ARTICLE

OPEN

Check for updates

Universal layer number in graphite

K. Sasaki [1,2] & K. Hitachi[2]

Graphene absorbs light in accordance with the fine-structure constant $\alpha \simeq 1/137$. The α value is universal in the sense that it is unrelated to material parameters but solely related to the elementary charge, which is a fundamental constant governing the coupling of light and matter. A new universality governed only by α has yet to be discovered in graphene optics. However, since α is a dimensionless quantity, it can be anticipated that the reciprocal of α appears as a characteristic number of layers in the light absorptance of an N-layer graphene. Here, we report that this number is $2/\pi\alpha$. We show simultaneously that for light in the infrared to visible range, an N-layer graphene with N above 1500 may be regarded as graphite. This also enables us to obtain the simplest expression for the optical constants of graphite, which is written in terms of α and interlayer distance only.

[1] NTT Research Center for Theoretical Quantum Physics, NTT Corporation, 3-1 Morinosato Wakamiya, Atsugi, Kanagawa 243-0198, Japan. [2] NTT Basic Research Laboratories, NTT Corporation, 3-1 Morinosato Wakamiya, Atsugi, Kanagawa 243-0198, Japan. ✉email: kenichi.sasaki.af@hco.ntt.co.jp

By a mechanical cleavage method[1], the number of layers in graphite is decreased from a huge number to unity, and graphene can be simply defined as a single layer of graphite. But, above how many layers of graphene can we regard it as if "graphite"? This is a natural question for many readers. We answer the question by calculating the optical properties of an N-layer graphene as a function of the number of layers N. In the process of solving this problem, we noticed that various interesting aspects lie behind it. They include not only scientific problems but also important problems related to applications. For example, what is the optimum N for absorbing light most efficiently? Interestingly, the answer is related to a fundamental physics constant, namely the fine-structure constant $\alpha \simeq 1/137$.

The exfoliation of a single-layer graphene from graphite provided a great opportunity to explore the behavior of massless Dirac fermions[2,3]. It is widely recognized that because of the conical band structure unique to massless Dirac fermions, graphene absorbs light in accordance with the fine-structure constant[2,4,5]. Considering the fact that graphite generally possesses massive Dirac fermions[6], there should be interesting physics relevant to a change in N from ∞ to 1. Furthermore, the "mass" is closely related to stacking order and interlayer distance which are changed by thermal expansion caused by absorption of light. Therefore, it is meaningful to investigate the optical properties of an N-layer graphene as a function of N.

In this paper, we show the universal layer number in graphite to be $2/\pi\alpha$. By employing the transfer matrix method, we show simultaneously that for light in the infrared to visible range, an N-layer graphene with N above 1500 may be regarded as graphite, on the basis of a convergence criterion. This also enables us to obtain the simplest expression for the optical constants of graphite, which is written in terms of α and interlayer distance only[5]. The validity of the method is proved by the fact that the calculated reflectance reproduces experimentally observed reflectivity of graphite[7]. When similar considerations are applied to the general van der Waals heterostructures, many insights besides those into graphite will be obtained.

