# Thermophysical Model for the Infrared Emissivity of Metals

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**We derive a thermophysical model for the infrared radiative response of common metals by modifying a recently proposed model to account for the presence of thermally driven dynamics. The temperature-dependence of our model is built upon the consistency of the equation of motion with the predictions of the relevant equilibrium theory for temperature-dependent carrier transport. The model parameters are systematically regressed over data representing a range of temperatures. The resulting model is valid over the approximate spectral range $\lambda \in [1, 16]$ μm and for the approximate temperature range $T \in [300, 700]$ K. Since the model is expressed as a complex-valued frequency response function, it can be directly incorporated into the Fresnel relations for use with more general optical and radiative frameworks.**

## I. Introduction

A first principles approach to dealing with design problems involving radiative transfer is one that considers the microscopic mechanisms that determine the macroscopic response. For the intraband response of conductive media—the primary focus of this work—the archetypical example of this methodology is the model proposed by Drude over a century ago [1]. At its most fundamental level, the Drude model is one that attempts to reconcile, from a microscopic viewpoint, the dynamics of free electrons. The Drude model may be interpreted as an ensemble realization that leads to complex-valued optical properties of interest. By applying the appropriate conditions of continuity at the interface between two media, one can describe the fraction of absorbed and reflected radiation in terms of these optical properties. The values that result from doing so are known as the Fresnel coefficients. When the Fresnel coefficients are known, the radiative parameters at a given point along the interface are readily computed.

The spectral range of the free-carrier response of metallic conductors corresponds roughly to the infrared spectrum. Models of the infrared optical response of metals are useful in a number of contexts ranging from the development of signature suppressing metamaterials [2] to the design of nanoscale IR antennas [3]. Likewise, models for the infrared temperature-dependent radiative properties of metals find a wide range of uses, such as predicting the effect of radiative forcing on heat shielding [4] and aiding in the development of reliable jet engine componentry [5]. In many practical situations, however, the Drude model fails to explain the detailed responses observed in experimental settings [6–10].

The problem of modeling these responses is accentuated when one seeks to characterize property variations as a function of temperature. This is due, in part, to the fact that not all spectrally dependent dynamics are driven by thermal excitations. A given spectrally resolved thermophysical model must therefore account for mechanisms that respond independently to variations in wavelength and temperature. In this work, we propose a model to accomplish this goal and illustrate its use by applying it to data for nickel, a transition metal whose infrared response exhibits complex dynamics.

## II. Theory

Drude's model for the free-carrier response of a bulk metallic solid to incident radiation derives from a microscopic equation of motion governing the behavior of an individual carrier. This has the Langevin form [11, 12]:

$$m^* \frac{dv(t)}{dt} + \zeta\, v(t) = q\, \mathcal{E}(t) + q\, \eta(t), \tag{1}$$

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where $v$ is the velocity of a carrier having an effective mass $m^*$, $\zeta = m^*/\tau_c$ is a damping related to momentum-randomizing scattering interactions occurring with an average period $\tau_c$, and $q$ is the elementary charge. In this description, $\mathcal{E}$ represents the ordered local field and we have modeled the noise force, $F_\eta = q\,\eta$, as resulting from random zero-mean local field noise, $\eta$.

The thermophysical modeling approach is one that extends our previously derived framework for the description of anomalous dynamics over a broadband infrared spectrum [13]. Here we have defined "anomalous" to mean intraband dynamics that represent a systematic departure from the Drude theory. The anomalous model accounts for these departures by generalizing the local field disturbance:

$$\widetilde{\eta}(t) = \int_{t_0}^{t} \mathcal{H}(t-s)\,\frac{d\mathcal{E}(s)}{ds}\,ds + \eta(t). \tag{2}$$

