

## Article

# Two-Step Relaxation of Non-Equilibrium Electrons in Graphene: The Key to Understanding Pump–Probe Experiments

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## S1. Time-dependent absorbance

In this section, we derive the time-dependent absorbance,  $A(t)$ , using the Fermi's Golden rule. The interband transition rate, under optical excitation, is [1]:

$$\Gamma_{\mathbf{k}} = \frac{2\pi}{\hbar} \frac{(ev_F)^2}{4} \frac{E_b^2}{\omega_b^2} \sin^2 \theta \delta(2\hbar v_F k - \hbar\omega_b) \{ [1 - g_h(-\varepsilon_{\mathbf{k}})] [1 - g_e(\varepsilon_{\mathbf{k}})] - g_h(-\varepsilon_{\mathbf{k}}) g_e(\varepsilon_{\mathbf{k}}) \}, \quad (\text{S1})$$

where  $g_e$  and  $g_h$  are the non-thermalized distribution functions for electrons and holes, respectively. Here,  $E_b$  is the pump's electric field amplitude. Then, integrating  $\Gamma_{\mathbf{k}}$  over  $\mathbf{k}$ , the transition rate per unit area is:

$$\Gamma = \frac{e^2 E_b^2}{8\hbar^2 \omega_b} \left\{ \left[ 1 - g_h \left( -\frac{\hbar\omega_b}{2} \right) \right] \left[ 1 - g_e \left( \frac{\hbar\omega_b}{2} \right) \right] - g_h \left( -\frac{\hbar\omega_b}{2} \right) g_e \left( \frac{\hbar\omega_b}{2} \right) \right\}. \quad (\text{S2})$$

Therefore, the power per unit area absorbed by the material reads:

$$W_{\text{abs}} = \Gamma \hbar\omega_b = \frac{e^2 E_b^2}{8\hbar} \left\{ \left[ 1 - g_h \left( -\frac{\hbar\omega_b}{2} \right) \right] \left[ 1 - g_e \left( \frac{\hbar\omega_b}{2} \right) \right] - g_h \left( -\frac{\hbar\omega_b}{2} \right) g_e \left( \frac{\hbar\omega_b}{2} \right) \right\}. \quad (\text{S3})$$

On the other hand, the incident power flux per unit area is given by:

$$W_{\text{inc}} = \frac{c}{8\pi} E_b^2. \quad (\text{S4})$$

The absorbance is given by the ratio between the absorbed and incident fluxes:

$$A(t) = \frac{W_{\text{abs}}}{W_{\text{inc}}} = \pi\alpha_F \left\{ \left[ 1 - g_h \left( -\frac{\hbar\omega_b}{2}, t \right) \right] \left[ 1 - g_e \left( \frac{\hbar\omega_b}{2}, t \right) \right] - g_h \left( -\frac{\hbar\omega_b}{2}, t \right) g_e \left( \frac{\hbar\omega_b}{2}, t \right) \right\} \quad (\text{S5})$$

with  $\alpha_F$  denoting the fine structure constant and:

$$\pi\alpha_F = \frac{4\pi}{c} \sigma_0. \quad (\text{S6})$$

Here  $\sigma_0$  is graphene's conductivity in equilibrium, at high frequencies. This result is valid for suspended graphene under normal incidence of the light. For graphene on top of a



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dielectric with a refractive index  $n$ , for an arbitrary incident angle  $\alpha$ , we can determine  $A(t)$  from the expression for the linear reflection and transmission coefficients [2]:

$$\begin{aligned} \hat{r}\left(\frac{\hbar\omega_b}{2}, t\right) &= \frac{n \cos \alpha - \cos \theta + \frac{4\pi}{cE_b^2} \mathbf{j} \cdot \mathbf{E}_b \cos \theta \cos \alpha}{n \cos \alpha + \cos \theta + \frac{4\pi}{cE_b^2} \mathbf{j} \cdot \mathbf{E}_b \cos \theta \cos \alpha} \\ \hat{t}\left(\frac{\hbar\omega_b}{2}, t\right) &= \frac{2 \cos \alpha}{n \cos \alpha + \cos \theta + \frac{4\pi}{cE_b^2} \mathbf{j} \cdot \mathbf{E}_b \cos \theta \cos \alpha} \end{aligned} \quad (\text{S7})$$

The Joule heating term containing  $\mathbf{j} \cdot \mathbf{E}_b$  is the power absorbed by graphene ( $\mathbf{j}$  is the current and  $\mathbf{E}_b$  the pump electric field) and  $\theta$  is the angle of refraction. The absorbance is related to the reflectivity  $R$  and transmittance  $T$  by:

$$A(t) = 1 - R(t) - T(t) \quad (\text{S8})$$

which can be expanded to the first order in  $\mathbf{j} \cdot \mathbf{E}_b$ :

$$A(t) \approx \frac{4 \cos \alpha \cos^2 \theta}{(n \cos \alpha + \cos \theta)^2} \frac{4\pi}{cE_b^2} \mathbf{j} \cdot \mathbf{E}_b. \quad (\text{S9})$$

We consider the situation where absorption by the substrate is negligible. This is a good approximation for the pump energies we are interested in and a substrate such as SiO<sub>2</sub>. Then, we have from Equation (S5):

$$\frac{4\pi}{cE_b^2} \mathbf{j} \cdot \mathbf{E}_b = \pi\alpha_F \left\{ \left[ 1 - g_h\left(-\frac{\hbar\omega_b}{2}, t\right) \right] \left[ 1 - g_e\left(\frac{\hbar\omega_b}{2}, t\right) \right] - g_h\left(-\frac{\hbar\omega_b}{2}, t\right) g_e\left(\frac{\hbar\omega_b}{2}, t\right) \right\}. \quad (\text{S10})$$

