# Supplemental Material:

# Tunable Ultrafast Thermal Relaxation in Graphene Measured by Continuous-Wave Photomixing

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### S1. NONLINEAR THERMAL MODEL

The electron temperature in the graphene may be modeled by the following nonlinear differential equation:

$$\alpha T \frac{dT}{dt} + \beta_1 (T - T_L) + \beta_3 (T^3 - T_L^3) = I(t)$$
(S1)

where T represents the graphene electron temperature,  $T_L$  is the lattice temperature, and I(t) is the absorbed optical power per unit area.  $\alpha T$  is the specific heat in the graphene and the terms proportional to  $\beta_1$  and  $\beta_3$  describe momentum-conserving cooling and disorder-assisted supercollision cooling, respectively.

We re-write these equations in terms of  $x \equiv T - T_L$ , the deviation from the lattice temperature:

$$\alpha (T_L + x) \frac{dx}{dt} + \beta_1 x + \beta_3 \left[ (T_L + x)^3 - T_L^3 \right] = I(t)$$
(S2)

We next assume that  $x \ll T_L$ , i.e., the photoinduced change in electron temperature is small in comparison to the equilibrium (lattice) temperature. With this assumption, x(t) may be expanded in a power series in the intensity I,

$$x(t) = x^{(1)}(t) + x^{(2)}(t) + x^{(3)}(t) + \dots$$
(S3)

Where  $x^{(n)} \propto I^n$ , and we are retaining terms up to third order. Substituting this expansion into (S2) gives

$$\alpha (T_L + x^{(1)} + x^{(2)} + x^{(3)}) \frac{d}{dt} (x^{(1)} + x^{(2)} + x^{(3)}) + \beta_1 (x^{(1)} + x^{(2)} + x^{(3)}) + \beta_3 \left[ (T_L + x^{(1)} + x^{(2)} + x^{(3)})^3 - T_L^3 \right] = I(t) \quad (S4)$$

Next, we expand (S4) and separately equate the orders to obtain the following inhomogeneous linear differential equations for  $x^{(1)}$ ,  $x^{(2)}$  and  $x^{(3)}$ ,

$$\alpha T_L \frac{dx^{(1)}}{dt} + (\beta_1 + 3\beta_3 T_L^2) x^{(1)} = I(t)$$
(S5)

$$\alpha T_L \frac{dx^{(2)}}{dt} + (\beta_1 + 3\beta_3 T_L^2) x^{(2)} = -\alpha x^{(1)} \frac{dx^{(1)}}{dt} - 3\beta_3 T_L [x^{(1)}]^2$$
(S6)

$$\alpha T_L \frac{dx^{(3)}}{dt} + (\beta_1 + 3\beta_3 T_L^2) x^{(3)} = -\alpha x^{(1)} \frac{dx^{(2)}}{dt} - \alpha x^{(2)} \frac{dx^{(1)}}{dt} - 6\beta_3 T_L x^{(1)} x^{(2)} - \beta_3 \left[x^{(1)}\right]^3$$
(S7)

which can be re-written as:

$$\frac{dx^{(1)}}{dt} + \gamma x^{(1)} = \frac{I(t)}{\alpha T_L} \tag{S8}$$

$$\frac{dx^{(2)}}{dt} + \gamma x^{(2)} = -\frac{1}{T_L} x^{(1)} \frac{dx^{(1)}}{dt} - \frac{3\beta_3}{\alpha} \left[ x^{(1)} \right]^2 \tag{S9}$$

$$\frac{dx^{(3)}}{dt} + \gamma x^{(3)} = -\frac{1}{T_L} x^{(1)} \frac{dx^{(2)}}{dt} - \frac{1}{T_L} x^{(2)} \frac{dx^{(1)}}{dt} - \frac{6\beta_3}{\alpha} x^{(1)} x^{(2)} - \frac{\beta_3}{\alpha T_L} \left[ x^{(1)} \right]^3$$
(S10)

where

$$\gamma \equiv \frac{\beta_1 + 3\beta_3 T_L^2}{\alpha T_L} \tag{S11}$$

represents the equivalent (linearized) cooling rate, taking into account both cooling mechanisms.

