

TRANSIENT ENERGY AND HEAT TRANSPORT IN METALS

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ABSTRACT

A recently developed Shastry formalism for energy transport is used to analyze the temporal behavior of the energy and heat transport in metals. Comparison with Cattaneo's equation is performed. Both models show the transition between ballistic and diffusive regimes. Furthermore, because the new model considers the discrete character of the lattice, it highlights some new phenomena such as oscillations in the energy transport at very short time scales. The energy relaxation of the conduction band electrons in metals is considered to be governed by the electron-phonon scattering, and the scattering time is taken to be averaged over the Fermi surface. Using the new formalism, one can quantify the transfer from ballistic modes to diffusive ones as energy propagates in the material and it is transformed into heat. While the diffusive contribution shows an almost exponentially decaying behavior with time, the non-diffusive part shows a damped oscillating behavior. The origin of this oscillation will be discussed as well as the effect of temperature on the dynamics of the energy modes transport.

INTRODUCTION

Development of high-power short-pulse laser sources with a pulse width in the sub-ps range has provided an opportunity to study the propagation of energy and heat at very short time scales; it has also created many applications in thin film analysis or in material processing. Ultrafast laser sources have made possible the study of many interesting fundamental physical phenomena in condensed matter such as electrons transitions in semiconductors [1, 2], electron-phonon coupling in metals [3-7], and electron dynamics in semiconductor superlattices [8, 9]. Shorter laser pulses in the sub-fs range have recently opened the field to explore electronic interactions within the atom itself [10].

Energy and heat transport during short-pulse laser heating of solid materials is an important phenomenon that needs to be fully understood to better control the abundant applications in

which short-pulse laser sources are used. The question of energy and heat transport mechanisms at short time scales is the basis of numerous theoretical and experimental papers. From the microscopic point of view, energy deposits into and propagates through a material in different ways, depending on the excitation, the structure of the material, and the nature of the energy carriers. At short time scales, Fourier's law becomes invalid and many Non-Fourier energy conduction models have been developed to overcome problems associated with the Fourier model (e.g. infinite speed of propagation of heat) [11-14]. Most importantly, the distinction between diffusive and non-diffusive (ballistic) regimes of energy transport becomes very relevant at these short time scales [15].

Recently, B. S. Shastry has developed a new formalism based on linear theory to describe coupled charge and energy transport in solid material systems [16]. The formalism is general and gives a set of equations for the electro-thermal transport coefficients in the frequency-wave vector domain. One of the most important results of this formalism is the introduction of new response functions describing the change in energy density, charge density, and the currents arising from the input excitation (coefficients M_1 , M_2 , N_1 , and N_2 as defined in the reference article [16]). Among these response functions, N_2 is of particular interest since this new function gives a measure of the change in energy density and hence temperature at various points in the system in response to the applied excitation at the top free surface of the system, and as such represents the energy (heat) Green's function of the system.

The objective of the current paper is to analyze the transient energy and heat transport in a metal occurring after application of a heating source at its top free surface in the frame work of the above mentioned Shastry's formalism. In addition, the analysis will consider a comparison with Cattaneo's model [17], both in time and frequency domains.

NOMENCLATURE

- a : lattice constant (Å).
 C_e : specific heat per unit volume (J/m³/K).
 D_e : electronic thermal diffusivity (m²/s).
 q : electronic wave vector (m⁻¹).
 P : input power (W/m³).
 t : time (s).
 T : temperature (K).
 v_F : Fermi velocity (m/s).
 Z : thermoelectric figure of merit (K⁻¹).
 β_e : electronic thermal conductivity (W/m/K).
 δ : Dirac delta function.
 τ_F : average relaxation time of conduction band electrons over the Fermi surface of a metal (fs).
 ω : angular frequency (rd/s).
 η : nondimensional time.
 δK : energy density (J/m³).
 ϕ_e : heat flux of electrons in the conduction band of the metal (W/m²).
 ξ : charge-energy modes coupling factor.

THEORY

SHASTRY'S MODEL

We follow the same steps of calculations we have performed in a recent paper [18], and the starting point of our analysis will be the Shastry-Green function N_2^S in the decoupled limit for metals. According to Shastry's work [16], the coupling factor ξ between charge and energy modes can be expressed using the high frequency value of the thermoelectric figure-of-merit Z^*T :

$$\xi = \frac{Z^*T}{Z^*T + 1} \quad (1)$$

Here Z^* is the high frequency limit of the Seebeck coefficient square times the electrical conductivity divided by the thermal conductivity. It is well known however; that metals are very poor thermoelectric materials with a very low ZT [19]. The decoupled limit is thus justified. By turning off the coupling between the charge and energy modes ($\xi=0$), N_2^S can be expressed as:

$$N_2^S(\omega, q) = \frac{-i + \tau_q \omega}{\omega + i\tau_q \omega^2 - iD_e q^2} \quad (2)$$

We should note here that Eq (2) is given for an arbitrary applied power function $P(t)$ at the top free surface of a metal. This expression is a generalization of the one given by Shastry in the case of a periodic power function [16]. ω is the angular frequency, q is the electron wave vector, D_e is the electronic thermal diffusivity and τ_q is the total electron scattering time, which, in general, is a function of q . Remarkably, in the case of a q -independent τ_q , the form of N_2^S in the frequency-wave vector domain, resembles the expression of the energy density change at the top free surface of the metal, one would have derived using Cattaneo's model and solving the energy density

equation for electrons in the case of a delta power excitation applied to the same surface. We will discuss Cattaneo's model more in detail in the next section.

In the following we consider a one dimensional energy transport problem, in which case we assume the top metal free surface being excited by an input laser pulse of power $P(t)$. The one dimensional approximation is reasonable at short time scales considering the ratio of the size of the laser pulse spot to the diffusion length which in this case is small on the order of the optical penetration depth. The latter quantity depends on the wavelength of the laser, but it is less than $10nm$ over a large range of wavelengths for most metals [20]. The optical penetration depth becomes even much shorter on the order of $1nm$ if very short wavelengths are used (e.g. UV with a frequency lower than the Plasmon frequency of the corresponding metal) [20]. This is very useful since it validates the assumption we are making of a surface excitation.