Results

Universal layer number and optical definition of graphite. Figure 1a shows the N-dependence of the absorptance A_N. The solid curves are obtained by the transfer matrix method for different wavelengths, while the dashed curve at the top is from a simpler model that neglects the reflection. There are three noticeable points in this figure. First, for a small N value below 20, it is hard to distinguish between the results of the two models. This means that the reflection is suppressed and negligible for such N values, which are the systems that were studied extensively after the discovery of graphene. The simplified model is justified for a small N although it fails to explain the fact that graphite gleams. Second, there is a lump-like structure at around 90 that is almost independent of the wavelength. This suggests the presence of a universal number of layers. Figure 1b, which shows the N-dependence of the reflectance R_N and transmittance T_N for a wavelength at 1550 nm, reveals that the lump-like structure corresponds to the layer number at which R_N and T_N cross each other. In other words, because R_N increases and T_N decreases with increasing N, $R_N + T_N$ takes an extremal value at the crossing point where the condition $R_N = T_N$ is satisfied. To confirm that the crossing point is exactly given by a universal layer number $N = 2/\pi\alpha$, we take the $\omega \to 0$ limit in Eq. (4) which immediately gives $R_N = \left(\frac{\pi\alpha N}{2+\pi\alpha N}\right)^2$ and $T_N = \left(\frac{2}{2+\pi\alpha N}\right)^2$. The emergence of the universal layer number in light absorption is intriguing, because the lump-like structure exhibits a maximum efficiency of 50% for a wide range of wavelengths (>1500 nm) at this universal layer
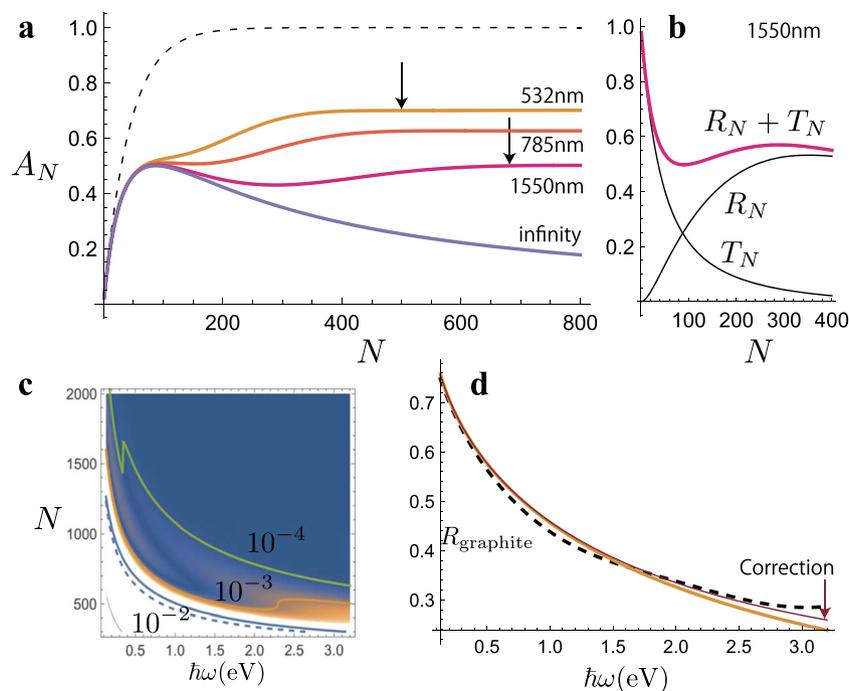
Fig. 1 Calculated results. a The light absorptance A_N is plotted as a function of the number of graphene layers N for different wavelengths. The arrows indicate the N values above which satisfy the convergence criterion $|A_N - A_\infty| \leq 10^{-3}$. The dashed curve is the result of the simplified model which neglects the reflection. **b** The N-dependence of the reflectance R_N and transmittance T_N for 1550 nm. The intersection of R_N and T_N appears at $N = 2/\pi\alpha$. **c** A contour plot of $|A_N - A_\infty|$ is shown with the curve of the more stricter convergence criterion $|A_N - A_\infty| \leq 10^{-4}$. The dashed curve is $2\delta(\omega)/d$. The kinks in the 10^{-3} and 10^{-4} curves arise because $|A_N - A_\infty|$ approaches zero as increasing N like a damped oscillation in a manner dependent on photon energy. **d** The theoretical results reproduce satisfactory the experimental reflectivity of graphite (dashed curve). The correction to $\pi\alpha$ improves.

number ($2/\pi\alpha \approx 87$). Physically, maximum efficiency is achieved by the fact that the electric field is not decaying and almost constant (due to boundary reflection). As a result, each layer absorbs an almost equal amount of light most efficiently. Third, A_N is almost saturated above about 500 and 670 for 532 and 1550 nm, respectively. The critical layer number, defined more precisely by the tolerance $|A_N - A_\infty| \leq 10^{-3}$, increases with decreasing photon energy, as shown in Fig. 1c. The critical layer number is closely related to the light frequency of interest, and the energy dependence must be relevant to that of the field localization, because the convergence of A_N means that T_N approaches 0. For light in a wide range of frequencies from infrared to visible, Fig. 1c clearly shows that for $N > 1500$, A_N meets the convergence criterion. Therefore, the condition $N > 1500$ serves as the definition of "graphite" or more exactly, the lower limit of the number of layers that can be considered graphite from the optics point of view.