For the two-laser illumination considered here, the optical intensity absorbed in the graphene is given by

$$I(t) = I_1 + I_2 + 2\sqrt{I_1 I_2} \cos \Omega t$$
 (S12)

where  $I_1$  is the absorbed intensity of laser 1,  $I_2$  is the absorbed intensity of laser 2, and  $\Omega \equiv \omega_1 - \omega_2$  is the heterodyne beat frequency between the two lasers.

Substituting this expression into (S8), one can find a solution for  $x^{(1)}(t)$ , which is used in turn to find  $x^{(2)}(t)$  from (S9), and  $x^{(3)}(t)$  from (S10).

The photovoltage produced through the Seebeck effect can be expressed as

$$V(t) = rT(T - T_L) = rx(x + T_L)$$
 (S13)

where rT is the Seebeck coefficient of graphene. Substituting  $x = x^{(1)} + x^{(2)} + x^{(3)} + \dots$  into (S13), evaluating only the DC component of V(t), and retaining only terms up to the third order in I, one finds, after simplification:

$$V(I_1, I_2) = r \left\{ \frac{I_1 + I_2}{\alpha \gamma} + \beta_1 \frac{(I_1 + I_2)^2}{(\alpha \gamma T_L)^3} - (3\beta_3^2 T_L^4 + 7T_L^2 \beta_1 \beta_3) \frac{(I_1 + I_2)^3}{T_L^6 \alpha^5 \gamma^5} \dots \right\}$$
(S14)

$$+2I_{1}I_{2}\left[\frac{\beta_{1}}{(\alpha\gamma T_{L})^{3}}-(9T_{L}^{4}\beta_{3}^{2}+15T_{L}^{2}\beta_{1}\beta_{3}+2\beta_{1}^{2})\frac{(I_{1}+I_{2})}{T_{L}^{6}\alpha^{5}\gamma^{5}}\right]\frac{\gamma^{2}}{\Omega^{2}+\gamma^{2}}\quad\dots\quad(S15)$$

$$-2I_{1}I_{2}\left[(6T_{L}^{2}\beta_{1}\beta_{3}-2\beta_{1}^{2})\frac{(I_{1}+I_{2})}{T_{L}^{6}\alpha^{5}\gamma^{5}}\right]\left(\frac{\gamma^{2}}{\Omega^{2}+\gamma^{2}}\right)^{2}\right\}$$
(S16)

For the room-temperature conditions reported here  $(T_L = 300 \text{ K})$ , we may make the additional approximation that  $\beta_1 \ll \beta_3 T_L^2$ . In this regime, the linearized cooling rate  $(\gamma)$  is determined primarily by supercollision cooling, even though both cooling processes contribute to the measured nonlinearity in the response. With this assumption, (S14)-(S16) simplify to:

$$V(I_1, I_2) = r \left\{ \frac{I_1 + I_2}{\alpha \gamma} + \beta_1 \frac{(I_1 + I_2)^2}{(\alpha \gamma T_L)^3} - 3\beta_3^2 \frac{(I_1 + I_2)^3}{T_L^2 \alpha^5 \gamma^5} \dots \right.$$
(S17)

$$+2I_{1}I_{2}\left[\frac{\beta_{1}}{(\alpha\gamma T_{L})^{3}}-9\beta_{3}^{2}\frac{(I_{1}+I_{2})}{T_{L}^{2}\alpha^{5}\gamma^{5}}\right]\frac{\gamma^{2}}{\Omega^{2}+\gamma^{2}}\bigg\}$$
(S18)

