Electron heating and mechanical properties of graphene

Jose Angel Silva-Guillén [*]

Key Laboratory of Artificial Micro- and Nano-structures of Ministry of Education and School of Physics and Technology,
Wuhan University, Wuhan 430072, China

Francisco Guinea

Fundación IMDEA Nanociencia, C/Faraday 9, Campus Cantoblanco, E-28049 Madrid, Spain;
Department of Physics and Astronomy, University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom;
and Donostia International Physics Center (DIPC)–UPV/EHU, E-20018 San Sebastián, Spain

The heating of electrons in graphene by laser irradiation, and its effects on the lattice structure, are studied. Values for the temperature of the electron system in realistic situations are obtained. For sufficiently high electron temperatures, the occupancy of the states in the σ band of graphene is modified. The strength of the carbon-carbon bonds changes, leading to the emergence of strains, and to buckling in suspended samples. While most applications of "strain engineering" in two-dimensional materials focus on the effects of strains on electronic properties, the effect studied here leads to alterations of the structure induced by light. This optomechanical coupling can induce deflections in the order of ~50 nm in micron-sized samples.

Introduction. Graphene, and other two-dimensional materials, show a unique coupling between the electronic and mechanical properties [1,2]. As a result, electronic transport and optical transitions depend on the shape of the sample, and on strains which may be present. The term "strain engineering" is commonly used [3] to describe techniques which use modifications of the strains in the system to induce desirable electronic properties. The inverse effect, the modification of structural properties by changes in the electronic structure, is hampered by the high mechanical stiffness of these materials. The low optical absorption of a graphene single layer is an additional difficulty, if the changes in the electronic distribution are induced by light. Proposals for the creation of significant forces by optical means rely on nontrivial combinations of graphene and dielectric layers [4,5]. Unusual effects of light on macroscopic, graphenelike systems has also been reported [6].

It is well documented that intense laser pulses lead to the excitation of high-energy electron-hole pairs, and, ultimately, to an electron plasma in thermal equilibrium at a temperature much higher than the lattice temperature [7–12]. The cooling of a hot electron plasma is mediated by optical and acoustic phonons [13,14]. The decoupling between electronic and lattice degrees of freedom has been studied extensively. The difference between electronic and sound velocities suppresses the phase space available for electron-phonon scattering [15,16], and reduces the transfer of energy from electrons to phonons. This obstruction is partially relieved by coherent processes involving phonons and impurities [15],

named supercollisions, which have been observed in different experiments [17–20].

In order to analyze the influence of a high-temperature electron gas on the structural properties of graphene, we consider the setup sketched in Fig. 1. A region in a suspended graphene layer of radius R is illuminated by a laser. The graphene layer absorbs energy from the laser beam, at a rate defined by the laser power W. We calculate the electron temperature once a steady state regime has been reached. The electron temperature modifies the occupancy of the graphene bands, which, in turn, changes the forces between atoms and induce strains and deformations in the lattice, irrespective of the lattice temperature, which is assumed to be much lower than the electron temperature. The effect of the electron temperature on the lattice constant is obtained from a self-consistent band-structure calculation, using a Boltzmann distribution for the occupancy of the electronic states. This calculation includes the non-negligible coupling between the σ bands and the lattice parameter [21,22]. For completion, we include a brief discussion of the radiation pressure due to the momentum transfer from laser photons to the graphene layer in the Supplemental Material [23].

Electron and lattice temperature. We assume that the laser energy is absorbed by the graphene layer via the creation of electron-hole pairs of energies comparable to $\hbar\nu$, where ν is the frequency of the laser. We study a suspended layer, and we do not need to take into account the degrees of freedom of a substrate. A steady state is reached through the combined effect of electron-electron interactions, the scattering between electrons and optical phonons, and heat diffusion, which transfers energy away from the region illuminated by the laser. The electron-electron interactions, which thermalize the electron plasma, include plasmon emission processes [24].
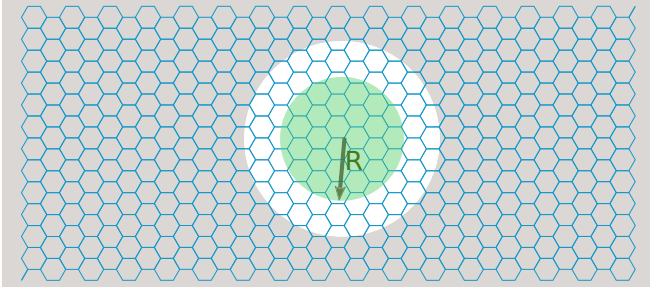
[*]josilgui@gmail.com

FIG. 1. Schematic drawing of the device used to heat up electrons in a graphene lattice. The substrate is depicted in gray and has a hole. A region of suspended graphene is illuminated by a laser beam (depicted in green) of radius R.