Finally, the general expression for the absorbance is:

$$A(t) = A_0(\alpha, \theta) \left\{ 1 - g_h\left(-\frac{\hbar\omega_b}{2}, t\right) - g_e\left(\frac{\hbar\omega_b}{2}, t\right) \right\} \quad (\text{S11})$$

where

$$A_0(\alpha, \theta) = \frac{4\pi\alpha_F}{(n \cos \alpha + \cos \theta)^2} \cos \alpha \cos^2 \theta. \quad (\text{S12})$$

## S2. Determination of $\tilde{g}(\vec{r}, t)$

To determine  $\tilde{g}(t)$ , we notice that the transient evolution of the non-thermalized population of charge carriers dictated by the balance equation, may be also calculated using graphene's density of states,  $\rho(\epsilon) = 2|\epsilon| / [\pi(\hbar v_F)^2]$ :

$$\begin{aligned} p_{\text{nt}}(\vec{r}, t) &= n_{\text{nt}}(\vec{r}, t) = \int_0^\infty d\epsilon \rho(\epsilon) g(\epsilon, \vec{r}, t) \\ &= \tilde{g}(\vec{r}, t) \int_0^\infty d\epsilon \rho(\epsilon) \exp\left(-\frac{(\epsilon - \hbar\omega_b/2)^2}{2\Delta_\epsilon^2}\right). \end{aligned} \quad (\text{S13})$$

Since  $\Delta_\epsilon \ll \hbar\omega_b$ , the integral can be approximated and yields:

$$p_{\text{nt}}(\vec{r}, t) = n_{\text{nt}}(\vec{r}, t) = \sqrt{2\pi}\Delta_\epsilon \tilde{g}(\vec{r}, t) \rho\left(\frac{\hbar\omega_b}{2}\right). \quad (\text{S14})$$

Consequently, the time-dependent amplitude can be written as a function of the non-thermalized density:

$$\tilde{g}(\vec{r}, t) = \frac{n_{nt}(\vec{r}, t)}{\sqrt{2\pi}\Delta_\epsilon\rho\left(\frac{\hbar\omega_b}{2}\right)}. \quad (\text{S15})$$

Therefore, we may rewrite (S15) as:

$$\tilde{g}(\vec{r}, t) = \frac{n_{nt}(\vec{r}, t)}{2n_{nt}^{\max}}, \quad (\text{S16})$$

where we the maximum concentration of non-thermalized electrons is defined as

$$n_{nt}^{\max} = \sqrt{\frac{\pi}{2}}\Delta_\epsilon\rho\left(\frac{\hbar\omega_b}{2}\right). \quad (\text{S17})$$

### S3. Diffusion coefficient and thermal diffusivity for a strongly degenerate electron gas

In this section, our objective is to establish a relation between the thermal diffusivity, denoted as  $D_\epsilon$ , and the diffusion coefficient, denoted as  $D$ , for the 2D electron gas in graphene. To accomplish this, we will employ Boltzmann's equation that, in the relaxation time approximation, reads:

$$\frac{\partial f}{\partial t} + \frac{\partial \vec{r}}{\partial t} \frac{\partial f}{\partial \vec{r}} + \frac{\partial \vec{k}}{\partial t} \frac{\partial f}{\partial \vec{k}} = -\frac{f - f_0}{\tau}, \quad (\text{S18})$$

where  $f$  and  $f_0$  represent the out-of-equilibrium and equilibrium distribution functions, respectively, and  $\tau$  is the momentum relaxation time. The system is out of equilibrium because of the presence of an external electric field and gradients of concentration and temperature. To the first order in these perturbation, the out-of-equilibrium distribution function can be written as

$$f(\vec{k}, \vec{r}) = f_0(\vec{k}, \vec{r}) + f_1(\vec{k}, \vec{r}), \quad (\text{S19})$$

where  $f_0(\vec{k}, \vec{r})$  is  $\vec{r}$ -dependent through the chemical potential and temperature. The Boltzmann's equation becomes:

$$\vec{v} \frac{\partial f_0}{\partial \vec{r}} + \frac{\partial \vec{k}}{\partial t} \frac{\partial f_0}{\partial \vec{k}} = -\frac{f_1}{\tau}. \quad (\text{S20})$$

It is solved using the standard ansatz [3]:

$$f_1 = -\left(\frac{\partial f_0}{\partial E}\right)\tau\left\{e\vec{E} + \vec{\nabla}\mu + \frac{E(\vec{k}) - \mu}{T}\vec{\nabla}T\right\} \cdot \vec{v}. \quad (\text{S21})$$