The results in Fig. 1a, b, c can be qualitatively understood with the basic knowledge about the absorption of light in thin films[8]. For a very thin film, absorption indeed scales linearly with the real part of the dynamical conductivity and thus also with the number of layers, shown by the simplified model. If the dynamical conductivity does not depend on the frequency, then also the absorption is necessarily dispersionless. Above a certain thickness, this linear approximation fails, while the wave nature of light starts to play a role (thickness is still small, but no longer fully negligible as compared with the wavelength). The absorption then becomes dispersive and it does not go linearly (not even monotonically) with the thickness anymore. Such behavior is well described in classical works on the optical properties of solids[8]. The only difference here is the non-dispersive conductivity of graphene due to interband transitions.

Simple formula for optical constant of graphite. We now derive a simple formula for the refractive index n and extinction coefficient κ of graphite. The proof consists of two logical steps. First, the optical constants are determined by the dynamical conductivity of graphite $\sigma_{graphite}$ as $(n + i\kappa)^2 = 1 + i\sigma_{graphite}/\epsilon_0\omega$. As a result, we can obtain a theoretical $R_{graphite}$ by the standard formula; $R_{graphite} = [(n-1)^2 + \kappa^2]/[(n+1)^2 + \kappa^2]$, if $\sigma_{graphite}$ is known. Second, by the ansatz $\sigma_{graphite} = \sigma_{graphene}/d$[5,9], it can be shown that the resultant $R_{graphite}$ exactly reproduces the infinitely large N of the transfer matrix model ($A_\infty = 1 - R_{graphite}$). Therefore, with the transfer matrix model we establish the following simple analytical expression of the optical constants of graphite,

$$n(\omega) = \sqrt{\frac{1 + \sqrt{1 + \left(\frac{\pi\alpha c}{\omega d}\right)^2}}{2}}, \quad \kappa(\omega) = \frac{1}{2n(\omega)}\frac{\pi\alpha c}{\omega d}. \quad (1)$$

These can be used to capture the changes in d caused, for example, by a high pressure[10], temperature increase (thermal expansion) due to light absorption, and the propagation of a strain pulse[11], through the reflectivity of graphite. We note that the frequency dependence of the critical layer number shown in Fig. 1c is explained by the field localization characterized by the skin-depth $\delta(\omega) \equiv c/\omega\kappa(\omega) = (2/\pi\alpha)n(\omega)d$, since $n(\omega)$ increases as ω decreases. Note also that it contains $2/\pi\alpha$ as the characteristic layer number.

We note that the α value cannot change with pressure, so any pressure-induced change to the linear-band structure results in a change of the reflectance. But it is not due to a pressure-induced changes of α but due to a breakdown of the simple description of the reflectance in terms of α and d only.

Discussion

Here, we compare the calculation with an experiment for graphite (highly oriented pyrolithic graphite)[7]. By using the above-mentioned formula with the optical constants measured for an ordinary ray, we plot the reflectivity as a function of photon energy in Fig. 1d (dashed curve). We compare it with the result calculated with $N = 1500$, for which there is little discrepancy between theory and experiment at least for photon energy below 0.5 eV. The difference seen from 0.5 to 1.5 eV means extra absorption, which may be the effects of thermal expansion and diffusion[12]. This speculation is consistent with the fact that $R_{graphite}$ decreases with increasing d. The discrepancy between theory and experiment seen at high energy above 1.5 eV is suppressed by the inclusion of the correction $\pi\alpha(1 + 0.05(\hbar\omega/t)^2)$, where $t = 3$ eV is the hopping integral. The need to correct the conductivity arises partly because of the breakdown of the Dirac cone approximation at high energy[13]. Our model of graphite, based on the assumption that electrons at different layers interact only through electromagnetic fields[14], satisfactory reproduces the experimental result for the reflectance of graphite, despite its simplicity. Our aim was to describe the optical properties of an N-layer graphene in a simplified situation, namely, in the absence of a substrate. In particular, for a small N with non-negligible transmittance, there is a possibility that the transmittance (and therefore the absorptance) is modified by a special substrate. The transfer matrix method can be modified to incorporate the effect of a substrate, which might be necessary if we are to understand the results for a complicated situation.