The steady state is characterized by a temperature $T(W, R)$ which describes both the electron gas and the optical phonons [25]. The temperature depends on the laser power W and the radius of the laser spot R.

The rate at which the energy flows away from the illuminated area depends on the electron thermal conductivity $\kappa_{\rm el}$, which is given by [14]

$$\kappa_{\rm el} = \frac{18\zeta(3)k_B^3 T_{e\text{-}h}^2}{\pi^2\hbar^2 v_F^2 a} v_F \ell_{\rm el}, \tag{1}$$

where $\zeta(x)$ is the Riemann zeta function, $a \approx 3.5$ Å is the thickness of the graphene layer, k_B is the Boltzmann constant, v_F the Fermi velocity, and $\ell_{\rm el}$ is the electronic mean free path. At high temperatures, $k_B T_{e\text{-}h} \gg \mu$, where μ is the chemical potential, the value of ℓ_{el} is given by

$$\ell_{\rm el} \approx \frac{e^2}{k_B T_{e\text{-}h}} \approx \frac{\hbar v_F}{k_B T_{e\text{-}h}}. \tag{2}$$

Hence,

$$\kappa_{\rm el} \approx \frac{18\zeta(3)}{\pi^2}\frac{k_B^2 T_{e\text{-}h}}{\hbar a} = \frac{c_\kappa k_B^2 T_{e\text{-}h}}{\hbar a}, \tag{3}$$

where $c_\kappa \approx 18\zeta(3)/\pi^2$ is a dimensionless constant. This result, as well as the existence of a universal electrical conductivity $\sigma \sim e^2/\hbar$, are a consequence of the fact that neutral graphene is a critical system.

If we take values for the thermal conductivity for the lattice from previous works, that is, $\kappa_l \approx 5000$ W/m K [26,27], Eq. (1) implies that $\kappa_l \gg \kappa_{\rm el}$, even for electron-hole temperatures $T_{e\text{-}h} \gtrsim 10^3$ K. Therefore, in the following, we can assume that the lattice dissipates heat rapidly, and remains in equilibrium with the external environment.

The rate of heat flow from the electrons to the acoustic modes can be divided into two contributions, one where the total momentum is conserved [13], and the other from supercollisions, which is mediated by elastic scattering [15]. The heat flow rates per unit area for these processes are

$$\left.\frac{\partial\mathcal{Q}}{\partial t}\right|_{\rm ac1} \approx \frac{D^2(k_B T_{e\text{-}h})^5}{\hbar^5\rho v_F^6},$$

$$\left.\frac{\partial\mathcal{Q}}{\partial t}\right|_{\rm ac2} \approx \frac{D^2(k_B T_{dis})^2(k_B T_{e\text{-}h})^3}{\hbar^5\rho v_F^4 c^2}, \tag{4}$$
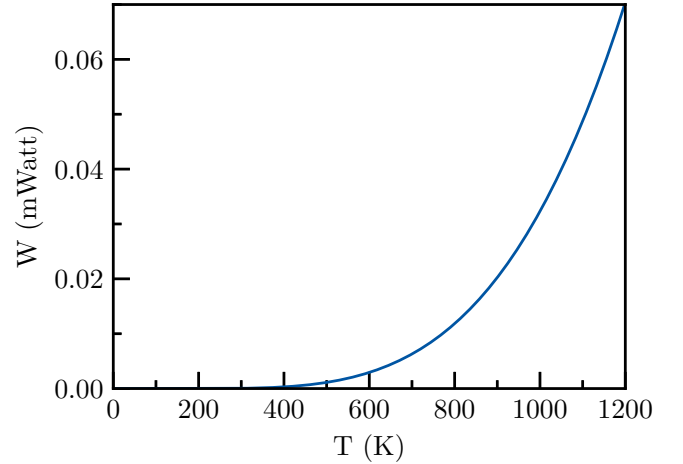