The 2D flux density of electrons is:

$$\vec{j} = \frac{4}{(2\pi)^2} \int \vec{v} f_1 d\vec{k} = \frac{4}{(2\pi)^2} \int \vec{v} \left(\frac{\partial f_0}{\partial E}\right)\tau(\vec{k}) \left\{e\vec{E} + \vec{\nabla}\mu + \frac{E(\vec{k}) - \mu}{T}\vec{\nabla}T\right\} \cdot \vec{v} d\vec{k}, \quad (\text{S22})$$

where the factor of 4 accounts for spin and valley degeneracy on graphene. To determine the diffusion coefficient, we consider only the second term in (S22), which involves the chemical potential gradient:

$$\vec{j}_D = -\frac{4}{(2\pi)^2} \left(\frac{\partial \mu}{\partial n}\right)_T \int (\vec{v} \cdot \vec{\nabla}n) \vec{v} \frac{\partial f_0}{\partial E} \tau(k) d^2k \equiv -D\vec{\nabla}n. \quad (\text{S23})$$

where  $D$  is the diffusion coefficient. For graphene,  $E(k) = \hbar v_F k$  and we have:

$$D = -\frac{1}{\pi\hbar^2} \left(\frac{\partial \mu}{\partial n}\right)_T \int_0^\infty E \frac{\partial f_0}{\partial E} \tau(E) dE. \quad (\text{S24})$$

In order to find an expression for the thermal diffusivity, we evaluate the thermal flux density, defined as:

$$\begin{aligned}\vec{w} &= \frac{4}{(2\pi)^2} \int (E(\vec{k}) - \mu) \vec{v} f_1 d\vec{k} \\ &= \frac{4}{(2\pi)^2} \int \vec{v} \left( \frac{\partial f_0}{\partial E} \right) \tau(\vec{k}) (E(\vec{k}) - \mu) \left\{ e\vec{E} + \vec{\nabla} \mu(\vec{r}) + \frac{E(\vec{k}) - \mu}{T} \vec{\nabla} T \right\} \cdot \vec{v} d\vec{k}.\end{aligned}\quad (\text{S25})$$

The relevant term now is the one with the temperature gradient, which yields:

$$\vec{w}_D = \frac{4}{(2\pi)^2 T} \int (\vec{v} \cdot \vec{\nabla} T) \cdot \vec{v} \frac{\partial f_0}{\partial E} \tau(k) (E(k) - \mu)^2 d^2k \equiv -\kappa \vec{\nabla} T \quad (\text{S26})$$

where  $\kappa$  is the electronic contribution to the thermal conductivity of graphene, given by:

$$\kappa = -\frac{1}{\pi \hbar^2 T} \int_0^\infty E \frac{\partial f_0}{\partial E} \tau(E) (E - \mu)^2 dE. \quad (\text{S27})$$

It can be related to the thermal diffusivity as follows:

$$D_\varepsilon = \frac{\kappa}{nc_p} = -\frac{1}{\pi \hbar^2 T c_p n} \int_0^\infty E \frac{\partial f_0}{\partial E} \tau(E) (E - \mu)^2 dE, \quad (\text{S28})$$

where  $c_p$  is the specific heat per particle. Thus, we have

$$\frac{D_\varepsilon}{D} = \frac{1}{nc_p T} \left( \frac{\partial \mu}{\partial n} \right)_T^{-1} \frac{\int_0^\infty E \frac{\partial f_0}{\partial E} (E - \mu)^2 \tau(E) dE}{\int_0^\infty E \frac{\partial f_0}{\partial E} \tau(E) dE}. \quad (\text{S29})$$

To calculate the integrals analytically, we need to employ an approximation. Two limiting cases can be considered here: the Boltzmann approximation and the strongly degenerate electron gas approximation. The Boltzmann approximation is applicable when most electrons in the system have an energy much larger than the chemical potential, i.e.,  $E \gg \mu$ . On the other hand, the strongly degenerate electron gas approximation is suitable when the majority of electrons follow  $\mu \gg k_B T$ . As indicated by the results in the Figure 3 of the main text, the electronic thermal energy is consistently smaller than the electronic chemical potential, suggesting that the strongly degenerate gas approximation is more appropriate in this case.

In this limit, the distribution function can be expressed as a step function,

$$f_0(E) \approx 1 - \Theta(E - \mu_e), \quad (\text{S30})$$

where  $\Theta$  denotes the Heaviside function. Consequently, its derivative gives rise to the Dirac delta-function

$$\frac{\partial f_0}{\partial E} = -\delta(E - \mu_e). \quad (\text{S31})$$

Within this approximation, we can carry out the integral in the denominator of Equation (S29), leading to:

$$\frac{D_\varepsilon}{D} = -\frac{1}{nc_p T \mu \tau(\mu)} \left( \frac{\partial \mu}{\partial n} \right)_T^{-1} \int_0^\infty E \frac{\partial f_0}{\partial E} (E - \mu)^2 \tau(E) dE. \quad (\text{S32})$$

However, applying the same procedure to the numerator yields in the integral vanishing. To avoid this, we write:

$$\mathcal{I} = \int_0^\infty E \frac{\partial f_0}{\partial E} (E - \mu)^2 \tau(E) dE = - \int_0^\infty f_0(E) \frac{d}{dE} [E(E - \mu)^2 \tau(E)] dE, \quad (\text{S33})$$

where we used integration by parts. Now, we can express the integral as

$$\mathcal{I} = - \int_0^\infty \frac{F(E)}{1 + \exp\left[\frac{E - \mu}{k_B T}\right]} dE = -k_B T \int_{-\mu/k_B T}^\infty \frac{F(\mu + x k_B T)}{1 + e^x} dx \quad (\text{S34})$$

with

$$F(E) = \frac{d}{dE} [E(E - \mu)^2 \tau(E)]. \quad (\text{S35})$$

Now, dividing the integration domain into two parts, we have:

$$\mathcal{I} = -k_B T \int_0^{\mu/k_B T} \frac{F(\mu - x k_B T)}{1 + e^{-x}} dx - k_B T \int_0^\infty \frac{F(\mu + x k_B T)}{1 + e^x} dx. \quad (\text{S36})$$