After excitation of the top metal free surface with an input power $P(t)$, the change of the energy density in the frequency-wave vector domain $\overline{\delta K_s}(\omega, q)$ can be expressed as [16]:

$$\overline{\delta K_s}(\omega, q) = N_2^S(\omega, q) \times \overline{P}(\omega) \quad (3)$$

where $\overline{P}(\omega)$ is the Fourier transform of $P(t)$ in the frequency domain.. The change of the energy density at the top free surface of the metal as function of time is obtained by a double inverse Fourier transforms with respect to ω and q :

$$\delta K_s(t, 0) = \frac{1}{(2\pi)^2} \int_{-\pi/a}^{\pi/a} \left[\int_{-\infty}^{+\infty} N_2^S(\omega, q) \overline{P}(\omega) e^{i\omega t} d\omega \right] dq \quad (4)$$

The integration over q is taken over the First Brillouin Zone (FBZ) in the one dimensional case, where "a" refers to the lattice constant of the metal. The power source $P(t)$ can be of any form, but we will limit our study to the ideal case of a Dirac delta function $P(t) = P_0 \times \delta(t)$ in order to capture the intrinsic evolution of the energy density $\delta K(t, 0)$ as a function of time: *the temporal behavior of the energy density Green's function at the top free surface of the metal.*

The integral within the square brackets in Eq (4) can be analytically calculated using the residue theorem. As a matter of fact, the integrand of this integral has two single poles that lie in the upper complex half plane. These poles are given respectively by:

$$\omega_{\pm} = i \frac{1 \pm \sqrt{1 - 4D_e \tau_q q^2}}{2\tau_q} \quad (5)$$

A straightforward calculation of the residues at these two single poles leads to:

$$\int_{-\infty}^{+\infty} N_2^s(\omega, q) e^{i\omega t} d\omega = 2\pi e^{-\frac{t}{2\tau_q}} \left[ch\left(\frac{R_q^s t}{2\tau_q}\right) + \frac{sh\left(\frac{R_q^s t}{2\tau_q}\right)}{R_q^s} \right]; \quad (6)$$

$$R_q^s = \sqrt{1 - 4D_e \tau_q q^2}$$

Equation (4) can then be re-expressed as:

$$\delta K_s(t, 0) = \frac{P_0}{2\pi} \int_{-\pi/a}^{\pi/a} e^{-\frac{t}{2\tau_q}} \left[ch\left(\frac{R_q^s t}{2\tau_q}\right) + \frac{sh\left(\frac{R_q^s t}{2\tau_q}\right)}{R_q^s} \right] dq \quad (7)$$

Up to now, the equations are completely general regardless the dependence of the relaxation time on the wave vector. Electron relaxation in the conduction band of metals is governed by two scattering processes; (i) electron-electron scattering process and (ii) electron-phonon scattering process [21]. In most metals, the second process is generally the dominant one and the transport of energy by phonons can be neglected. Using the fact that electrons and phonons in a metal can be characterized by different temperatures, it has been shown that scattering of electron by phonons can be either elastic or inelastic, and the relaxation time is inversely proportional to the lattice temperature [4, 22-24]. In the following, we consider the case of a constant relaxation time $\tau_q = \tau_F$, which we consider to be the average scattering time of electrons over the Fermi surface of the metal. Eq (7) can be split into two parts, depending on the sign of the argument of R_q^s . We can write it down as:

$$\left\{ \begin{array}{l} \delta K_s(t, 0) = \delta K_s^<(t, 0) + \delta K_s^>(t, 0) \\ \delta K_s^<(t, 0) = \frac{P_0}{\pi} e^{-\frac{t}{2\tau_F}} \int_0^{q_0^s} \left[ch\left(\frac{R_q^s t}{2\tau_F}\right) + \frac{sh\left(\frac{R_q^s t}{2\tau_F}\right)}{R_q^s} \right] dq \quad (a) \\ \delta K_s^>(t, 0) = \frac{P_0}{\pi} e^{-\frac{t}{2\tau_F}} \int_{q_0^s}^{q_m} \left[\cos\left(\frac{R_q^s t}{2\tau_F}\right) + \frac{\sin\left(\frac{R_q^s t}{2\tau_F}\right)}{R_q^s} \right] dq \quad (b) \\ q_m = \frac{\pi}{a}; q_0^s = \frac{1}{2\sqrt{D_e \tau_F}} \text{ and } R_q^s = \sqrt{4D_e \tau_F q^2 - 1} \end{array} \right. \quad (8)$$

The first part in Eq (8) describes the diffusive contribution and is exponentially decaying as function of time. On the other hand, the second part describes the non-diffusive part. It is interesting to notice the oscillating character of the integrand in Eq 8(b) which will result after integration over q in a damped oscillating behavior.

In the next section, we will show that a similar decomposition in the time domain can be performed using Cattaneo's model.

CATTANEO'S MODEL

Our starting point here is the one dimensional Cattaneo's equation applied to electrons in the conduction band of a metal. This equation relates the heat flux of electrons to their temperature gradient and is given by [17]:

$$\tau_F \frac{\partial \varphi_e}{\partial t} + \varphi_e = -\beta_e(T_e) \frac{\partial T_e}{\partial x} \quad (9)$$

where β_e represents the thermal conductivity of the electrons. To this equation we add the energy conservation equation for a metal, which is given by:

$$\frac{\partial [\delta K_C]}{\partial t} + \frac{\partial \varphi_e}{\partial x} = P(t, x) \quad (10)$$

where P represents the input power applied to the top free surface of the metal. On the other hand, the energy density of electrons is related to their temperature via the equation [21, 22]:

$$\delta K_C(t, x) = \frac{1}{2} C_e(T_e) T_e(t, x) \quad (11)$$

where C_e is the temperature dependent specific heat per unit volume of the electronic system.