FIG. 2. Power dissipated by optical phonons over an area $A = 1$ μm^2 as a function of electron temperature.

where D is the deformation potential, ρ is the mass density, and c is the sound velocity. We describe supercollisions in terms of an effective temperature related to elastic scattering $T_{\rm dis}$. We assume that elastic scattering leads to a mobility independent of the carrier density. Then, $(k_B T_{\rm dis})^2 \approx \epsilon_F(\hbar v_F/\ell_{\rm el}^{\rm elastic})$, where $\ell_{\rm el}^{\rm elastic}$ is the electronic elastic mean free path. For $\ell_{\rm el}^{\rm elastic} \sim 100$ nm, $T_{\rm dis} \sim 10^2$ K.

The rate of heat flow to the optical modes is

$$\left.\frac{\partial\mathcal{Q}}{\partial t}\right|_{\rm op} \approx \alpha_{\rm op}\frac{(k_B T_{e\text{-}h})^3}{(\hbar v_F)^4}\mathcal{F}\left(\frac{\hbar\omega_{\rm op}}{k_B T_{e\text{-}h}}\right), \tag{5}$$

where $\omega_{\rm op}$ is an average optical phonon frequency, and the parameter $\alpha_{\rm op}$ and the function $\mathcal{F}$ are described in the Supplemental Material (see also Refs. [8,28,29]). The power dissipated to optical modes in an area $A = 1$ μm^2 as function of electron temperature is plotted in Fig. 2.

By comparing Eqs. (4) and (5), we conclude that the energy transfer from high-temperature electrons to optical phonons is much larger than the energy transfer to acoustic phonons, for physically accessible temperatures, $T_{e\text{-}h} \lesssim 10^4$ K. Therefore, in the following, we can consider only the role of the optical phonons.

The fraction of the laser power W absorbed by the electron-hole pairs in the graphene layer is $\pi\alpha W$, where $\alpha \approx 1/137$ is the fine-structure constant, and $\pi\alpha$ is the optical absorption of a graphene layer [30]. In order to obtain the steady state temperature of the electron plasma, we take into account the energy dissipated away from the laser spot, which depends on the electron heat conductivity, and the transfer of energy from electrons to optical phonons. We obtain

$$c_\kappa\frac{k_B^2}{\hbar}\partial_r[T(r)\partial_r T(r)] + \frac{\alpha_{\rm op}[k_B T(r)]^3}{(\hbar v_F)^4}\mathcal{F}\left(\frac{\hbar\omega_{\rm op}}{k_B T}\right)$$

$$= \begin{cases} \frac{\alpha W}{\pi R^2}, & r \leqslant R, \\ 0, & R < r, \end{cases} \tag{6}$$

where c_κ was defined in Eq. (3). As mentioned previously, we assume that the laser has power W, and it irradiates uniformly a circular spot of radius R. Qualitatively, the two terms in Eq. (6) allow us to define two cooling regimes: (1) For low
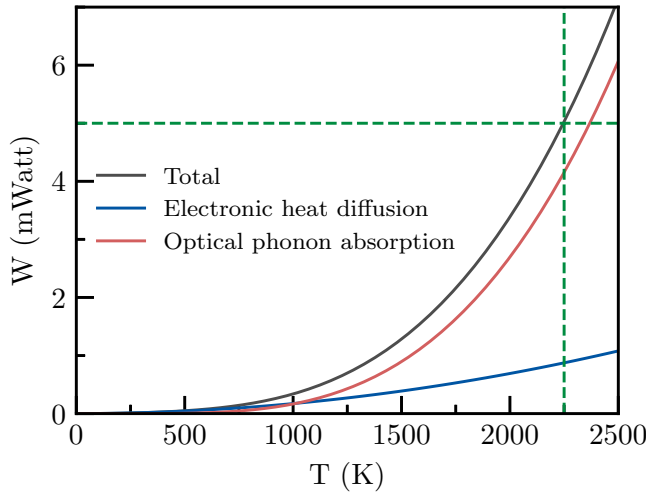
FIG. 3. Temperature of the electron-hole plasma vs laser power for a laser spot of radius $R = 1$ μm. Red: Dissipation by electronic heat diffusion. Blue: Dissipation by optical phonon absorption. Black: Total dissipation. For a laser power of $W = 5$ mW, the calculated temperature is $T = 2250$ K.