The history integral in Eq. (2) may be understood by considering an impulsive perturbation, for which the integral records a history of the change rates of the field as it relaxes to equilibrium. This history is shaped by the dimensionless history kernel, $\mathcal{H}$. The particular history kernel was chosen to balance the need for model performance with the desire for a succinct description:

$$\mathcal{H}(t) = \frac{(\tau_f\,/\,t)^\mu}{\Gamma(1-\mu)}, \tag{3}$$

where $\tau_f$ is the characteristic time of field relaxation, $\Gamma(\,\cdot\,)$ is the gamma (generalized factorial) function, and $\mu \in [0, 1)$ represents the strength of field memory decay. When $\mu = 0$, the local field has "perfect memory" of the fluctuation. Whenever $\mu > 0$, the field fluctuation exhibits an asymptotic relaxation with a decay strength dependent on the value of $\mu$. When $\mu \to 1$, the history kernel behaves as a Dirac delta, $\delta(t)$, which describes the process associated with a "perfectly forgetful" local field (*i.e.*, Markovian relaxation). After combining Eqs. (2) and (3), substituting the result into Eq. (1), and then taking the ensemble average, $\langle\,\cdot\,\rangle$, one arrives at the macroscopic carrier transport model

$$\tau_c\,\frac{dj(t)}{dt} + j(t) = \left(\frac{n_d\,q^2\,\tau_c}{m^*}\right)\left(E(t) + \tau_f^\mu\,\frac{d^\mu E(t)}{dt^\mu}\right), \tag{4}$$

where $\langle\eta\rangle = 0$, $\langle v\rangle = j/n_d\,q$, $\langle\mathcal{E}\rangle = E$, and $n_d$ is the number density.

In order to extend Eq. (4) to account for temperature effects, we consider a temperature-dependent conductivity. This is motivated, *e.g.*, by the solution to the Boltzmann equation in the Relaxation Time Approximation (BRTA) [12, 14]:

$$\sigma_\gamma(T) = \frac{n_d\,q^2}{m^*}\tau_c(T), \tag{5}$$

where the temperature-dependence of the relaxation time derives from the collision integral in the BRTA equation. The temperature-dependence in Eq. (5) is obtained empirically from experimental observations in Sec.III.A.

To account for the possibility of superposed macroscopic anomalous carrier dynamics in localized regimes that may be distinct from the bulk Drude behavior, we assume a single effective carrier type with a relaxation time that may, in general, be modified in the anomalous regimes. For this purpose, we introduce the dimensionless scaling parameter $\alpha(T)$ and define $\tau_a = \alpha\,\tau_c$. Under a Fourier transform, the transport model then leads to the wavelength-dependent susceptibility model

$$\chi_\phi(\lambda, T) = \chi_d(\lambda, T) + \chi_a(\lambda), \tag{6}$$

where we have set $\alpha(T)\,\tau_c(T) =$ constant in accordance with empirical observations described further on. The Drude contribution is

$$\chi_d(\lambda, T) = -\frac{\lambda^2}{2\,\pi\,c_0\,\varepsilon_0}\left(\frac{\sigma_\gamma(T)}{i\,\lambda + \lambda_\gamma(T)}\right), \tag{7}$$

where $\lambda_\gamma = 2\,\pi\,c_0\,\tau_c$, $c_0$ is the speed of light in a vacuum, and $\varepsilon_0$ is the permittivity of free space. The anomalous contribution is

$$\chi_a(\lambda) = -(-i)^\mu\,\frac{\lambda^2}{2\,\pi\,c_0\,\varepsilon_0}\left(\frac{\lambda_f}{\lambda}\right)^\mu\left(\frac{\sigma_a}{i\,\lambda + \lambda_a}\right), \tag{8}$$

with $\lambda_a = 2\,\pi\,c_0\,\tau_a$ and $\sigma_a = n_d\,q^2\,\tau_a/\,m^*$ defining the anomalous relaxation wavelength and anomalous conductivity, respectively. In the frequency domain setting, the parameter $\mu$ is best understood as a tuning parameter for the energetic partitioning of the anomalous term. The energetic partitioning property of nonlocal models has been recently described in detail [15]. The conductivity relation in Eq. (5) implies physical constraints that are observed when regressing the model parameters: $\sigma_\gamma\,/\,\lambda_\gamma = \sigma_a\,/\,\lambda_a =$ constant. The relative permittivity is then given by the relation $\varepsilon = 1 + \chi$:

$$\varepsilon(\lambda, T) = \varepsilon_\beta + \chi_\phi(\lambda, T), \tag{9}$$

where $\varepsilon_\beta$ is the contribution from higher energy bound states [16]. Here we have assumed that the characteristic timescales of the interband dynamics and the intraband dynamics are well separated. Accordingly, $\varepsilon_\beta$ may be approximated as a real constant over the infrared band of interest, $\lambda \gtrsim 1$ μm.

### A. Optical and Radiative Properties

The refractive index is directly related to the permittivity:

$$\widetilde{n} = \sqrt{\varepsilon}, \tag{10}$$

where $\widetilde{n} = n + i\,k$, and with $n$ being the dispersive index and $k$ being the absorptive index. When coupled with Fresnel's relations, the refractive indices can be used to obtain the relevant radiative properties. For an optically smooth metal at thermodynamic equilibrium emitting into free space, the spectral normal emissivity is

$$\epsilon_n = \frac{4\,n}{(n+1)^2 + k^2}, \tag{11}$$

which is valid along any spectral band.

## III. Application to Nickel

Nickel is an ideal candidate for this study since it is a commonly used material in engineering applications that also has the nontrivial valency [Ar] $3d^8\,4s^2$. In nickel, band theoretical calculations predict absorption in the near-infrared response as a direct result the lower level d-orbital valencies, which become active at higher energies [17]. The overall effect of this is a distortion of the ideal profile generated by the Drude-Sommerfeld model, leading to a profile determined in part by an anomalous component.

The data used in this study were taken from the study of Edwards and Bayard de Volo [4]. They measured the emissivity of nickel at room temperature and at higher temperatures using a heated cavity directional reflectometer. The study provides measurements over the mid-infrared regime corresponding approximately to $\lambda \in [1, 16]$ μm and at the temperatures $T \in \{306, 583, 722\}$ K. The samples were polished to ensure a smooth surface prior to experimentation.

### A. Implementation

The model parameters are realized in three steps. At each step requiring regression, the parameters were obtained by minimizing Pearson's chi-squared objective [18]. The first step determines the temperature-independent parameters by regressing these on the data obtained at the lowest available temperature, $T = 306$ K. This is done to reduce uncertainty caused by the dominant lattice absorption at higher temperatures. The second step involves fixing the temperature-independent parameters, and then regressing the temperature-dependent parameters for each data set independently. The third-and-final step involves extracting a material function—the temperature-dependent conductivity—from the independently regressed parameter sets.

At each step in the fitting procedure, the bound state contribution is fixed to $\varepsilon_\beta = 4.396$. This value is determined from the long-wavelength limit applied to the bound electron portion of the model in [10], which was obtained in terms of our recently derived, physically consistent bound oscillator model [19]. After determining and then fixing the resulting temperature-independent model constraints, the remaining temperature-dependent parameters are regressed on each data set independently. Subsequent to this step, it was found that

$$\alpha(T)\,\sigma_\gamma(T) \;\propto\; \alpha(T)\,\tau_c(T) \approx \text{constant}. \tag{12}$$

In other words, by explicitly allowing the anomalous time constant scaling law to be temperature-dependent, the optimal values for this parameter obtained on independent data suggest a temperature-independent time constant, $\tau_a = \alpha\,\tau_c$, in anomalous regimes.