$C_e(T) = \pi^2/3 k_B^2 g(\varepsilon_F) T = \gamma T$ where $g(\varepsilon_F)$ is the electronic density of states at the Fermi energy ε_F . For gold, the linearity coefficient $\gamma = 66 \text{ J/m}^3/\text{K}^2$ [23].

Combination of Eqs (9-11) allows us to write the energy density equation as:

$$\tau_F \frac{\partial^2 [\delta K_C]}{\partial t^2} + \frac{\partial [\delta K_C]}{\partial t} - D_e \frac{\partial^2 [\delta K_C]}{\partial x^2} = \tau_F \frac{\partial P}{\partial t} + P \quad (12)$$

As we have done in Shastry's model, we assume the metal to be excited at its top free surface by a laser delta pulse of power $P(t, x) = P_0 \times \delta(t, x)$. After a double nonunitary Fourier transform with respect to time and space, Eq (12) becomes:

$$(-\tau_F \omega^2 + i\omega + D_e q^2) \overline{\overline{\delta K_C}} = (1 + i\tau_F \omega) P_0 \quad (13)$$

From which we can easily extract the expression of the energy density in the frequency-wave vector domain:

$$\begin{aligned} \overline{\overline{\delta K_C}}(\omega, q) &= \frac{1 + i\tau_F \omega}{-\tau_F \omega^2 + i\omega + D_e q^2} P_0 \\ &= \frac{-i + \tau_F \omega}{\omega + i\tau_F \omega^2 - iD_e q^2} P_0 \end{aligned} \quad (14)$$

It is very interesting to notice the resemblance between Eqs (2) and (14). Both Shastry and Cattaneo models, give similar

expressions to the ratio $\frac{\overline{\overline{\delta K_C}}(\omega, q)}{P_0}$. Let us

$$\text{note } N_2^c = \frac{\overline{\overline{\delta K_C}}(\omega, q)}{P_0}.$$

We have derived similar expressions from both models. That means we can do the same time decomposition of the electronic energy density at the top free surface of a metal using Cattaneo's model. The diffusive contribution will be expressed using a similar formula to Eq 8(a). On the other hand, because Cattaneo's model is a continuous model, the upper boundary of the integral in Eq 8(b) is infinity, and the non-diffusive regime shows a different behavior.

$$\left\{ \begin{aligned} \delta K_c(t,0) &= \delta K_c^<(t,0) + \delta K_c^>(t,0) \\ \delta K_c^<(t,0) &= \frac{P_0}{\pi} e^{-\frac{t}{2\tau_f}} \int_0^{q_0^c} \left[ch\left(\frac{R_q^c t}{2\tau_f}\right) + \frac{sh\left(\frac{R_q^c t}{2\tau_f}\right)}{R_q^c} \right] dq \quad (a) \\ \delta K_c^>(t,0) &= \frac{P_0}{\pi} e^{-\frac{t}{2\tau_f}} \int_{q_0^c}^{\infty} \left[\cos\left(\frac{R_q^c t}{2\tau_f}\right) + \frac{\sin\left(\frac{R_q^c t}{2\tau_f}\right)}{R_q^c} \right] dq \quad (b) \\ q_0^c &= \frac{1}{2\sqrt{D_e\tau_f}}; R_q^c = \sqrt{1-4D_e\tau_f q^2} \text{ and } \overline{R_q^c} = \sqrt{4D_e\tau_f q^2 - 1} \end{aligned} \right. \quad (15)$$

Using the same expression of the separation wave vector $q_0^{S,C}$, the time decomposition can be translated to decomposition in the frequency domain. For both Shastry and Cattaneo models, the Green's functions $N_2^{S,C}$ are directly integrated in the wave vector domain.

$$\left\{ \begin{aligned} \delta K_{S,C}(\omega,0) &= \delta K_{S,C}^<(\omega,0) + \delta K_{S,C}^>(\omega,0) \\ \delta K_{S,C}^<(\omega,0) &= \frac{P_0}{\pi} \int_0^{q_0^{S,C}} N_2^{S,C}(\omega,q) dq \quad (a) \\ \delta K_{S,C}^>(\omega,0) &= \frac{P_0}{\pi} \int_{q_0^{S,C}}^{\infty} N_2^S(\omega,q) dq \quad (b) \\ \delta K_c^>(\omega,0) &= \frac{P_0}{\pi} \int_{q_0^c}^{\infty} N_2^C(\omega,q) dq \quad (c) \end{aligned} \right. \quad (16)$$

The diffusive and non-diffusive contributions to the total energy density Green's function variation at the top free surface of a metal, are given in the frequency domain by the following expressions for both Shastry [Eqs (17)] and Cattaneo [Eqs (18)] models:

$$\left\{ \begin{aligned} \delta K_S^<(\omega,0) &= \frac{P_0}{\pi} \sqrt{\frac{1+i\tau_f\omega}{iD_e\omega}} \text{Atan}\left(\frac{1}{2\sqrt{i\tau_f\omega - \tau_f^2\omega^2}}\right) \quad (a) \\ \delta K_S^>(\omega,0) &= \frac{P_0}{\pi} \sqrt{\frac{1+i\tau_f\omega}{iD_e\omega}} \left[\text{Atan}\left(\frac{\pi}{a} \sqrt{\frac{D_e}{i\omega - \tau_f\omega^2}}\right) - \text{Atan}\left(\frac{1}{2\sqrt{i\tau_f\omega - \tau_f^2\omega^2}}\right) \right] \quad (b) \end{aligned} \right. \quad (17)$$

$$\left\{ \begin{aligned} \delta K_c^<(\omega,0) &= \frac{P_0}{\pi} \sqrt{\frac{1+i\tau_f\omega}{iD_e\omega}} \text{Atan}\left(\frac{1}{2\sqrt{i\tau_f\omega - \tau_f^2\omega^2}}\right) \quad (a) \\ \delta K_c^>(\omega,0) &= \frac{P_0}{\pi} \sqrt{\frac{1+i\tau_f\omega}{iD_e\omega}} \left[\frac{\pi}{2} \text{Atan}\left(\frac{1}{2\sqrt{i\tau_f\omega - \tau_f^2\omega^2}}\right) \right] \quad (b) \end{aligned} \right. \quad (18)$$