FIG. 4. Equilibrium lattice constant (blue) and gap between the σ bands (red) vs electronic temperature.

values of R, or large values of W, the dissipation is dominated by electronic thermal conduction into the nonirradiated region, $r > R$, described by the first term in Eq. (6). (2) If W is sufficiently low, or R is large enough, dissipation is mostly the local transfer of heat to optical modes, given by the second term in Eq. (6).

The values W_* and R_*, which define the crossover between these regimes takes place approximately, are

$$\alpha W_* R_*^4 \sim \frac{(\hbar v_F)^8}{\alpha_{\rm op}^2 \hbar^3}, \qquad (7)$$

where we have replaced $\mathcal{F}[(\hbar\omega_{\rm op})/(k_B T)]$ by its constant value in the limit $(\hbar\omega_{\rm op})/(k_B T) \to \infty$ (see Supplemental Material for more details).

A more precise determination can be obtained from computing the electron temperature as a function of W and R considering only one relaxation mechanism. The crossover between the two regimes takes place when the two temperatures are similar. Figure 3 shows the relation between plasma temperature and laser power when the laser is focused on a region of radius $R = 1$ μm. The optical phonon absorption dominates for $W \gtrsim 0.2$ mW. For this laser power, the electron plasma reaches a temperature $T \approx 1300$ K. For a power $W \sim 5$ mW, in the regime dominated by optical phonons, the electron temperature is $T \approx 2250$ K.

Outside the region illuminated by the laser, electronic thermal conduction will bring the electron-hole plasma to equilibrium with the external environment. From Eq. (6) we can define a length scale

$$\ell_{\rm eq}^2 = \pi R^2 \frac{c_\kappa (k_B T)^2}{\alpha W}. \qquad (8)$$

For $T \sim 2200$ K and $W \sim 5$ mW, we obtain $\ell_{\rm eq} \sim 600$ nm.

Effect of the electronic temperature on the graphene lattice. As we have just seen, it is possible to change the temperature of the electr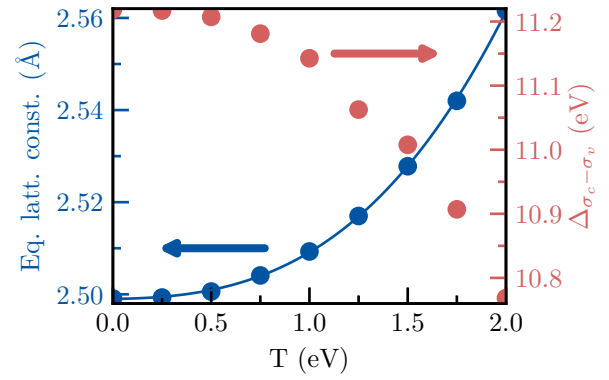ons in graphene without modifying the actual temperature of its lattice. Now, we center our attention on the possible consequences that the change of the electronic temperature has on the lattice of graphene. For that, we carried out first-principles calculations. These were performed using a numerical atomic orbitals approach to density functional theory (DFT) [31,32], which was developed for efficient calculations in large systems and implemented in the SIESTA code [33,34]. We have used the generalized gradient approximation (GGA) and, in particular, the functional of Perdew, Burke, and Ernzerhof [35]. Only the valence electrons are considered in the calculation, with the core being replaced by norm-conserving scalar relativistic pseudopotentials [36] factorized in the Kleinman-Bylander form [37]. The nonlinear core-valence exchange-correlation scheme [38] was used for all elements. We have used a split-valence triple-ζ basis set including polarization functions [39]. The energy cutoff of the real-space integration mesh was set to 1000 Ry. To build the charge density (and, from this, obtain the DFT total energy and atomic forces), the Brillouin zone (BZ) was sampled with the Monkhorst-Pack scheme [40] using grids of $(60 \times 60 \times 1)$ k points. To simulate the effect of increasing the electronic temperature of graphene, we changed the electronic temperature of the Fermi-Dirac (FD) distribution of the electrons. It is important to note that, once a finite temperature has been chosen, the relevant energy is not the Kohn-Sham (KS) energy, but the free energy since the atomic forces are derivatives of this [41–43]. The change of the lattice constant with electronic temperature is shown in Fig. 4, where we can see that with increasing temperature, the lattice constant becomes larger.