Finally, we show the correction to A_N caused by an electronic coupling between layers that is expected to exist for natural graphite with AB stacking dominance[10,15]. The energy dispersion relation changes from massless Dirac fermions to massive Dirac fermions with the "mass" $m_r = \gamma_1 \cos\left(\frac{r\pi}{N+1}\right)$, where $r (=1, \cdots, N)$ is the wavenumber of the standing wave formed along the c-axis by an interlayer hopping of γ_1 ($= 0.4$ eV)[6,16]. We calculated interband dynamical conductivity of an N-layer graphene with AB stacking and found that it is expressed in terms of the mass variables as

$$\sigma_N(\omega) = \frac{\pi\alpha}{d}\frac{\epsilon_0 c}{N}\sum_{r=1}^{N}\left\{\left(1 - \frac{2m_r}{\hbar\omega - 2m_r}\right)\Theta(\hbar\omega - 2(m_r + |m_r|))\right.$$
$$\left. + \left(\frac{2m_r}{\hbar\omega}\right)^2 \Theta(\hbar\omega - 2|m_r|)\right\},$$

$$(2)$$

where $\Theta(x)$ denotes the step function satisfying $\Theta(x) = 1$ for $x \geq 0$ and 0 otherwise. This formula reproduces the results obtained previously for small N values[17–19] and infinite N[20]. By defining the relative permittivity as $\varepsilon_N(\omega) \equiv 1 + i\frac{\sigma_N(\omega)}{\epsilon_0\omega}$, we can obtain the reflection amplitude as $c_0^r = \frac{i\left(\sqrt{\varepsilon_N} - \frac{1}{\sqrt{\varepsilon_N}}\right)\sin\left(\sqrt{\varepsilon_N}\frac{\omega(z_N - z_1)}{c}\right)}{2\cos\left(\sqrt{\varepsilon_N}\frac{\omega(z_N - z_1)}{c}\right) - i\left(\sqrt{\varepsilon_N} + \frac{1}{\sqrt{\varepsilon_N}}\right)\sin\left(\sqrt{\varepsilon_N}\frac{\omega(z_N - z_1)}{c}\right)}$. Figure 2 shows the resultant A_N for three photon energies $\hbar\omega = 0.8$, 0.4, and 0.2 eV. The correction to the lump-like structure is seen. Interestingly, the correction is most pronounced when photon energy is near $2\gamma_1$ and is suppressed by decreasing photon energy. The former originates from the fact that $\sigma_N(\omega)$ is enhanced by direct interband transitions at $\hbar\omega = 2\gamma_1$[10,15]. The latter is relevant to the fact that the effect of the γ_1 is removed from $\sigma_N(\omega)$ in the $\omega \to 0$ limit: indeed, $\lim_{\omega\to 0}\sigma_N(\omega) = \pi\alpha\epsilon_0 c/d$ provided that the system is undoped. Our analysis presented here is limited to AB stacking, and there is a possibility that $\sigma_N(\omega)$ undergoes further correction because the
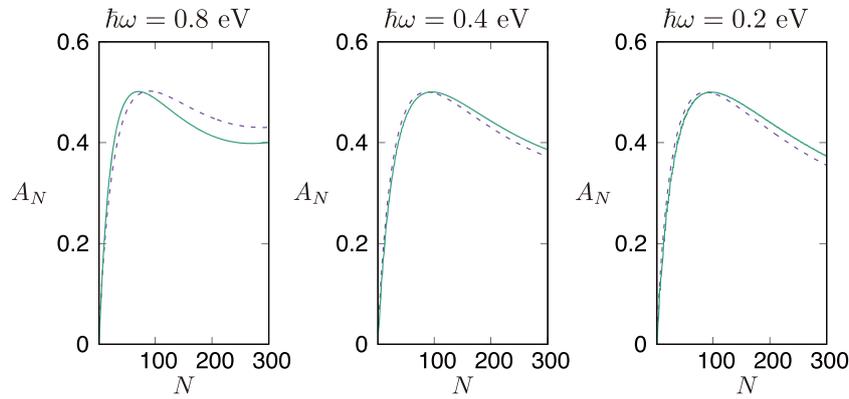
Fig. 2 Correction to universal layer number by interlayer electronic coupling. The N-dependence on the absorptance A_N is shown for several photon energies $\hbar\omega = 0.8$, 0.4, and 0.2 eV. The solid (dashed dotted) curves are the results calculated with (without) the interlayer electronic coupling. The correction appears as a slight change in the lump-like structure.

low-energy band structure is perturbed by an interlayer interaction in a stacking dependent manner[6,21].