In these equations, (a) and (b) describe the diffusive and non-diffusive contributions, respectively. The total energy density

Green's function variation in the frequency domain at the top free surface of a metal is given by:

$$\left\{ \begin{aligned} \delta K_S(\omega,0) &= \frac{P_0}{\pi} \sqrt{\frac{1+i\tau_f\omega}{iD_e\omega}} \text{Atan}\left(\frac{\pi}{a} \sqrt{\frac{D_e}{i\omega - \tau_f\omega^2}}\right) \quad (a) \\ \delta K_c(\omega,0) &= \frac{P_0}{2} \sqrt{\frac{1+i\tau_f\omega}{iD_e\omega}} \quad (b) \end{aligned} \right. \quad (19)$$

We can easily check that Eqs 17(a), 18(a), 19(a) and 19(b) tend to a Fourier type equation at low frequency:

$$\delta K_S^<(\omega \rightarrow 0,0) = \delta K_c^<(\omega \rightarrow 0,0) = \frac{P_0}{2} \sqrt{\frac{1}{iD_e\omega}} = \delta K_F(\omega,0) \quad (20)$$

RESULTS AND DISCUSSION

At electron temperatures $T_e \leq T_F$, where T_F is the Fermi temperature, the electron thermal conductivity is given by $\beta_e = C_e v_F^2 \tau_f / 3$ [21], where v_F is the Fermi velocity, and τ_f is the scattering relaxation time of electrons averaged over the Fermi surface of the metal. Then, the thermal diffusivity of the electronic system in the conduction band of the metal takes the

$$\text{simple expression } D_e = \frac{\beta_e}{C_e} = \frac{v_F^2 \tau_f}{3}.$$

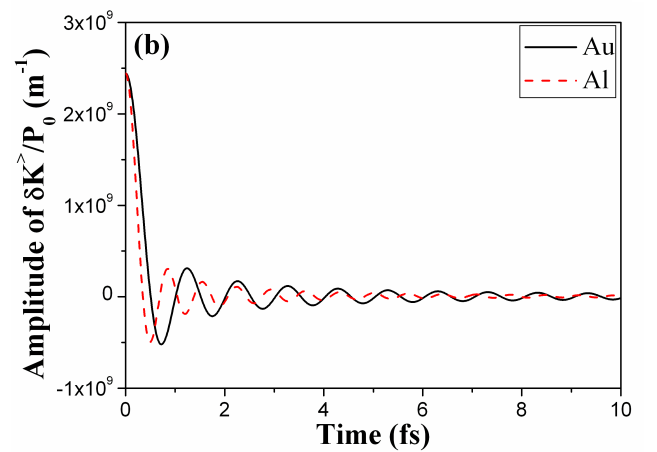
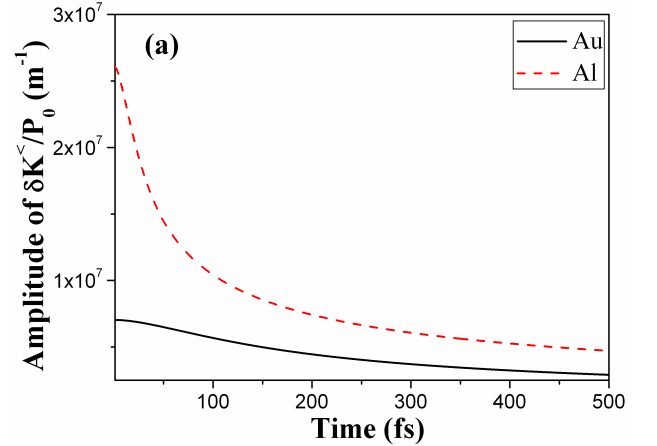


Figure 1: Temporal behavior of the energy density Green's function in Shastry's model at the top free surface of gold and aluminum at room temperature: (a) Eq 8(a). (b) Eq 8(b).

Table 1: Properties of gold and aluminum used in the calculation at room temperature.

Metal	Au	Al
Lattice constant (\AA)	4.08	4.05
Relaxation time τ_f (fs)	28	5.2
Fermi velocity v_F (10^6 m/s)	1.4	2.03
Electronic thermal diffusivity D_e (m^2/s)	0.0183	0.0071

In Figs 1, we have plotted the temporal behavior of the different contributions to the energy density Green's function in Shastry's model at the top free surface of two metals, gold and aluminum, at room temperature $T=300K$, as given by Eqs 8(a) and 8(b). More specifically the vertical axis in Figs 1(a) and 1(b) represents the quantity $\delta K_s(t,0)/P_0$ which has the unit of the absorption coefficient (m^{-1}). The higher is this quantity the higher is the energy density and hence the temperature at the top free surface of the metal. The values of the scattering relaxation time τ_f are estimated based on the values of the electrical resistivity using Drude theory [21]. Table 1 above summarizes these values as well as the values of the Fermi velocities and the electronic thermal diffusivities of gold and aluminum at room temperature.

The left side of the integral as described by Eq. 8(a) shows a smooth decaying behavior as a function of time which is almost an exponential [Fig 1(a)]. This behavior is characteristic of the diffusive regime of the heat transport by electrons. On the other hand, the right side of the integral described by Eq. 8(b) shows an oscillating behavior as a function of time [Fig 1(b)]. The oscillations are damped out exponentially with time and are characterized by a period that can be easily derived from Eq 8(b). The period of these oscillations has the expression [18]:

$$\theta_F = 2\sqrt{3} \frac{a}{v_F} \quad (21)$$

The oscillation period is function only of the lattice constant of the metal and its Fermi velocity, and is independent of the scattering relaxation time of the electrons in the conduction band. For almost all metals $a \sim 4\text{\AA}$ and v_F is of the order of 1.4×10^6 m/s, a simple application of Eq (21) shows then that the period of this oscillation is very small $\theta_F \approx 1\text{fs}$. Furthermore, by changing the temperature, only the scattering relaxation time is affected; the relaxation time τ_f increases by decreasing the temperature [21, 22, 25]. Since the oscillation period is independent of τ_f , this period is also independent of the temperature [18].

