon(\lambda_X, T) \) in the spectral thermophysical emissivity of the medium such that

$$\frac{\partial \epsilon(\lambda, T)}{\partial T} \bigg|_{\lambda=\lambda_X} \approx 0 \quad \forall T. \quad (31)$$

The nonexistence of “true” X-points has been discussed at length within a band-theoretical framework. In fact, these “points” are more accurately described as finite regions and are related to nearly invariant transitions within small specific wavelength ranges resulting in approximately intersecting emissivity isotherms. That is, these regions occur somewhat by happenstance as a result of the specific lattice (and defect) composition (and resulting band structure) rather than by any distinct mechanism. As such, these regions, if observed in the model, should ideally arise naturally from the model mechanics rather than by explicit imposition. As evidenced in Fig. 3, this behavior is more naturally expressed in the proposed model, where \( \lambda_X \approx 1.5 \mu \text{m} \).

At very low temperatures (i.e., much lower than the Debye temperature), the large accumulation of error in the EBdV model is due to the embedded assumption of an ideal lattice, which does not account for the residual resistivity that is present in real materials. Due to the fact that the EBdV model is realized as a normal emissivity model, it lacks phase information and is therefore also incapable of providing estimates for the spectral directional emissivity. We expand upon our foregoing analysis by plotting in Fig. 4 the surface representing the normal spectral reflectivity generated by the proposed model over the valid temperature range.

The nontrivial structure of the multivariate model reflectivity is made immediately apparent by comparison of the low- and high-temperature profiles, and by examination of the interpolatory surface marrying these extremes. Inspection of the plot reveals that the profile is fundamentally generated by two asymptotic behaviors that are joined at low temperatures by a corner-wavelength of roughly 6 \( \mu \text{m} \). As the temperature is increased, the primary effect of the temperature-dependent lattice distortion is to apply a smoothing effect about the corner-wavelength that leads, at higher temperatures, to a semiparabolic spectral reflectivity profile. Included in the plot are experimental values for the spectral normal reflectivity computed from the ambient temperature (we assume \( T = 294 \) K) measurements of Ordal et al. [44]
FIG. 3. Comparison of temperature-dependent spectral emissivity models. In plot (a): the model of Edwards and Bayard de Volo. In plot (b): the spectral normal emissivity realized by combining the proposed model in Eqs. (15)–(17), (29), and (30) with the optical and radiative relations in Eqs. (19) and (25). Parameters for the proposed model are given in Tbl. I. The model in plot (a) was originally developed for and applied to the data for $T = \{305, 583, 722\}$ K. The relative error for the proposed model in plot (b) is everywhere less than 10%.

FIG. 4. Multivariate reflectivity of nickel. The surface is generated by combining the proposed seven-degrees-of-freedom model in Eqs. (15)–(17), (29), and (30) with the optical and radiative relations in Eqs. (19), (23), and (25). Parameters for the proposed model are given in Tbl. I. Black markers indicate data from which the model parameters were regressed. Gray markers indicate reflectivity computed from the complex-valued optical measurements obtained by Ordal et al. which are available over a broadband infrared regime $\lambda \in [1, 286]$ µm. Although the procedure used to prepare the sample (if any) is not discussed in that study, we can at least confirm that the sample purity is commensurate with the previously established guidelines. As demonstrated in the figure, the model accurately reproduces the reflectivity profile over the entire spectral range.

We bring our analysis full circle in Fig. 5, where the model has been used to generate an estimate of the complex-valued material properties at $T = 294$ K. We note that, aside from the $T = 4$ K data, all data used to develop the model were collected as real-valued emissivity measurements and therefore lack complex phase information. Nonetheless, the model possesses structural fidelity in both settings (optical and radiative) and is therefore capable of producing meaningful estimates. In other words, the figure portrays an extrapolatory estimate in the complex-valued optical space supported by the model structure determined in the real-valued space of the emissivity. This functionality of the model—that is, to estimate phase information from real-valued measurements—provides a suitable alternative to other such methods for doing the same (e.g., Kramers-Kronig analysis). Furthermore, since the template formalism from which the thermophysical model was derived has been previously shown to adhere to the Kramers-Kronig relations, we are assured that the same is true for estimates produced by the proposed model at any tempera-
ture in the prescribed range.

IV. CONCLUDING REMARKS

Design objectives involving the radiant exchange of electromagnetic fields require practical modeling approaches that reproduce the optical or radiative properties, often with prescribed levels of accuracy. Optical response models characterize the dispersion of electromagnetic waves through and between the participating media. These models typically take the form of complex-valued macroscopic functions of radiative wavelength whose origin is a microscopic governing equation. Surface radiative properties, on the other hand, are real-valued quantities that characterize the balanced exchange of energy at relevant interfaces. By applying conditions of continuity at the interfaces, one obtains the Fresnel relations relating the optical and radiative properties.