The photoinduced voltage can be rewritten as

$$V(I_1, I_2) = a_1(I_1 + I_2) + a_2(I_1^2 + I_2^2) - a_3(I_1^3 + I_2^3) \quad \dots$$
(S19)

$$+2a_2I_1I_2\left[1+\frac{\gamma^2}{\Omega^2+\gamma^2}\right] - 3a_3I_1I_2(I_1+I_2)\left[1+\frac{2\gamma^2}{\Omega^2+\gamma^2}\right]$$
(S20)

where the coefficients  $a_1$ ,  $a_2$  and  $a_3$  are given by

$$a_1 \equiv \frac{r}{\alpha\gamma}, \quad a_2 \equiv \frac{\beta_1}{(\alpha\gamma T_L)^3}, \quad a_3 \equiv \frac{3\beta_3^2}{T_L^2\alpha^5\gamma^5}$$
 (S21)

When the two beams  $I_1$  and  $I_2$  are double-chopped and synchronously detected at the chopper difference frequency, the lock-in amplifier produces a signal proportional to (S20):

$$V_{\Delta} = V(I_1, I_2) - V(I_1, 0) - V(0, I_2) + V(0, 0)$$
(S22)

$$= 2a_2I_1I_2\left(1 + \frac{\gamma^2}{\Omega^2 + \gamma^2}\right) - 3a_3I_1I_2(I_1 + I_2)\left(1 + \frac{2\gamma^2}{\Omega^2 + \gamma^2}\right)$$
(S23)

The DC photovoltage therefore has a Lorentzian dependence on the heterodyne difference frequency  $\Omega \equiv \omega_1 - \omega_2$ , with a spectral width that is proportional to the carrier cooling rate  $\gamma$ , as shown schematically in Fig. S1

#### **S2. NONLINEAR PHOTORESPONSE OF THE LOWER MOBILITY SAMPLE**

Fig. S2 shows a measurement similar to Fig. 2 performed on lower-mobility exfoliated graphene on SiO<sub>2</sub>. In this device, the diffusion length is estimated to be only 500 nm, which is about one order of magnitude smaller than for the encapsulated device. Because of this difference, the majority of the photoresponse in this device originates from the Fermi-level pinned region near the contact, where the carrier concentration is not as easily controlled by the applied gate voltage. For positive gate voltages, Fermi level pinning produces a pn junction and charge-neutral region near the contact[34, 35], which contributes to the



FIG. S1. DC photovoltage  $V_{\Delta}$  as a function of the heterodyne difference frequency  $\Omega = \omega_1 - \omega_2$ .

observed sub-linear response. Otherwise, the response is qualitatively similar to that of the HBN-encapsulated device, and we observe a similar expected transition from supercollision cooling to conventional cooling under negative gate bias.

From the data in Fig. S2, the sublinear-superlinear transition occurs at  $V_g = -6$  V where the estimated Fermi level is  $E_F = 80$  meV. Assuming a disorder mean-free-path of l = 40 nm (which was independently determined from DC electrical measurements), we can use equation (5) in the main text to determine the ratio of the two rate coefficients,  $\beta_1/\beta_3 = 5300$  K<sup>2</sup>.

# S3. LINEARIZED COOLING RATE AT THE CHARGE NEUTRAL POINT

The thermal model presented in the manuscript and in (S1) ignores the fact that when the graphene is gated at the charge neutral point, the carriers are no longer degenerate, and under these conditions, the specific heat  $(\alpha T)$  and conventional cooling coefficient  $(\beta_1)$  must be modified to [14, 22, 36]:

$$\alpha T \to \alpha_2 T^2$$
, where  $\alpha_2 \equiv 18\zeta(3)k_B^3/\pi\hbar^2 V_F^2$  (S24)

 $\beta_1 \to \beta_5 T^4$ , where  $\beta_5 \equiv 7\pi^3 k_B^5 V_D^2 / 30\rho \hbar^5 v_F^6$  (S25)



FIG. S2. (a) Single-laser photovoltage  $(V_1)$ , and nonlinear photomixing signal  $(V_{\Delta})$  measured vs. the gate voltage  $V_g$ , for the exfoliated graphene on SiO<sub>2</sub>. (b) Measured photovoltage  $|V_1|$  vs. optical input power, showing clearly the sub-linear and super-linear behaviors.