The oscillating behavior in the energy (heat) transport that results from Shastry's formalism is a consequence of the band cut-off due to the discrete character of the lattice; the oscillations are caused by Bragg reflections of ballistically accelerated electrons at the boundaries of the First Brillouin

Zone (FBZ). These electrons can make many round-trips within the FBZ bouncing back and forth on the boundaries, before they damp out due scattering mechanisms inside this zone. The ballistic electrons become afterwards diffusive. This is illustrated by the difference of the amplitudes of $\delta K_s^</math>/ P_0 and $\delta K_s^>$ / P_0 in Figs 1(a) and 1(b). At short time scales, energy and heat are mostly transported ballistically; the amplitude of the ballistic contribution is higher than the amplitude of the diffusive contribution and as the time goes by, the ballistic regime transition to a diffusive regime. For higher electron energies (high Fermi velocities), the oscillation period is shorter and the number of reflections is increased before ballistic energy transport damps out to a diffusive "thermal" regime.$

This oscillating behavior in the energy density modes can be viewed as the analogous of the Bloch oscillations of the electronic charge density in the material subject to a uniform electric field [8, 9]. The period of charge density Bloch oscillations is inversely proportional to the lattice constant, while this period is proportional to the lattice constant for the energy density modes oscillations as shown in Eq (21).

In Figs 2(a) we have plotted the diffusive contribution to the energy density Green's function at the top free surface of the two metals as calculated based on Shastry's model [Eq 8(a)] as a function of the nondimensional time $\eta=t/\tau_f$, in comparison to Fourier's prediction which is simply given by

$$\delta K_F(t,0) = \frac{P_0}{\sqrt{4\pi D_e t}} .$$

The temporal behavior of the diffusive contribution $\delta K_s^<(t,0)$, can be divided into three separate regimes; two regimes at short time scales and the third regime for a long time scale. For $t < \tau_f$, before any scattering event happens, $\delta K_s^<(t,0)$ is almost constant, then it starts decaying exponentially with time up to about $8\tau_f$, from where it changes the trend and it starts following a Fourier type energy diffusion law. Fourier's prediction is calculated analytically using Green's function method for the energy density equation. As it can be seen in Fig 2(a), the temporal behavior of the diffusion contribution to the energy density Green's function at the top free surface of the two metals, as calculated based on Shastry's model and Fourier's prediction overlap perfectly at long time scales.

In Fig 2(b), we show separately the temporal behavior of the diffusive contribution and the sum of the ballistic and diffusive contributions to the total energy density Green's function at the top free surface of gold at room temperature, as calculated based on Shastry's model [Eqs 8(a), and 8(a+b)], in comparison to Fourier's model. While the ballistic contribution is the dominant one at short time scales, it becomes insignificant after about $8\tau_f - 10\tau_f$. After that moment, the total energy is transported via a diffusive regime in which case the temporal decay follows a Fourier type law.

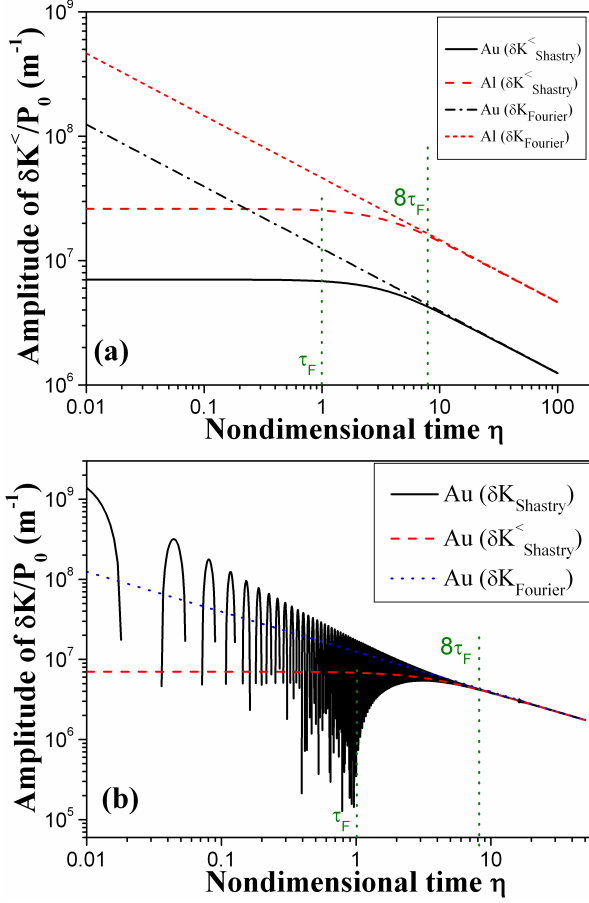


Figure 2: (a) Comparison between the diffusive contribution to the total energy density Green's function at the top free surface of gold and aluminum with Fourier's model at room temperature. (b) Comparison between the diffusive contribution (dashed line), the sum of the ballistic and the diffusive contributions (solid line) to the total energy density Green's function at the top free surface of gold at room temperature, with Fourier's model (dotted line).