Applying the identity,

$$\frac{1}{1 + e^{-x}} = 1 - \frac{1}{1 + e^x}, \quad (\text{S37})$$

allow us to write:

$$\mathcal{I} = - \int_0^\mu F(E) dE + k_B T \int_0^\infty \frac{F(\mu - x k_B T) - F(\mu + x k_B T)}{1 + e^x} dx. \quad (\text{S38})$$

Here we have extended the upper limit of one of the terms to infinity as we are interested in the strongly degenerate case. From our expression for  $F(E)$  it is clear that the integral vanishes in the first term. In the second one, we can apply a Taylor expansion which leads to:

$$\mathcal{I} = -2(k_B T)^2 F'(\mu) \int_0^\infty \frac{x}{1 + e^x} dx = \frac{1}{3} \pi^2 (k_B T)^2 \mu \tau(\mu). \quad (\text{S39})$$

Therefore, incorporating this result into Eq. (S32) yields:

$$\frac{D_\epsilon}{D} = \frac{1}{3} \frac{\pi^2 k_B^2 T}{n c_p} \left( \frac{\partial \mu}{\partial n} \right)_T^{-1}. \quad (\text{S40})$$

First, let us evaluate the electron density in graphene. Under the current approximation, it is given by:

$$n = \frac{4}{(2\pi)^2} \int_0^{2\pi} \int_0^\infty (1 - \theta(k - k_F)) k dk d\theta = \frac{\mu^2}{\pi \hbar^2 v_F^2} \quad (\text{S41})$$

Thus, the derivative of the chemical potential with respect to the concentration can be expressed as:

$$\frac{\partial \mu}{\partial n} = \frac{\mu}{2n}. \quad (\text{S42})$$

Finally, we need to evaluate the heat capacity. The general expression for the degenerated electronic gas is:

$$c_p = \frac{\pi^2}{3} k_B^2 T \frac{g(\mu)}{n}, \quad (\text{S43})$$

where  $g(\mu)$  is graphene's density of states at the Fermi level. Therefore, since the density of states is

$$g(E) = \frac{2}{\pi} \frac{E}{(\hbar v_F)^2} \quad (\text{S44})$$

we finally obtain:

$$\frac{D_\varepsilon}{D} = 1. \quad (\text{S45})$$

#### S4. Solution of the balance equations

In this section our goal is to solve the balance equations for the thermalized carriers as presented in the main text. We begin by addressing the balance equation for the thermalized carrier density, given by:

$$\frac{dn_t}{dt} = \frac{n_{nt}}{\tau_{ee}} + D\nabla^2 n_t - \frac{n_t - n_0}{\tau_r}. \quad (\text{S46})$$

Employing the Green's function method allows us to rewrite Equation (S46) as

$$\frac{dG(x, y, t)}{dt} - D\nabla^2 G(x, y, t) + \frac{G(x, y, t)}{\tau_r} = \delta(x)\delta(y)\delta(t), \quad (\text{S47})$$

and the solution for  $n_t$  is then found as the convolution between Green's function and the "perturbation",

$$n_t(x, y, t) = \int dx' dy' dt' G(x - x', y - y', t - t') \left\{ \frac{n_{nt}(t')}{\tau_{ee}} + \frac{n_0}{\tau_r} \right\}. \quad (\text{S48})$$

The Green's function is given by [4]:

$$G(x, y, t) = \begin{cases} 0 & , \text{ for } t < 0; \\ \frac{e^{-t/\tau_r}}{(2\pi)^2} \frac{\pi}{Dt} \exp\left[-\frac{r^2}{4Dt}\right] & , \text{ for } t > 0. \end{cases} \quad (\text{S49})$$

Thus, we obtain:

$$\begin{aligned} n_t(\vec{r}, t) &= \int_{-\infty}^t dt' \int d^2r' \frac{1}{4\pi D(t-t')} \exp\left[-\frac{t-t'}{\tau_r} - \frac{(r-r')^2}{4D(t-t')}\right] \left\{ \frac{n_{nt}(r', t')}{\tau_{ee}} + \frac{n_0}{\tau_r} \right\} \\ &= n_0 + \frac{1}{\tau_{ee}} \int_{-\infty}^t dt' \int d^2r' \frac{n_{nt}(r', t')}{4\pi D(t-t')} \exp\left[-\frac{t-t'}{\tau_r} - \frac{(r-r')^2}{4D(t-t')}\right]. \end{aligned} \quad (\text{S50})$$

As mentioned in the main text, it is useful to do an spatial average on this expression. Performing the spatial average with the weight function introduced in the main text yields:

$$\begin{aligned} \langle n_t(t) \rangle &= \int d^2r n_t(\vec{r}, t) f(\vec{r}) = \frac{\ln 2}{\pi w_0^2} \int d^2r n_t(\vec{r}, t) \exp\left[-\frac{\ln 2}{w_0^2} (\vec{r} - \vec{r}_0)^2\right] \\ &= n_0 + \frac{2\ln 2}{\tau_{ee}} \int_{-\infty}^t dt' \int_0^\infty r' dr' \frac{e^{-(t-t')/\tau_r} n_{nt}(r', t')}{w_0^2 + 4\ln 2 D(t-t')} \exp\left[-\frac{\ln 2 (r' - r_0)^2}{w_0^2 + 4\ln 2 D(t-t')}\right]. \end{aligned} \quad (\text{S51})$$