This result can be understood by looking at the effect that the electronic temperature has on the σ bands which are responsible for the bonds in graphene and, therefore, its lattice constant. Looking at Fig. 4, we can see that changing the electronic temperature slightly changes the population of these bands. As a result, the σ bonds will be become weaker, and the lattice will expand.

Electronic temperature and strains. We have just seen that the temperature of the electron-hole plasma can modify the interatomic forces and the local lattice constant. Hence, strains are induced in the graphene layer when shining a laser beam to a graphene layer.

The results in the preceding text suggest that a lattice expansion of order $\epsilon = \Delta\ell/\ell \sim 0.01\%$ is possible when the
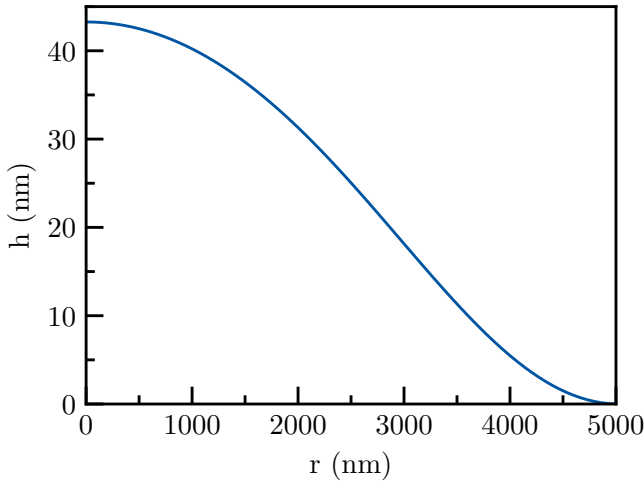
FIG. 5. Profile of a disk-shaped suspended graphene flake with clamped edges of radius $R = 5000$ nm with a thermally generated stress of $\epsilon = 0.01\%$.

FIG. 6. As in Fig. 3 for a graphene bilayer. The calculated temperature is $T \approx 4570$ K.

temperature of the electron plasma is $T \sim 1000$–2000 K. In a suspended system with clamped edges (see Fig. 1), such an expansion will cause the sheet to buckle. A simple calculation, using the techniques developed for graphene bubbles in Ref. [44], and for a circular region of radius $R = 5$ μm, gives the profile shown in Fig. 5. Note that the average strain is $\epsilon \approx h_{\mathrm{max}}^2/R^2$.

Generalization to multilayer graphene: *A graphene bilayer.* The rate of heat transfer in a graphene bilayer from the electron-hole plasma to optical modes is calculated in the Supplemental Material. The main change is a suppression in the heat transfer, due to interference effects in the electron-phonon matrix element, partially compensated by an increase in the electronic density of states. Note that, for a given power, the absorption is $\alpha \approx 2\pi/137$, twice the absorption of a monolayer. Results are shown in Fig. 6. The temperature of the electron-hole plasma, for a given laser power, is significantly increased in bilayer graphene.

Graphene stacks with more than two layers. In a system with N layers, the absorbed energy per unit time is $\partial Q/\partial t = N\alpha W$, distributed over the N layers, so that the energy absorbed per layer does not change. In order to estimate the electronic thermal conductivity, we make use of the fact that the low-energy band structure of multilayered graphene can be described as a combination of quadratic and linear bands touching at the Dirac point [45]. The resulting electronic thermal conductivity is determined by the quadratic bands. Its temperature dependence is $\kappa_{el}(N) \approx [k_B^3 T^2 \tau_N(T)]/(\hbar^2 a)$, where we assume that, at high temperatures, the scattering time $\tau_N(T)$ is determined by electron-electron interactions. These interactions couple with a similar strength of an elec-
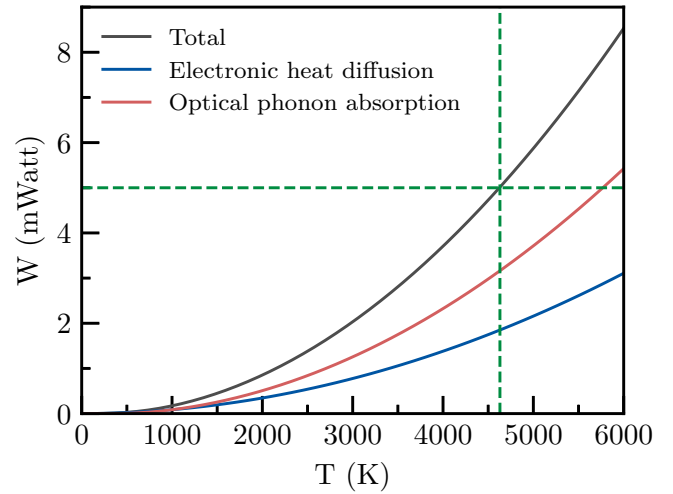
tron in a given layer and electron-hole pairs in any layer. Combining this result with the criticality provided by the band touching, we obtain $\tau_N(T) \sim \hbar/(Nk_BT)$, so that $\kappa_{el}(N) \sim (k_B^2 T)/(N\hbar a)$. Finally, we obtain that the electron temperature scales as $T(N) \propto \sqrt{N}$.