In summary, we have proposed the concept of a universal number of layers $2/\pi\alpha \approx 87$. When the optical properties of an N-layer graphene are viewed as a function of N, $2/\pi\alpha$ is much larger than the layer numbers that have been studying extensively after the discovery of the graphene monolayer. Our approaches based on the simple approximation of separated, electrically uncoupled graphene N layers is applicable to other graphene-like materials, multilayer epitaxial graphene and turbostratic graphite[22], besides highly oriented pyrolithic graphite. We extended the study to natural graphite, by including interlayer electronic coupling, and found that the N-dependence of absorptance would exhibit a correction to the universal layer number for specific photon energy. When similar considerations are applied to the general van der Waals heterostructures, many insights besides those into graphite will be obtained.

Methods

The transfer matrix method is useful for determining the propagation of waves such as electrons, light, and phonons[23] in a superlattice and has also been used for a superlattice containing graphene[24–26]. Our superlattice is shown in Fig. 3, where the previously unreported key idea relates to the interlayer space between adjacent graphene layers as a constituent of the superlattice. In other words, graphite is a superlattice consisting of a vacuum and an atomic layer. The arrows along the z-axis indicate the propagation direction of light; the first graphene layer transmits and reflects the incident light in the forward and backward directions with the amplitudes c_1^t and c_0^r, which are to be determined. Such transmission and reflection are repeated at each layer. The absolute square of c_N^t and c_0^r corresponds to the transmittance T_N and reflectance R_N, respectively. The total absorptance is given by $A_N = 1 - R_N - T_N$, which is equivalent to the sum of the energies absorbed by each graphene layer.

The electromagnetic fields of adjacent layers are related by the transfer matrix T given by

$$\begin{pmatrix} E_{i+1} \\ B_{i+1} \end{pmatrix} = \begin{pmatrix} \cos\left(\frac{\omega d}{c}\right) & ic\sin\left(\frac{\omega d}{c}\right) \\ \frac{i}{c}\sin\left(\frac{\omega d}{c}\right) & \cos\left(\frac{\omega d}{c}\right) \end{pmatrix} \begin{pmatrix} 1 & 0 \\ -\frac{\pi\alpha}{c} & 1 \end{pmatrix} \begin{pmatrix} E_i \\ B_i \end{pmatrix}. \quad (3)$$

The T matrix is obtained from Maxwell's equations and is actually the product of two matrices. The first matrix expresses the propagation of electromagnetic fields in the interlayer vacuum space, which is fixed by the interlayer distance d, angular frequency of light ω, and speed of light c. The second matrix represents the boundary condition of graphene; the electric field is continuous ($E'_{i+1} = E_i$), while the magnetic field is discontinuous ($B'_{i+1} = B_i - (\pi\alpha/c)E_i$). The discontinuity is given by the current in graphene, $J_i = \sigma_{\text{graphene}}E_i$, where $\sigma_{\text{graphene}} = \pi\alpha\epsilon_0 c$ is the graphene's dynamical conductivity, divided by $-\epsilon_0 c^2$ according to Ampère's circuital law. By multiplying the transfer matrix with the field at an infinitesimal distance above the top layer $N-1$ times, we can determine the field at an infinitesimal distance below the N-th layer,

$$\begin{pmatrix} E'_N(z_N) \\ B'_N(z_N) \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ -\frac{\pi\alpha}{c} & 1 \end{pmatrix} T^{N-1} \begin{pmatrix} E_0(z_1) \\ B_0(z_1) \end{pmatrix}. \quad (4)$$