For the energy density, the balance equation is:

$$\dot{\varepsilon}_t \approx \frac{\hbar\omega_b}{2} \frac{n_{nt}(\vec{r}, t)}{\tau_{ee}} + D_\varepsilon \nabla^2 \varepsilon_t - \frac{\varepsilon_t - \varepsilon'_0(t)}{\tau_\varepsilon}. \quad (\text{S52})$$

The procedure to solve this equation is entirely similar to the one for the electronic density. Therefore, after performing the average one obtains:

$$\langle \varepsilon_t(t) \rangle = \varepsilon'_0(t) + \frac{\ln 2 \hbar\omega_b}{\tau_{ee}} \int_{-\infty}^t dt' \int_0^\infty r' dr' \frac{e^{-(t-t')/\tau_\varepsilon} n_{nt}(r', t')}{w_0^2 + 4\ln 2 D_\varepsilon(t-t')} \exp\left[-\frac{\ln 2 (r' - r_0)^2}{w_0^2 + 4\ln 2 D_\varepsilon(t-t')}\right]. \quad (\text{S53})$$

### S5. General expression for the differential reflectivity in the presence of hot electrons

Let us begin by considering that a TM polarized wave is focused onto a layer of graphene situated on top of a substrate, at a specific incident angle,  $\alpha$ , as depicted in Figure S1. The electric fields both above and below the graphene layer can be described in a general manner as follows:

$$\mathcal{E}_x^{(i)} = A_i \left( t - \sin \alpha \frac{x}{c} \right) \cos \alpha e^{i(\sin \alpha k_a x + \cos \alpha k_a z - \omega_a t)} ; \quad (\text{S54})$$

$$\mathcal{E}_x^{(r)} = A_r \left( t - \sin \alpha \frac{x}{c} \right) \cos \alpha e^{i(\sin \alpha k_a x - \cos \alpha k_a z - \omega_a t)} ; \quad (\text{S55})$$

$$\mathcal{E}_x^{(t)} = A_t \left( t - n \sin \theta \frac{x}{c} \right) \cos \theta e^{i(n \sin \theta k_a x + n \cos \theta k_a z - \omega_a t)} . \quad (\text{S56})$$

Here,  $i$ ,  $r$ , and  $t$  stand for incident, reflected, and transmitted fields, while  $k_a$  and  $\omega_a$  represent the wavevector and frequency of the probe beam. Additionally,  $\theta$  denotes the refracted angle,  $n$  is the refractive index of the substrate, and  $A_{i(r,t)}$  signifies the amplitude of the respective fields. These amplitudes dictate the temporal evolution of the fields. We will describe the probe beam amplitude as a Gaussian function:

$$A_{i(r,t)}(t) = a_{i(r,t)} \exp \left[ -\frac{t^2}{\tau_a^2} \right] , \quad (\text{S57})$$

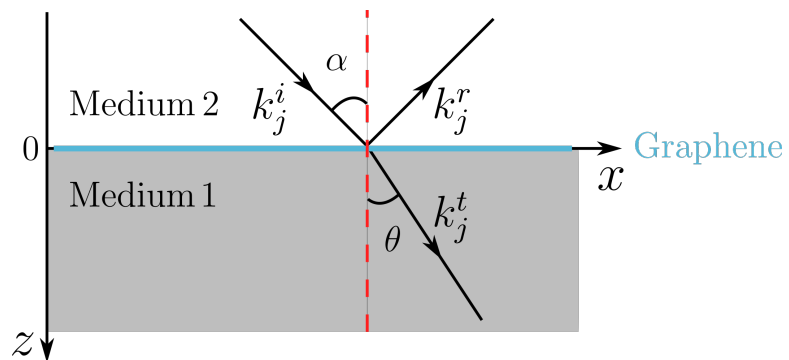
where  $\tau_a$  is the duration time of the probe beam.

By applying Maxwell's equations, we can derive the corresponding magnetic fields, resulting in the following expressions:

$$\mathcal{H}_y^{(i)} = \frac{\omega_a}{k_a c \cos \alpha} A_i \left( t - \sin \alpha \frac{x}{c} \right) \cos \alpha e^{i(\sin \alpha k_a x + \cos \alpha k_a z - \omega_a t)} ; \quad (\text{S58})$$

$$\mathcal{H}_y^{(r)} = -\frac{\omega_a}{k_a c \cos \alpha} A_r \left( t - \sin \alpha \frac{x}{c} \right) \cos \alpha e^{i(\sin \alpha k_a x - \cos \alpha k_a z - \omega_a t)} ; \quad (\text{S59})$$

$$\mathcal{H}_y^{(t)} = \frac{n \omega_a}{k_a c \cos \theta} A_t \left( t - n \sin \theta \frac{x}{c} \right) \cos \theta e^{i(n \sin \theta k_a x + n \cos \theta k_a z - \omega_a t)} . \quad (\text{S60})$$



**Figure S1.** Scheme of TM polarized waves propagating from medium 1 to medium 2, with graphene at the interface  $z = 0$ . The incident angle for wave  $j$  is  $\alpha$ , while the transmitted is  $\theta$ .  $k_j^i$ ,  $k_j^t$  and  $k_j^r$  are the incident, transmitted and reflected wavevectors respectively.