In lieu of modeling the conductivity directly, we obtain an expression for the resistivity $\rho_\gamma = 1/\sigma_\gamma$. This is done since the latter is more aptly expressed in terms of the underlying physics:

$$\rho_\gamma(T) = \rho_r + \rho_T(T). \tag{13}$$

This form is appropriate since the resistivity is proportional to the collision integral in the BRTA. This proportionality extends to superpositions of independent scattering mechanisms [12], a property which is more commonly known as Matthiessen's rule. The temperature-independent residual resistivity $\rho_r > 0$ is due to lattice defects, while $\rho_T$ arises due to electron-phonon interactions, the latter being strongly temperature-dependent. The phononic contribution is accurately described by the power-law relation

$$\rho_T(T) = \rho_{\text{ref}}\,(T\,/\,T_{\text{ref}})^k, \tag{14}$$

where $k = 2.140$, and $\rho_{\text{ref}} = 0.072$ μohm·m denotes the value obtained at a reference temperature $T_{\text{ref}} = 306$ K. The residual resistivity is $\rho_r = 0.1134$.

### B. Analysis of Results

The central result of this study is the seven-degree-of-freedom model obtained by combining Eqs. (6) – (9), (13), and (14) with the parameters listed in Table 1. Coupling the model with Eq. (11) then yields the normal spectral emissivity of nickel over the mid-infrared regime $\lambda \in [1, 16]$ μm and for the approximate temperature range $T \in [300, 700]$ K.

**Table 1 Parameters for the proposed model applied to nickel. The model is obtained by combining Eqs. (6) – (9), (13), and (14). Units of resistivity are μohm·meter. Units of wavelength are μm. The high-frequency bound state contribution and the memory decay parameter are both dimensionless. The scaling parameter $\kappa = n_d\, q^2 / 2\,\pi\, c_0\, \varepsilon_0\, m^*$ is used with the physical constraints $\sigma_\gamma\,/\,\lambda_\gamma = \sigma_a\,/\,\lambda_a = \kappa$ to compute the remaining characteristic wavelengths.**

| | Drude | | | Anomalous | | | |
|---|---|---|---|---|---|---|---|
| $\varepsilon_\beta$ | $\rho_r$ | $\rho_{\text{ref}}$ | $k$ | $\rho_a$ | $\lambda_f$ | $\mu$ | $\kappa$ |
| 4.396 | 0.113 | 0.072 | 2.140 | 3.932 | 33.389 | 0.276 | 4.697 |

Few examples of closed-form, temperature-dependent spectral emissivity models for nickel are found in the literature. For this reason, we appeal to the spectral normal emissivity model provided by Edwards and Bayard de Volo [4], which we refer to as the EBdV model. The EBdV model was obtained from a detailed reductive analysis of the Drude-Roberts model [6]. Its parameters were regressed directly from the emissivity data used in the present study. Thus, we expect the EBdV model to provide a competitive baseline for assessment of our model. The performance of both models is displayed in Fig. 1. The error for each model is given in Table 2 for each of the respective sets of measurements. The errors given in Table 2—as well as the frequency-dependent relative errors in Fig. 1—demonstrate that the proposed model represents an across the board improvement.

**Table 2 Mean absolute relative error (given in %) for the temperature-dependent emissivity models in the plots of Fig. 1.**

| | 306 K | 583 K | 722 K |
|---|---|---|---|
| EBdV [4] | 5.6 | 6.2 | 6.2 |
| proposed | 1.4 | 5.0 | 5.3 |