Because $E_0(z_1) = e^{i\omega z_1/c} + c_0^r e^{-i\omega z_1/c}$ and $cB_0(z_1) = e^{i\omega z_1/c} - c_0^r e^{-i\omega z_1/c}$ for the light
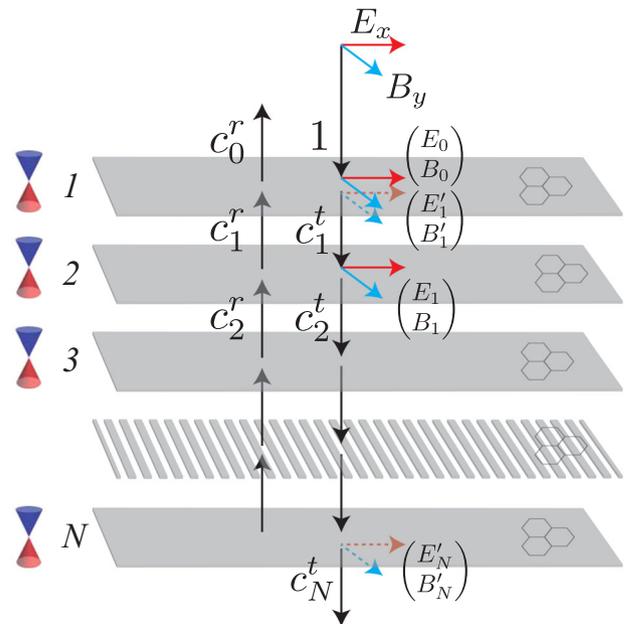
Fig. 3 N-layer graphene with light. Light propagation in an N-layer graphene superlattice is shown schematically. A linearly polarized light expressed by E_x and B_y, is assumed in the transfer matrix method. The electromagnetic fields at the i-th interlayer space ($z_i \le z \le z_{i+1}$) are written in terms of the amplitudes c_i^t and c_i^r as $E_i(z) = c_i^t e^{i\omega z/c} + c_i^r e^{-i\omega z/c}$ and $cB_i(z) = c_i^t e^{i\omega z/c} - c_i^r e^{-i\omega z/c}$. The interlayer distance d is 0.335 nm.

at the entrance, and $E'_N(z_N) = c_N^t e^{i\omega z_N/c}$ and $cB'_N(z_N) = c_N^t e^{i\omega z_N/c}$ for the field at the exit, Eq. (4) provides two equations for determining the amplitudes c_0^r and c_N^t. Once c_0^r is known, c_i^t and c_i^r can be calculated by using Eq. (3), and the field configuration is locally determined. Please note that in the $\omega \to 0$ limit in Eq. (4), we obtain

$$\begin{pmatrix} E'_N(z_N) \\ B'_N(z_N) \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ -\frac{\pi\alpha N}{c} & 1 \end{pmatrix} \begin{pmatrix} E_0(z_1) \\ B_0(z_1) \end{pmatrix} \quad (5)$$

which immediately gives $R_N = \left(\frac{\pi\alpha N}{2+\pi\alpha N}\right)^2$ and $T_N = \left(\frac{2}{2+\pi\alpha N}\right)^2$.

For comparison with the transfer matrix model, we use a simpler model that neglects the reflection. The first layer absorbs $\pi\alpha$ of the incident light and transmits the remaining $1 - \pi\alpha$. Because the second layer absorbs $\pi\alpha$ of the transmitted light, the amount of transmitted light after the second layer becomes $(1 - \pi\alpha)^2$. By repeating the calculation, we find that the transmittance after N layers is given by $(1 - \pi\alpha)^N$ and that the absorptance becomes $1 - (1 - \pi\alpha)^N$. This result is independent of ω in contrast to A_N.