As we have mentioned above, the closest Non-Fourier model to Shastry's model is Cattaneo's model [11, 17]. We have shown that both models allow the separation between the diffusive and the non-diffusive contributions to the total energy density variation as a function of time at the top free surface of a metal. Both models describe the diffusive regime using similar expression [Eqs 8(a) and 15(a)]. On the other hand, because of the continuous character of Cattaneo's model, the upper limit in the integral of Eq 15(b) is infinity, and the non-diffusive regime shows a different behavior. For values of the wave vector q between q_0^C and infinity, we can with a very good approximation neglect 1 in the argument of R_q^C , the latter becomes then $\overline{R_q^C} \approx 2q\sqrt{D_e\tau_F}$. The first term in Eq 15(b) vanishes basically after integration and only the second term will remain. Eq. 15(b) can be rewritten as:

$$\delta K_c^>(t,0) = \frac{P_0}{2\pi} e^{-\frac{t}{2\tau_F}} \int_{q_0^C}^{\infty} \frac{\sin\left(q\sqrt{\frac{D_e t}{\tau_F}}\right)}{q\sqrt{D_e\tau_F}} dq \quad (22)$$

This equation can be calculated analytically and the result is given by:

$$\delta K_c^>(t,0) = \frac{P_0}{2\pi} e^{-\frac{t}{2\tau_F}} \left[\frac{\frac{\pi}{2} - Si\left(\frac{t}{2\tau_F}\right)}{\sqrt{D_e\tau_F}} \right] \quad (23)$$

where Si represents the Sine integral function given by

$$Si(z) = \int_0^z \frac{\sin(x)}{x} dx \quad [26].$$

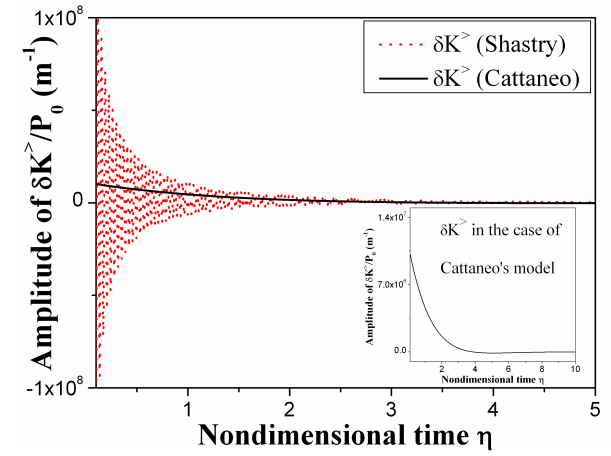


Figure 3: Comparison between the temporal behaviors of the non-diffusive contribution to the total energy density Green's function at the top free surface of gold at room temperature, as calculated based on Shastry's model (dotted line) and Cattaneo's model (solid line). The inset shows the behavior of Cattaneo's model over longer time scale.

In order to shed more light on the difference between the non-diffusive contribution to the total energy density at the top free surface of a metal, as described by Shastry's model and Cattaneo's model, we plot in Fig 3 the results of these two models in the case of gold at room temperature for comparison. Due to the band cut-off effect in Shastry's model, the non-diffusive contribution shows an exponentially damped oscillating behavior as a function of time. On the other hand, because of the continuous character of Cattaneo's model, the oscillating behavior disappears and the non-diffusive contribution shows an exponential decay as a function of time, much faster than the diffusive contribution. As we can see in the inset of Fig 3, the non-diffusive contribution to the total energy density in Cattaneo's model becomes almost insignificant after about $4\tau_F - 6\tau_F$. This is faster than the time constant decay of the non-diffusive contribution as calculated by Shastry's model.

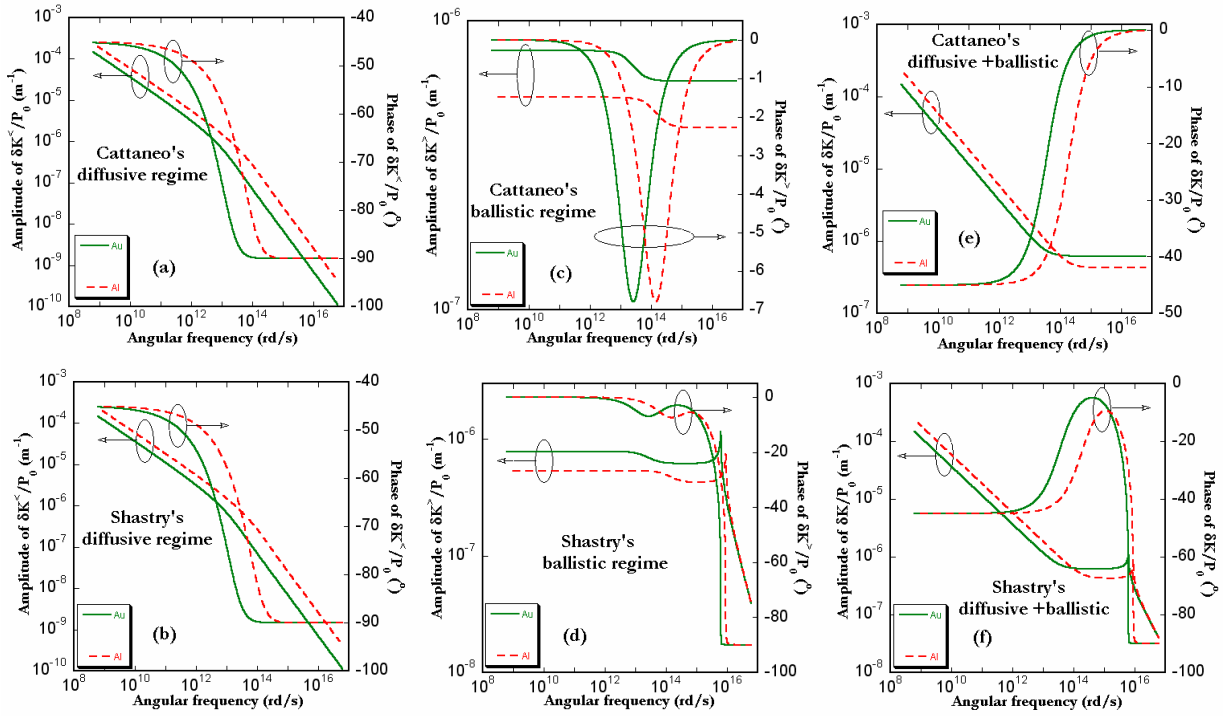


Figure 4: Frequency behavior of the diffusive contribution (a, b), the non-diffusive contribution (c, d), and the total energy density Green's function (e, f) at the top free surface of gold and aluminum at room temperature in both Cattaneo's model (a-c) and Shastry's model (d-f).