The next step involves determining the field amplitudes to compute the transmittance and the reflectivity. With these expressions at hand, we can proceed to apply the following boundary conditions at  $z = 0$ :

$$\mathcal{E}_x^{(i)} + \mathcal{E}_x^{(r)} = \mathcal{E}_x^{(t)} ; \quad (\text{S61})$$

$$\mathcal{H}_y^{(i)} + \mathcal{H}_y^{(r)} = \mathcal{H}_y^{(t)} + \frac{4\pi}{c} j_x(x, t) , \quad (\text{S62})$$

which translate the continuity of the electric field and the discontinuity of the magnetic field due to the presence of graphene. The current density can be generally expressed as:

$$j_x(t) = \int_{-\infty}^{\infty} \sigma(t, t') \mathcal{E}_x^{(t)}(t') dt', \quad (\text{S63})$$

where  $\sigma$  represents the conductivity of graphene. In the scenario without pumping, where graphene is at equilibrium, the conductivity is time-independent. Therefore, the current density is simply written as:

$$j_x(x, t) = \sigma_{\text{eq}}(\omega_a) \mathcal{E}_x^{(t)}(x, t). \quad (\text{S64})$$

By substituting these expressions for the fields and current into Eqs. (S61) and (S62), the following equations are obtained:

$$A_i \cos \alpha e^{i(k_a \sin \alpha x - \omega_a t)} + A_r \cos \alpha e^{i(k_a \sin \alpha x - \omega_a t)} = A_t \cos \theta e^{i(n \sin \theta k_a x - \omega_a t)}; \quad (\text{S65})$$

$$A_i e^{i(k_a \sin \alpha x - \omega_a t)} - A_r e^{i(k_a \sin \alpha x - \omega_a t)} = n A_t e^{i(n \sin \theta k_a x - \omega_a t)} + \frac{4\pi}{c} \sigma_{\text{eq}} A_t \cos \theta e^{i(n \sin \theta k_a x - \omega_a t)}. \quad (\text{S66})$$

Using these equations we can express the transmitted and reflected amplitudes in terms of the incident amplitude as:

$$A_t = A_i \frac{2 \cos \alpha}{n \cos \alpha + \cos \theta + \frac{4\pi}{c} \sigma_{\text{eq}} \cos \theta \cos \alpha}; \quad A_r = -A_i \frac{n \cos \alpha - \cos \theta + \frac{4\pi}{c} \sigma_{\text{eq}} \cos \theta \cos \alpha}{n \cos \alpha + \cos \theta + \frac{4\pi}{c} \sigma_{\text{eq}} \cos \theta \cos \alpha}. \quad (\text{S67})$$

Let us now focus on the case with pumping. In this scenario, the conductivity becomes time-dependent due to the transient evolution of the distribution functions, as depicted in the left panel of Figure 4 of the main article. Here, we can express  $\sigma(t, t')$  as:

$$\begin{aligned} \sigma(t, t') &= -\frac{ie^2}{2\pi^2 \hbar} \int_0^\infty d\varepsilon \left( 1 - f^{(e)}(\varepsilon, t') - f^{(h)}(\varepsilon, t') \right) \int_{-\infty}^\infty d\omega \frac{\hbar(\omega + i\gamma_{\text{inter}}) e^{-i\omega(t-t')}}{(2\varepsilon - \hbar(\omega + i\gamma_{\text{inter}}))(2\varepsilon + \hbar(\omega + i\gamma_{\text{inter}}))} \\ &= \frac{e^2}{\pi \hbar} \theta(t - t') e^{-\gamma_{\text{inter}}(t-t')} \int_0^\infty d\varepsilon \cos \left[ \frac{2\varepsilon(t-t')}{\hbar} \right] \left( 1 - f^{(e)}(\varepsilon, t') - f^{(h)}(\varepsilon, t') \right). \end{aligned} \quad (\text{S68})$$

Thus, by substituting these results into the boundary conditions, we arrive at the subsequent expression:

$$\begin{aligned} 2 \cos \alpha A_i(t) &= (n \cos \alpha + \cos \theta) A_t(t) + \\ &+ \frac{4\pi e^2}{\pi \hbar c} \int_{-\infty}^\infty dt' \theta(t - t') e^{i(\omega_a + i\gamma_{\text{inter}})(t-t')} \int_0^\infty d\varepsilon \cos \left[ \frac{2\varepsilon(t-t')}{\hbar} \right] \left( 1 - f^{(e)}(\varepsilon, t') - f^{(h)}(\varepsilon, t') \right) \cos \theta \cos \alpha A_t(t'). \end{aligned} \quad (\text{S69})$$

Fourier transforming this equation yields:

$$\begin{aligned} 2 \cos \alpha \tilde{A}_i(\nu) &= (n \cos \alpha + \cos \theta) \tilde{A}_t(\nu) + \frac{4\pi e^2}{\pi \hbar c} \int_{-\infty}^\infty dt' \int_{t'}^\infty dt e^{i(\omega_a + i\gamma_{\text{inter}})(t-t') + i\nu t} \times \\ &\times \int_0^\infty d\varepsilon \cos \left[ \frac{2\varepsilon(t-t')}{\hbar} \right] \left( 1 - f^{(e)}(\varepsilon, t') - f^{(h)}(\varepsilon, t') \right) \cos \theta \cos \alpha A_t(t') \end{aligned} \quad (\text{S70})$$

where the Fourier transform of the amplitude coefficients is defined as

$$\tilde{A}_{i,t}(\nu) = \int_{-\infty}^\infty A_{i,t}(t) e^{i\nu t} dt. \quad (\text{S71})$$