Conclusions. We have estimated the electron temperature in a graphene layer under laser irradiation. The temperature is determined by a balance between the power input from the laser, the transfer of energy to optical phonons, and the conduction of heat away from the irradiated region. Temperatures in the order of 1000–2000 K can be reached for a laser power $W \approx 5$ mW in regions of radius $R \approx 1$ μm. Similar, or higher, temperatures can be expected in multilayer stacks. The weak coupling between electrons and acoustic phonons, and the large heat conductivity of these phonons imply that the lattice temperature changes only slightly.

The electron temperature leads to changes in the lattice constant of graphene, even if the lattice temperature does not vary. We find that strains of order $\epsilon \approx 0.01\%$–0.02% are likely. These strains can induce a significant buckling in a suspended sample. Our analysis suggests that light can be used to modify the structural properties of graphene and other two-dimensional materials.

[1] B. Amorim, A. Cortijo, F. de Juan, A. G. Grushin, F. Guinea, A. Gutiérrez-Rubio, H. Ochoa, V. Parente, R. Roldán, P. San-Jose *et al.*, Phys. Rep. **617**, 1 (2016).

[2] R. Roldán, L. Chirolli, E. Prada, J. A. Silva-Guillén, P. San-Jose, and F. Guinea, Chem. Soc. Rev. **46**, 4387 (2017).

[3] V. M. Pereira and A. H. Castro Neto, Phys. Rev. Lett. **103**, 046801 (2009).

[4] S. H. Mousavi, P. T. Rakich, and Z. Wang, ACS Photonics **1**, 1107 (2014).

[5] M. M. Salary, S. Inampudi, K. Zhang, E. B. Tadmor, and H. Mosallaei, Phys. Rev. B **94**, 235403 (2016).

[6] T. Zhang, H. Chang, Y. Wu, P. Xiao, N. Yi, Y. Lu, Y. Ma, Y. Huang, K. Zhao, X.-Q. Yan *et al.*, Nat. Photonics **9**, 471 (2015).

[7] T. Winzer, A. Knorr, and E. Malic, Nano Lett. **10**, 4839 (2010), 1008.1904.

[8] C. H. Lui, K. F. Mak, J. Shan, and T. F. Heinz, Phys. Rev. Lett. **105**, 127404 (2010).

[9] J. C. Johannsen, S. Ulstrup, F. Cilento, A. Crepaldi, M. Zacchigna, C. Cacho, I. C. E. Turcu, E. Springate, F. Fromm, C. Raidel *et al.*, Phys. Rev. Lett. **111**, 027403 (2013).

[10] I. Gierz, J. C. Petersen, M. Mitrano, C. Cacho, E. Turcu, E. Springate, A. Stöhr, A. Köhler, U. Starke, and A. Cavalleri, Nat. Mater. **12**, 1119 (2013).

[11] J. C. Johannsen, S. Ulstrup, A. Crepaldi, F. Cilento, M. Zacchigna, J. A. Miwa, C. Cacho, R. T. Chapman, E. Springate, F. Fromm *et al.*, Nano Lett. **15**, 326 (2015).