As we have mentioned above in the theory section, the same time decomposition can be made in the frequency domain for both Shastry and Cattaneo models. In Fig 4, we show the frequency behaviors of the amplitude and phase of the diffusive and the non-diffusive contributions to the total energy density Green's function at the top free surface of gold and aluminum at room temperature, as calculated based on both models. The behavior of the total energy density is also reported for comparison. In Fig 5, we show only the result for gold at room temperature, to which we added Fourier's law prediction to check the behavior at low frequency regime.

As we can see in both Figs 4 and 5, the diffusive contributions have similar behaviors in both models. On the other hand, the non-diffusive contributions show different behaviors. In Cattaneo's model, the amplitude and phase are constant up to a certain frequency where their trends start to change. The amplitude decreases to stabilize at a lower value at high frequencies, and the phase goes through a minimum and then comes back to the initial zero value. In Shastry's model, the non-diffusive contribution shows a similar behavior to Cattaneo's model up to certain frequency, after which, it has a different behavior. The amplitude goes through a sharp maximum before it starts decaying at high frequency, and the phase does not come back to the initial value, but it falls rapidly to a value of $\pi/2$. These interesting additional features in the frequency behavior of the non diffusive contribution in

Shastry's model are a consequence of the discrete character of the lattice.

Also we have reported in Fig 5(c) the behavior of the total energy density Green's function as a function of frequency as calculated according to Cattaneo, Shastry and Fourier models. We can see the perfect overlapping of the three models at low frequency regime both for the amplitude and phase.

In Fig 6, we report the temperature effect on the frequency behaviors of the amplitude and phase of the diffusive and the non-diffusive contributions to the total energy density Green's function at the top free surface of gold, as calculated based on both Cattaneo and Shastry models. By decreasing the temperature, the total relaxation time τ_F increases and the characteristic features in each models shift to low frequency regime.

Let us get back to the time domain. Many authors have reported the observation of an oscillating behavior in the time domain of the reflectivity change at the top free surface of semi-metals using the femtosecond Pump-Probe Transient Thermoreflectance technique [27-29]. Probing the relative change of the surface reflectivity is proportional to probing the change of the energy density at this surface. Nevertheless, these oscillations have been identified as due to a generation and relaxation of coherent phonon in such semi-metals. The frequencies of which have been confirmed using Raman Spectroscopy techniques [27-29]. By consequence, these

oscillations are not related to the Bloch oscillating behavior in the energy transport by conduction band electrons in metals predicted by Shastry's formalism.

temperature in both Cattaneo's model (solid line), and Shastry's model (solid-dashed line). The dashed line in (c) describes Fourier's model.

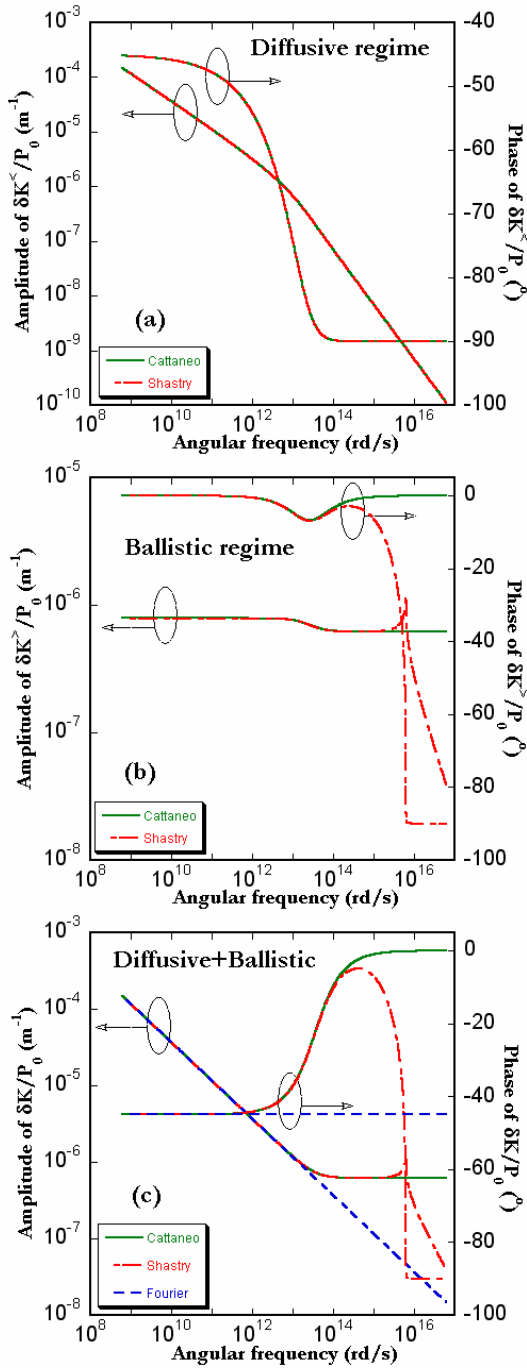


Figure 5: Frequency behavior of the diffusive contribution (a), the non-diffusive contribution (b), and the total energy density Green's function (c) at the top free surface of gold at room

No experiment has reported such behavior in the energy density change at the free surface of metals due to electrons transport. Three main reasons can explain the lack of observation: (i) the smallness of the oscillation period ($I\tau$), (ii) the optical penetration depth of metals at long excitation laser wavelengths, and (iii) the convolution effect due to the laser pulse width which smoothes out these oscillations.