We can readily perform the integration over  $t$  in Eq. (S70). Keeping only the relevant terms, one gets:

$$\int_{t'}^{\infty} dt e^{i(\omega_a + i\gamma_{\text{inter}})(t-t') + i\nu t} \cos\left[\frac{2\varepsilon(t-t')}{\hbar}\right] = -ie^{i\nu t'} \left\{ \frac{\hbar^2(\omega_a + \nu + i\gamma_{\text{inter}})}{4\varepsilon^2 - \hbar^2(\omega_a + \nu + i\gamma_{\text{inter}})^2} \right\}. \quad (\text{S72})$$

Therefore, Eq. (S70) is rewritten as:

$$2 \cos \alpha \tilde{A}_i(\nu) = (n \cos \alpha + \cos \theta) \tilde{A}_t(\nu) - \frac{4\pi}{c} \left( \frac{ie^2}{\pi\hbar} \right) \int_{-\infty}^{\infty} dt' e^{i\nu t'} \int_0^{\infty} d\varepsilon \hbar(\omega_a + \nu + i\gamma_{\text{inter}}) \frac{(1 - f^{(e)}(\varepsilon, t') - f^{(h)}(\varepsilon, t'))}{4\varepsilon^2 - \hbar^2(\omega_a + \nu + i\gamma_{\text{inter}})^2} \cos \theta \cos \alpha A_t(t') \quad (\text{S73})$$

and, once again, we can identify here the expression for the conductivity and rewrite:

$$2 \cos \alpha \tilde{A}_i(\nu) = (n \cos \alpha + \cos \theta) \tilde{A}_t(\nu) + \frac{4\pi}{c} \int_{-\infty}^{\infty} dt' e^{i\nu t'} \sigma_{\text{ne}}(\omega + \nu, t') \cos \theta \cos \alpha A_t(t'). \quad (\text{S74})$$

The last term of the equation represents a convolution of both pulses, as the non-equilibrium conductivity arises due to the pump beam. If there is a delay,  $\delta t$ , between the pump and probe, we can simply modify the effective conductivity as:

$$\sigma_{\text{ne}}(\omega + \nu, t') \rightarrow \sigma_{\text{ne}}(\omega + \nu, t' + \delta t). \quad (\text{S75})$$

Now, we need to solve Eq. (S74), which can be achieved through iterations. The zeroth order iteration consists of neglecting the second term on the right-hand side, resulting in:

$$\tilde{A}_t^{(0)}(\nu) = \frac{2 \cos \alpha}{n \cos \alpha + \cos \theta} \tilde{A}_i(\nu). \quad (\text{S76})$$

To obtain the first order of the transmitted amplitude, we substitute the expression for the zeroth order into the integral in Equation (S74), which allows us to obtain the first order amplitude for the transmitted field:

$$\tilde{A}_t^{(1)}(\nu) = t^{(0)} \tilde{A}_i^{(0)}(\nu) - \frac{8\pi}{c} \frac{\cos \theta \cos^2 \alpha}{(n \cos \alpha + \cos \theta)^2} \int_{-\infty}^{\infty} dt' e^{i\nu t'} \sigma_{\text{ne}}(\omega + \nu, t') A_i(t'). \quad (\text{S77})$$

For the reflected wave, using boundary condition (S61), we can write:

$$\tilde{A}_r^{(1)}(\nu) = r^{(0)} \tilde{A}_i^{(0)}(\nu) - \frac{8\pi}{c} \frac{\cos^2 \theta \cos \alpha}{(n \cos \alpha + \cos \theta)^2} \int_{-\infty}^{\infty} dt' e^{i\nu t'} \sigma_{\text{ne}}(\omega + \nu, t') A_i(t'), \quad (\text{S78})$$

where

$$r^{(0)} = -\frac{n \cos \alpha - \cos \theta}{n \cos \alpha + \cos \theta}. \quad (\text{S79})$$

Finally, let us define the reflectivity of the entire structure under pumping as:

$$R'_a(\delta t) = \frac{\int_{-\infty}^{\infty} d\nu |\tilde{A}_r(\nu)|^2}{\int_{-\infty}^{\infty} d\nu |\tilde{A}_i(\nu)|^2}. \quad (\text{S80})$$

If we consider the expression obtained at Equation (S78) up to first-order in conductivity, we see that the reflectivity of the system under pumping is given by:

$$R'_a = R_a^{(0)} + \frac{2}{W_a} \frac{n \cos \alpha - \cos \theta}{(n \cos \alpha + \cos \theta)^3} \frac{8\pi}{c} \cos \alpha \cos^2 \theta \text{Re} \left\{ \int_{-\infty}^{\infty} d\nu \int_{-\infty}^{\infty} dt \tilde{A}_i(\nu) A_i(t) e^{i\nu t} \sigma_{\text{ne}}(\omega_a + \nu, t + \delta t) \right\} \quad (\text{S81})$$

with

$$R_a^{(0)} = |r^{(0)}|^2 \quad ; \quad W_a = \int_{-\infty}^{\infty} d\nu |\tilde{A}_i(\nu)|^2. \quad (\text{S82})$$