[12] Q. Ma, T. I. Andersen, N. L. Nair, N. M. Gabor, M. Massicotte, C. H. Lui, A. F. Young, W. Fang, K. Watanabe, T. Taniguchi *et al.*, Nat. Phys. **12**, 455 (2016).

[13] R. Bistritzer and A. H. MacDonald, Phys. Rev. Lett. **102**, 206410 (2009).

[14] W.-K. Tse and S. Das Sarma, Phys. Rev. B **79**, 235406 (2009).

[15] J. C. W. Song, M. Y. Reizer, and L. S. Levitov, Phys. Rev. Lett. **109**, 106602 (2012).

[16] J. C. W. Song and L. S. Levitov, J. Phys.: Condens. Matter **27**, 164201 (2015).

[17] N. M. Gabor, J. C. W. Song, Q. Ma, N. L. Nair, T. Taychatanapat, K. Watanabe, T. Taniguchi, L. S. Levitov, and P. Jarillo-Herrero, Science **334**, 648 (2011).

[18] K. J. Tielrooij, J. C. W. Song, S. A. Jensen, A. Centeno, A. Pesquera, A. Zurutuza Elorza, M. Bonn, L. S. Levitov, and F. H. L. Koppens, Nat. Phys. **9**, 248 (2013).

[19] J. C. W. Song, K. J. Tielrooij, F. H. L. Koppens, and L. S. Levitov, Phys. Rev. B **87**, 155429 (2013).

[20] K. J. Tielrooij, L. Piatkowski, M. Massicotte, A. Woessner, Q. Ma, Y. Lee, K. S. Myhro, C. N. Lau, P. Jarillo-Herrero, N. F. van Hulst *et al.*, Nat. Nanotechnol. **10**, 437 (2015).

[21] F. Mazzola, J. W. Wells, R. Yakimova, S. Ulstrup, J. A. Miwa, R. Balog, M. Bianchi, M. Leandersson, J. Adell, P. Hofmann *et al.*, Phys. Rev. Lett. **111**, 216806 (2013).

[22] F. Mazzola, T. Frederiksen, T. Balasubramanian, P. Hofmann, B. Hellsing, and J. W. Wells, Phys. Rev. B **95**, 075430 (2017).

[23] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.101.060102 for a brief description of the radiation pressure and the heat transfer to optical phonons on a graphene layer.

[24] J. M. Hamm, A. F. Page, J. Bravo-Abad, F. J. Garcia-Vidal, and O. Hess, Phys. Rev. B **93**, 041408(R) (2016).

[25] Note that, as we are considering a suspended system, we do not include substrate modes [46].

[26] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, and C. N. Lau, Nano Lett. **8**, 902 (2008).

[27] A. A. Baladin, Nat. Mater. **10**, 569 (2011).

[28] A. H. Castro Neto and F. Guinea, Phys. Rev. B **75**, 045404 (2007).

[29] D. Yadav, M. Trushin, and F. Pauly, Phys. Rev. B **99**, 155410 (2019).

[30] R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, and A. K. Geim, Science **320**, 1308 (2008).

[31] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[32] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[33] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys.: Condens. Matter **14**, 2745 (2002).

[34] E. Artacho, E. Anglada, O. Diéguez, J. D. Gale, A. García, J. Junquera, R. M. Martin, P. Ordejón, J. M. Pruneda, D. Sánchez-Portal *et al.*, J. Phys.: Condens. Matter **20**, 064208 (2008).

[35] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[36] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[37] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[38] S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982).

[39] E. Artacho, D. Sánchez-Portal, P. Ordejón, A. García, and J. M. Soler, Phys. Status Solidi B **215**, 809 (1999).

[40] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[41] R. M. Wentzcovitch, J. L. Martins, and P. B. Allen, Phys. Rev. B **45**, 11372 (1992).

[42] S. de Gironcoli, Phys. Rev. B **51**, 6773 (1995).

[43] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).

[44] E. Khestanova, F. Guinea, L. Fumagalli, A. K. Geim, and I. V. Grigorieva, Nat. Commun. **7**, 12587 (2016).

[45] F. Guinea, A. H. Castro Neto, and N. M. R. Peres, Phys. Rev. B **73**, 245426 (2006).

[46] T. Low, V. Perebeinos, R. Kim, M. Freitag, and P. Avouris, Phys. Rev. B **86**, 045413 (2012).