A possible candidate to observe the temporal oscillating behavior in the energy transport is a metallic superlattice. As suggested by Eq (21), the period of these oscillations is proportional to the lattice constant, which is a consequence of the integration over the FBZ. It is well known however that superlattices structures are characterized by a subdivision of the electronic and phononic bands into mini-bands. Particularly the FBZ is divided into mini Brillouin zones of width π/d where d is the superlattice period. This spatial period d can be one to two orders of magnitude larger than the lattice constant a , which will increase the energy density oscillating period by the same order of magnitude and bring its value from the femtosecond regime to the picosecond regime. This latter regime can be probed by the state of the art in femtosecond laser metrology. As a matter of fact, the conventional Bloch oscillations have been only observed in superlattices structures [8, 9].

In addition, short pulse laser sources are in continuous development and attosecond width pulses have been developed [10]. Even though many other resonance phenomena of condensed matter have to be taken into account when using these ultra-short laser pulses, these sources, especially with short laser wavelengths but are still longer than the Plasmon wavelength of the corresponding metal, can be used to observe this fundamental energy transport oscillation.

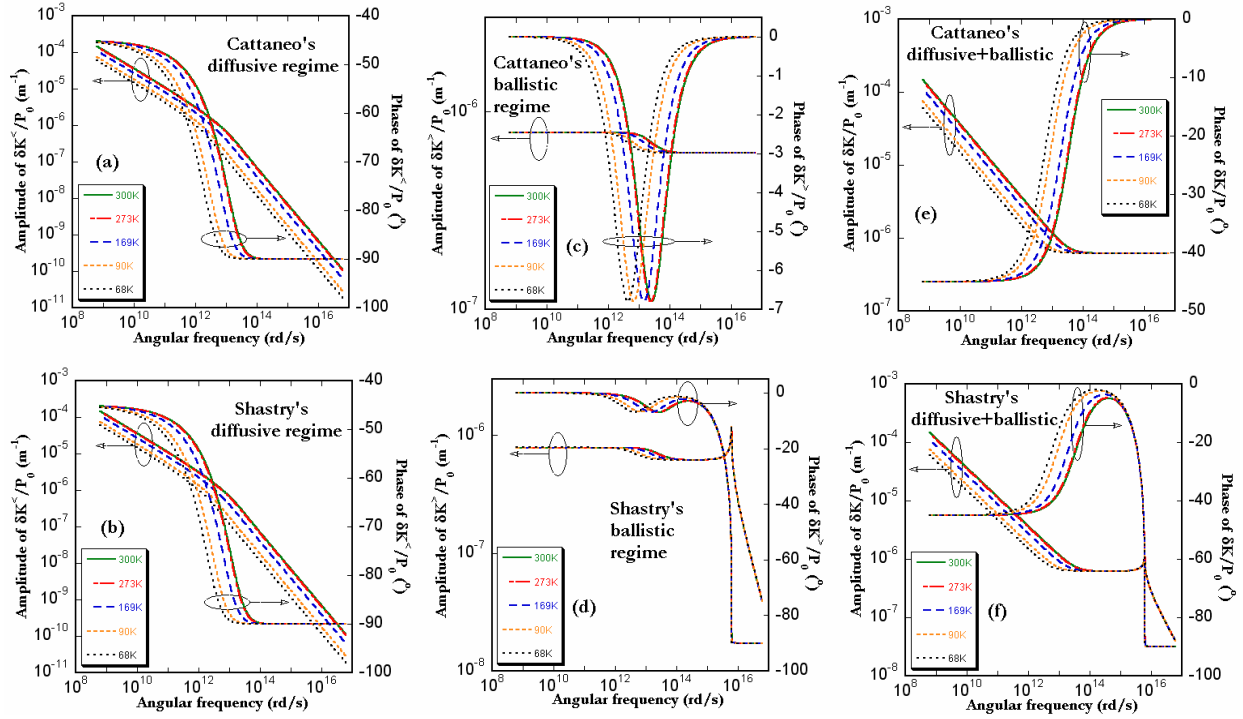


Figure 6: Frequency behavior of the diffusive contribution (a, b), the non-diffusive contribution (c, d), and the total energy density Green's function (e, f) at the top free surface of gold at different temperatures in both Cattaneo's model (a-c) and Shastry's model (d-f).

CONCLUSION

We have analyzed the transition between ballistic and diffusive energy transport in metals using the recently developed Shastry's formalism. An interesting temporal oscillating behavior in the energy density Green's function at the top free surface of metals is reported. This behavior in the energy transport is a consequence of the band cut-off due to the discrete character of the crystalline lattice. This leads to Bragg reflection of electrons in a metal. The oscillating behavior in the energy transport can be viewed as an energetic analogous to the conventional Bloch oscillation in the charge density of the conduction band electrons of the metal. It is an interesting manifestation of the ballistic contribution to the energy transport that results from the electrons bouncing back and forth at the boundaries of the first Brillouin zone before they damp out into the diffusive regime due to scattering mechanisms.

Remarkably, Cattaneo's model shows similar features to Shastry's formalism. More specifically, a similar decomposition in the total energy density at the top free surface of the metal can be made. The diffusive contribution to the energy density is described using a formula similar to Shastry's model. On the other hand, because of the continuous character of Cattaneo's model, the non-diffusive contribution shows no oscillations and it decays on a time constant even faster than the one predicted by Shastry's model.

In the frequency domain, the total energy density Green's function phase variation as a function of frequency at the top free surface of a metal shows a $\pi/2$ phase variation at high frequencies. This difference in the phase behavior at high frequencies can be probed and used as an indication of the existing oscillations in the time domain.

The treatment in this paper for energy and heat transport by electrons in the conduction band of metals can easily be extended to semiconductors where the dominant energy and heat carriers are phonons. In this case, the total relaxation time in Shastry's model is wave vector dependent and can not be taken to be constant. The case of semiconductors is being investigated and will constitute the topic of a future work.

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