A practical, design-oriented approach is one that leads to a relatively low-complexity characterization of these properties in terms of a complex-valued macroscopic model, which nonetheless yields estimates of high enough fidelity to be useful in an applied setting. With respect to the technically-significant free-electron response of metals—corresponding, approximately, to the infrared regime—one of the earliest and most widely recognized approaches is that given by Drude over a century ago. Despite the relative fidelity provided by the Drude model in many idealized scenarios, there are a great number of practical situations where the model is insufficient to explain the experimental data. The issue is further complicated when one is also interested the temperature dependence of the material response. One reason for this is that not all spectrally-dependent responses that contribute significantly to the overall behavior possess a nonzero thermoderivative. The total response is comprised of dynamics that necessarily behave independently and non-uniformly as a function of temperature and wavelength. This is often the case for metals representing even a modest departure from the free-electron theory. That this is so is also evidenced by the relative sparse availability of such parsimonious models in the literature, despite their practical value.

Here we have addressed this problem by generalizing a Drude(-Langevin) transport equation to account for departures from the free electron model. The modification interprets these departures as anomalously diffusive particle-field interactions expressed in terms of temporally nonlocal field relaxations. Standard results and theory—such as, e.g., Boltzmann carrier transport, Matthiessen’s approximation, and the Bloch-Grüneisen equation—were leveraged to impart thermodynamics unto the anomalous carrier transport equation in a physically meaningful way. The practical efficacy and physical coherence of the resulting structure has been demonstrated by applying the model to nickel, a material known to deviate substantially from the free electron model due to its nontrivial valence configuration. Aside from the theoretical considerations, nickel is also an ideal candidate due to its wide use in applied contexts.

A systematic approach for determination of the model parameters from experimental data has been described. We demonstrate that the resulting seven-degrees-of-freedom model significantly outperforms previously proposed models, reproducing eight sets of measurements spanning four separate studies. The experimental data sets correspond to an approximate spectral bandwidth \( \lambda \in [1, 16] \mu m \) and an approximate temperature range \( T \in [0, 1400] \) K. The accuracy of the model is such that it is amenable for use in applied (e.g., design-oriented) contexts. Furthermore, although only one of the data sets used to develop the model includes complex-valued phase information, procedural regression of the model parameters, along with the physically motivated structure and thermal dependence, make it possible to form inverse estimates of phase information (i.e., at differing temperatures) that neither require a corresponding Kramers-Kronig analysis, nor the usual high- and low-frequency extrapolations.

Appendix A: Temporal Asymptotics of the Stretched Mittag-Leffler Relaxation

Combining the Mittag-Leffler function\(^{16}\) with the stretched exponential form of the Kohlrausch-Williams-Watts (KWW) dielectric relaxation model\(^{45,46}\) one arrives at the more general decay structure given by

\[
E_\mu(-t/t_\gamma)^\mu = \sum_{n=0}^{\infty} \frac{(-t/t_\gamma)^\mu^n}{\Gamma(\mu n + 1)}, \quad (A1)
\]

which we refer to as the stretched Mittag-Leffler relaxation (SMLR). The SMLR generalizes the conventional exponential decay such that one recovers \( \exp(-t/t_\gamma) \) when \( \mu = 1 \), a fact that is readily confirmed on examination of (A1). When \( t_\gamma \) is a bounded positive value, the long-time behavior of the SMLR is such that:\(^{47}\)

\[
\lim_{t \to \infty} E_\mu(-t/t_\gamma)^\mu = \frac{(t/t_\gamma)^{-\mu}}{\Gamma(1 - \mu)}, \quad (A2)
\]

so that this recovers expression (7) for the memory kernel, \( K(t) \). When the domain of \( \mu \) is that of the model described in this work, uniform convergence of the history integral yields the result:

\[
\lim_{t \to -\infty} E_\mu(-t/t_\gamma)^\mu \star \frac{d\mathcal{E}(t)}{dt} \equiv \lim_{t \to -\infty} t^{\mu} \frac{d^\mu \mathcal{E}(t)}{dt^\mu}, \quad (A3)
\]

where the fractional Leibniz notation on the right-hand side implies either of the Caputo or the Riemann-Liouville fractional derivative definitions, since these are equivalent as \( t \to \infty \).\(^{16}\) Thus, within the more general framework that utilizes the SMLR as the decay kernel, one nonetheless recovers (8) in the stationary limit.

FIG. 5. Real (dark, blue) and imaginary (light, orange) parts of the susceptibility (a) and the refractive index (b) for nickel. The lines for $T = 4$ K (solid) and $T = 294$ K (dashed) were generated with the proposed seven-degrees-of-freedom model in Eqs. (15)–(17), (29), (30), and (19), realized with the parameter values listed in Tbl. I. The markers indicate measurements taken at $T = 4$ K (filled) and $T = 294$ K (open). The complex-valued response model evaluated at $T = 294$ K represents an estimate of the experimental data at that temperature.