Data availability

References
1. Novoselov, K. S. et al. Two-dimensional atomic crystals. *Proc. Natl Acad. Sci. USA* **102**, 10451–3 (2005).
2. Novoselov, K. S. et al. Two-dimensional gas of massless Dirac fermions in graphene. *Nature* **438**, 197–200 (2005).
3. Zhang, Y., Tan, Y.-W., Stormer, H. L. & Kim, P. Experimental observation of the quantum Hall effect and Berryas phase in graphene. *Nature* **438**, 201–204 (2005).
4. Nair, R. R. et al. Fine structure constant defines visual transparency of graphene. *Science* **320**, 1308–1308 (2008).
5. Kuzmenko, A. B., van Heumen, E., Carbone, F. & van der Marel, D. Universal optical conductance of graphite. *Phys. Rev. Lett.* **100**, 117401 (2008).
6. Min, H. & MacDonald, A. H. Electronic structure of multilayer graphene. *Prog. Theor. Phys. Suppl.* **176**, 227–252 (2008).
7. Djurišić, A. B. & Li, E. H. Optical properties of graphite. *J. Appl. Phys.* **85**, 7404–7410 (1999).
8. Palik, E. D. & Furdyna, J. K. Infrared and microwave magnetoplasma effects in semiconductors. *Rep. Prog. Phys.* **33**, 307 (1970).
9. Blinowski, J. et al. Band structure model and dynamical dielectric function in lowest stages of graphite acceptor compounds. *J. de. Phys.* **41**, 47–58 (1980).
10. Hanfland, M., Syassen, K. & Sonnenschein, R. Optical reflectivity of graphite under pressure. *Phys. Rev. B* **40**, 1951–1954 (1989).
11. Thomsen, C., Grahn, H. T., Maris, H. J. & Tauc, J. Surface generation and detection of phonons by picosecond light pulses. *Phys. Rev. B* **34**, 4129–4138 (1986).
12. Marsden, B., Mummery, A. & Mummery, P. Modelling the coefficient of thermal expansion in graphite crystals: implications of lattice strain due to irradiation and pressure. *Proc. R. Soc. A: Math., Phys. Eng. Sci.* **474**, 20180075 (2018).
13. Stauber, T., Peres, N. M. R. & Geim, A. K. Optical conductivity of graphene in the visible region of the spectrum. *Phys. Rev. B* **78**, 085432 (2008).
14. Painter, G. S. & Ellis, D. E. Electronic band structure and optical properties of graphite from a variational approach. *Phys. Rev. B* **1**, 4747–4752 (1970).
15. Taft, E. A. & Philipp, H. R. Optical properties of graphite. *Phys. Rev.* **138**, A197–A202 (1965).
16. Partoens, B. & Peeters, F. M. Normal and Dirac fermions in graphene multilayers: Tight-binding description of the electronic structure. *Phys. Rev. B* **75**, 193402 (2007).
17. Abergel, D. S. L. & Fal'ko, V. I. Optical and magneto-optical far-infrared properties of bilayer graphene. *Phys. Rev. B* **75**, 155430 (2007).
18. Koshino, M. & Ando, T. Magneto-optical properties of multilayer graphene. *Phys. Rev. B* **77**, 115313 (2008).
19. Orlita, M. & Potemski, M. Dirac electronic states in graphene systems: optical spectroscopy studies. *Semiconductor Sci. Technol.* **25**, 063001 (2010).
20. Ichikawa, Y. H. & Kobayashi, K. Optical properties of graphite in the infrared region. *Carbon* **3**, 401–406 (1966).
21. Johnson, L. G. & Dresselhaus, G. Optical properies of graphite. *Phys. Rev. B* **7**, 2275–2285 (1973).
22. Hass, J. et al. Why multilayer graphene on 4H–SiC (000$\bar{1}$) behaves like a single sheet of graphene. *Phys. Rev. Lett.* **100**, 125504 (2008).
23. Mizuno, S., Ito, M. & Tamura, S.-i Time advance and delay of phonon packets scattered off superlattice systems. *Jpn. J. Appl. Phys.* **33**, 2880–2885 (1994).
24. Kaipa, C. S. R. et al. Enhanced transmission with a graphene-dielectric microstructure at low-terahertz frequencies. *Phys. Rev. B* **85**, 245407 (2012).
25. Zhan, T., Shi, X., Dai, Y., Liu, X. & Zi, J. Transfer matrix method for optics in graphene layers. *J. Phys.: Condens. Matter* **25**, 215301 (2013).
26. Cheng, Y. H., Chen, C., Yu, K. Y. & Hsueh, W. J. Extraordinary light absorptance in graphene superlattices. *Opt. Express* **23**, 28755 (2015).

Acknowledgements

Author contributions
K.S. and K.H. conceived of the presented idea. K.S. developed the theory and performed the computations. All authors discussed the results and contributed to the final paper.

Competing interests
The authors declare no competing interests.

Additional information