and the nonlinear thermal equation under these conditions becomes

$$\alpha_2 T^2 \frac{dT}{dt} + \beta_5 T^4 (T - T_L) + \beta_3 (T^3 - T_L^3) = I(t)$$
(S26)

If (S26) is linearized about the lattice temperature, one obtains, analogous to (S5)

$$\alpha_2 T_L^2 \frac{dx}{dt} + (\beta_5 T_L^4 + \beta_3 T_L^2) x = I(t)$$
(S27)

where  $x = T - T_L$  is the photoinduced change in electron temperature relative to the lattice. The linearized cooling rate is then

$$\gamma' = \frac{\beta_5 T_L^2 + 3\beta_3}{\alpha_2} \tag{S28}$$

which is shown by the red curve in Fig. 5b.

We expect that at low temperatures,  $k_bT$  will be much smaller than  $E_F^*$ , the chargepuddle-limited Fermi level, in which case the cooling can instead be accurately described by (S1). The boundary between the two regimes can be estimated by equating (S11) and (S28), which, for the parameters considered in Fig. 5 indicates that (S11) should only be applicable for  $T_L < 80$  K. This condition is represented by the intersection between the blue and red curves in Fig. 5. When the parameters determined from the low-temperature fit to (S11) are used in (S28), with no additional free parameters, we correctly predict the observed cooling rate above 80 K, which further supports the model.

# S4. DEVICE FABRICATION AND DC ELECTRICAL CHARACTERIZATION

Both devices considered here employed a doped silicon substrate ( $\rho_{\rm Si} = 100 \ \Omega \cdot {\rm cm}$ ), with 300 nm of thermally grown SiO<sub>2</sub> as a gate dielectric. The substrate served as a large-area gate contact for adjusting the carrier concentration.

The HBN-encapsulated device [20] was fabricated per the method described in [21]. A piece of polypropylene carbonate (PPC) coated polydimethylsiloxane (PDMS) was first used to pick up HBN, monolayer graphene and another piece of HBN, in that order. The resulting heterostructure was then transferred to the aforementioned SiO<sub>2</sub> substrate, where electron beam lithography (EBL) was used to define a hydrogen silses quioxane (HSQ) hard mask on poly(methy methacrylate) (PMMA). The surrounding areas were then etched in CHF<sub>3</sub> plasma to shape the device channel and expose the graphene edge. Afterwards, HSQ was lifted off and EBL was used again to define the contact leads and pads using PMMA, and 1.5 nm/20 nm/50 nm Cr/Pd/Au was e-beam evaporated and lifted off for edge contact. The HBN-encapsulated graphene channel length was 7  $\mu$ m and width 0.7  $\mu$ m .

For the second device, a single layer of graphene was mechanically exfoliated from bulk graphite and transferred directly to the SiO<sub>2</sub>/Si substrate. The exfoliated graphene exhibits a mobility about  $\mu = 5,000 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ , which was inferred from DC transport measurements. Electron-beam lithography was used to pattern a bi-layer resist comprised of methyl methacrylate (MMA) and polymethy methacrylate (PMMA). The contacts were deposited using successive angled evaporations of chromium (15 nm) and gold (30 nm), thereby providing dissimilar contacts to the opposing edges of the graphene channel. Dissimilar electrical contacts are not necessary when the optical beams are focused onto one contact, as for the measurements reported here, but this configuration also provides the thermal asymmetry needed for detection of spatially homogeneous or longer wavelength illumination. The graphene channel length was 2.5  $\mu$ m and width 7  $\mu$ m.

To quantify the electrical characteristics and gating behavior, we conducted unilluminated measurements of the DC resistance as a function of the gate voltage, for both the HBN- encapsulated device and the non-encapsulated device. Fig. S3 shows the DC measurements, along with optical micrographs showing the graphene active region, contact geometry, and cross-sectional diagram.



FIG. S3. The DC resistance R as a function of the applied gate voltage  $V_g$  and the optical micrograph for (a) the HBN-encapsulated graphene device and (b) the exfoliated graphene on SiO<sub>2</sub> device.

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