If we consider graphene without pumping, but with the same precision in the expansions, we get:

$$R_a = \left| \frac{n \cos \alpha - \cos \theta + \frac{4\pi}{c} \sigma_{\text{eq}} \cos \theta \cos \alpha}{n \cos \alpha + \cos \theta + \frac{4\pi}{c} \sigma_{\text{eq}} \cos \theta \cos \alpha} \right|^2 \approx R_a^{(0)} - \frac{4\pi}{c} \text{Re}\{\sigma_{\text{eq}}\} R_a^{(0)} \frac{\cos^2 \theta}{\cos \alpha} \frac{t^{(0)^2}}{r^{(0)}}.$$

Therefore, the differential reflectivity is given by:

$$\frac{\delta R_a(\delta t)}{R_a} \approx \frac{R'_a(\delta t) - R_a}{R_a^{(0)}} = -\frac{4\pi \cos^2 \theta}{c \cos \alpha} \frac{t^{(0)^2}}{r^{(0)}} \left\{ \frac{\text{Re}\{\Sigma_a(\delta t)\}}{W_a} - \text{Re}\{\sigma_{\text{eq}}\} \right\}, \quad (\text{S83})$$

where

$$\Sigma_a(\delta t) = \int_{-\infty}^{\infty} d\nu \int_{-\infty}^{\infty} dt \tilde{A}_i(\nu) A_i(t) e^{i\nu t} \sigma_{\text{ne}}(\omega_a + \nu, t + \delta t). \quad (\text{S84})$$

To simplify this expression, let us consider that  $\omega_a \gg \nu$ , which allows us to write:

$$\Sigma_a(\delta t) = \int_{-\infty}^{\infty} dt A_i(t) \sigma_{\text{ne}}(\omega_a, t + \delta t) \int_{-\infty}^{\infty} d\nu e^{i\nu t} \tilde{A}_i(\nu) = 2\pi \int_{-\infty}^{\infty} dt A_i^2(t) \sigma_{\text{ne}}(\omega_a, t + \delta t). \quad (\text{S85})$$

Inserting the explicit expression for  $A_i$  and dividing by  $W_a$  as required in Eq. (S83), we obtain:

$$\frac{\text{Re}\{\Sigma_a(\delta t)\}}{W_a} = \frac{1}{\tau_a} \sqrt{\frac{2}{\pi}} \int_{-\infty}^{\infty} dt \exp\left[-\frac{2t^2}{\tau_a^2}\right] \text{Re}\{\sigma_{\text{ne}}(\omega_a, t + \delta t)\}. \quad (\text{S86})$$

We are interested in the real part of  $\sigma_{\text{ne}}$ . In the limit of  $\gamma \rightarrow 0$ , using the Sokhotski–Plemelj theorem, it is easy to show that the real part of the conductivity can be simply written as

$$\text{Re}\{\sigma_{\text{ne}}\} = \sigma_0 \left[ 1 - f^{(e)}\left(\frac{\hbar\omega_a}{2}, t + \delta t\right) - f^{(h)}\left(\frac{\hbar\omega_a}{2}, t + \delta t\right) \right]. \quad (\text{S87})$$

## S6. Criterion of importance of the hot-electron effects

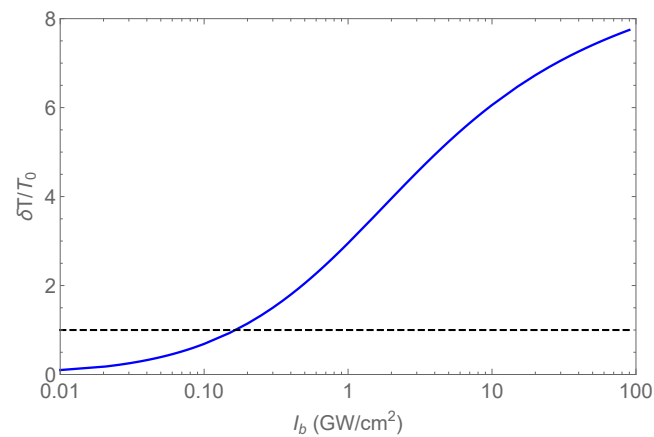
To evaluate the importance of the hot-electron effects, we introduce a criterion to measure how far away our system is from thermal equilibrium with the crystal lattice. Since the temperature is clearly a signature from the hot electron gas, we can compare the temperature of the hot electron gas with the one at equilibrium as

$$\frac{\delta T(t)}{T_0} = \frac{T(t) - T_0}{T_0} \quad (\text{S88})$$

and see how it evolves with the pumping intensity. Therefore, we can establish the following criterion: when this quantity exceeds unity, the hot-electron effects become essential, meaning that the electron temperature is at least twice the equilibrium temperature.

In Figure S2, we illustrate the variation of  $\delta T/T_0$  with the intensity of the pump beam. It is important to note that, for this analysis, we must fix the time to a specific value. Since our focus is on examining the behavior of the hot electrons, we cannot set  $t = 0$ , as we assume the thermalization to occur first for graphene. Therefore, we set  $t = 100$  fs. As shown, for intensities on the order of  $0.1 \text{ GW/cm}^2$ , our parameter already exceeds 1. This implies that, even for somewhat lower intensities, the hot electron effects are already highly

significant and most of the nonlinear experiments uses intensities well above this order of magnitude.



**Figure S2.** Variation of  $\delta T/T_0$  with the intensity for  $t = 100$  fs. We used the same parameters as in the left panel in Figure 5 of the main text.

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