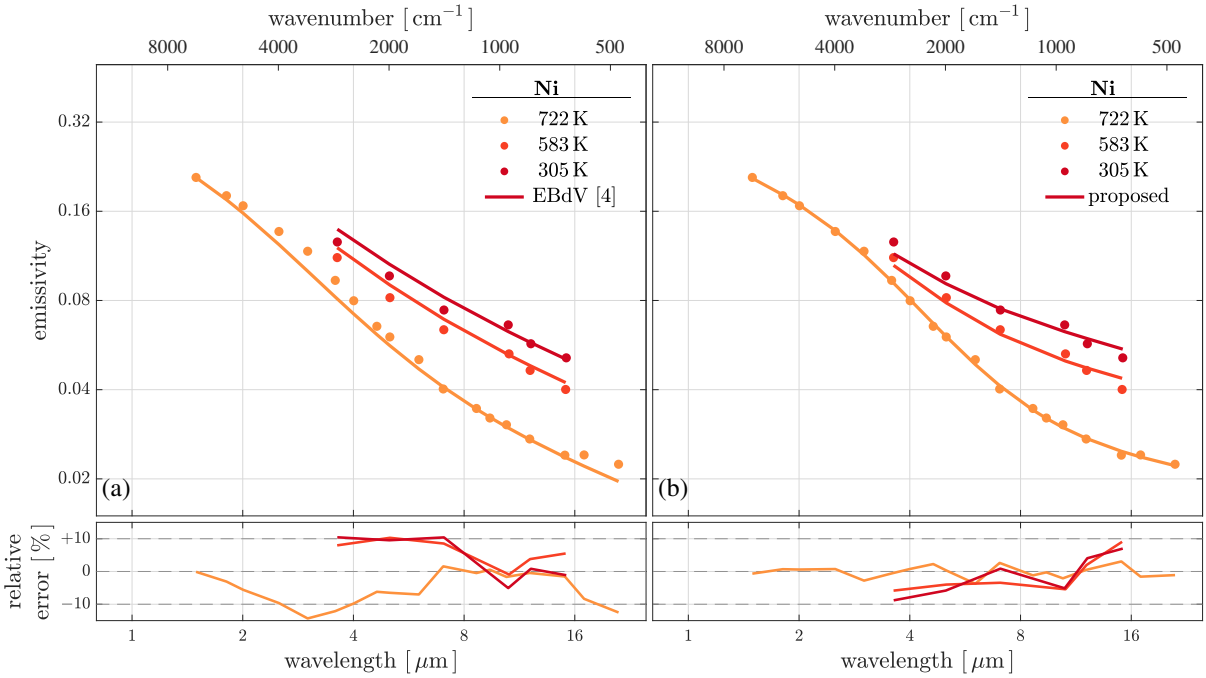


**Fig. 1 Comparison of temperature-dependent spectral emissivity models. In plot (a): the model of Edwards and Bayard de Volo. In plot (b): the spectral normal emissivity Eq. (11) realized with the proposed model. The relative error for the proposed model is everywhere less than 10 %. The parameters for the EBdV model in plot (a) were regressed by the authors of that study directly from the data represented in the plots.**

## IV. Concluding Summary

When dealing with the free-carrier response of conductive media, it is often the case that design constraints can be met from a first-principles approach that involves a low-dimensional microscopic equation of motion. In idealized media, such as monovalent metals over limited infrared regimes, the Drude model is sufficient for characterizing the optical and radiative responses. There are many important circumstances, however, where the Drude model insufficiently explains the experimental data. This issue is further convoluted when one is interested the spectral thermophysical response. One reason for this is that not all spectrally dependent model components have a nonzero thermoderivative over a given band, so that the observed behaviors may represent the result of multiple components that behave independently and nonuniformly as a function of temperature and wavelength. This is often the case for metals representing even a modest departure from the "free-electron" response. That this is so is evidenced by the relatively sparse availability of such models in the literature.

In this work, we have addressed this need by adapting a recently derived temporally nonlocal microscopic model to account for the presence of thermally driven dynamics. The model addresses departures from the free-electron theory by generalizing the Langevin description to account for structured fluctuations in the local field that decay with a nonzero time constant. The nonlocal component permits an imperfect memory of previous relaxed states. The model modification is based on consistency of the nonlocal equation of motion with the equilibrium predictions of the Boltzmann theory for thermal effects on carrier transport. A realization of the model structure has been obtained by systematic regression of the parameters over measurements taken for nickel at temperatures ranging from 306 K to 722 K. The empirical model realization has a multivariate (spectral and thermal) component and an anomalous temperature-independent component. The proposed model outperforms previously proposed models, yielding a mean absolute relative error of less than six percent for each of the data sets and a worst case relative error of less than ten percent on any single data point. Although the results are presented in terms of the spectral emissivity, the first principles origin of the model ensures that its use extends directly to more general Fresnel frameworks.

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