A reexamination of the effective fine structure constant of graphene, as measured in graphite

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Abstract

We present a refined and improved study of the influence of screening on the effective fine structure constant of graphene, $\alpha^*$, as measured in graphite using inelastic x-ray scattering. This follow-up to our previous study was carried out with two times better momentum resolution, five times better energy resolution, and improved techniques for reducing experimental background. We compare our results to RPA calculations and evaluate the relative importance of interlayer hopping, excitonic corrections, and screening from higher energy excitations. We find that the static, limiting value of $\alpha^*$ falls in the range 0.25 to 0.35, which is higher than our previous result of 0.14, but still below the value expected from RPA. Graphitic effects from interlayer hopping were found to play a negligible role in the range of momenta studied. Instead, the anomalous screening was found to arise from a combination of excitonic effects in the $\pi \rightarrow \pi^*$ continuum and screening from the tightly bound $\sigma$-bands. Both effects appear to fade in the limit of low momentum, suggesting a recovery of RPA in the asymptotic limit, but should have significant influence on low-energy measurements on length scales less than a few nm, such as STM.
I. INTRODUCTION

Since its synthesis a decade ago, graphene has been the subject of intense research\(^2\). In the long-wavelength limit, graphene satisfies the massless Dirac equation, where its electrons follow a linear band dispersion given by \( E = \pm \hbar v_f q \), where the \( \pm \) refers to the conduction/valence bands, \( v_f \approx 10^8 \text{ cm/s} \approx c/300 \) is the Fermi velocity, and \( q \) is the electron momentum (in 2D)\(^3\). As a result of this dispersion, the bare electron-electron interaction strength – as defined by the fine-structure constant \( \alpha = U/K \approx 2.2/\epsilon \), where \( \epsilon \) is the dielectric constant of the substrate on which the graphene is mounted (\( \alpha \approx 2.2 \) for suspended graphene) – is of order unity, in contrast to the interaction strength in QED, where \( \alpha = 1/137 \); thus, many-body effects should, in principle, play a significant role in graphene\(^6\). In particular, the screened value of \( \alpha \), which one could call a renormalized or effective fine structure constant \( \alpha^* \), is a subject of great theoretical interest, and is relevant to all Dirac systems including topological insulator surface states, some classes of transition metal dichalcogenides, Dirac and Weyl semimetals in three dimensions, etc.

Experiment and theory, however, give conflicting views on the value of \( \alpha^* \). Inelastic X-ray scattering (IXS) experiments performed on graphite\(^4\) found that for freestanding graphene \( \alpha^* \approx 0.15 \) as \( q \to 0 \) and \( \omega \to 0 \), and cited an excitonic shift in the \( \pi \)-band dispersion as a possible reason for this reduced \( \alpha^* \). Interpretation of this experiment is based on the assumption that the interaction between graphene sheets in graphite is primarily Coulombic, with interlayer hopping playing a secondary role\(^1\). The experiment, however, had an energy resolution of only 0.3 eV, with data taken at 0.5 eV intervals, when the features of primary interest range from 1 to 15 eV. Additionally, the lowest momenta measured were at 0.238 Å\(^{-1}\) and 0.476 Å\(^{-1}\) so the extrapolation of \( q \to 0 \) relied on only a few points. Subsequent calculations in the random-phase-approximation\(^7\) (RPA) using the full \( \pi \)-bands and including the interlayer hopping parameters \( \gamma_3 \) and \( \gamma_1 \) in graphite (see Fig. 2a) suggested that this discrepancy was due to graphitic effects, i.e., the presence of interlayer hopping terms. Experiments done on boron nitride\(^8\) find that \( \epsilon \approx 3 (\alpha^* \approx 0.9) \), but higher order corrections beyond the RPA have suggested that this is a result of substrate effects\(^9\). Additionally, an investigation of the Shubnikov-de Haas oscillations for the electrons and holes in suspended graphene samples suggested a logarithmic renormalization of the \( \pi \)-bands\(^12\).

In this paper, we present a refined measurement of \( \alpha^* \) in graphene as measured in graphite,
using an improved version of the previous method\textsuperscript{11}, with higher energy and momentum resolution, as well as reduced elastic background. We evaluate the importance of interlayer hopping, excitonic corrections, and the higher energy $\sigma$-bands to the effective fine-structure constant. We compare to theoretical results obtained within the RPA, and show that for $q > 0.212 \text{ Å}^{-1}$, $\alpha^*$ falls in the range 0.25 to 0.35, which is well below the RPA value for graphene. We identify the reason for the low value as a combination of screening from the $\sigma$-bonded electrons, which contribute significantly at finite momentum, and excitonic effects, which comprise a beyond-PRA correction to the screening. Both of these effects appear to fade in the small momentum limit, but should have significant influence on low-energy, local probes such as STM.

II. EXPERIMENT

IXS measurements were carried out at 7.81 keV beam energy at the Advanced Photon Source at Argonne National Laboratory on the Sector 9 beamline. Both ZYA-grade highly-ordered pyrolitic graphite (HOPG) and high quality, commercially obtained, natural single-crystal graphite samples were used. The spectra of the two were found to be indistinguishable for the momenta probed in our experiments. The total energy resolution ranged from 170-180 meV, and the corresponding momentum resolution was set to 0.15-0.3 \text{ Å}^{-1}, depending upon the scan region. Energy analysis was provided by a bent, Si-444, backscattering analyzer, which deflected the scattered photons into a MYTHEN microstrip detector. Our energy resolution is a factor of two better than the previous experiment, reducing the background from the quasielastic line, a key source of error as described in Appendix\textsuperscript{A}. We also removed the incident windows on our sample chamber and improved the reproducibility in beam stop positioning, which further reduced the background in our experiments, particularly in the 0-5 eV range crucial to the extraction of $\alpha^*$. Spectra were obtained for energy losses from 0 to 15 eV, at momentum transfers of $q = 0.212 \text{ Å}^{-1}$ up to $q = 0.563 \text{ Å}^{-1}$, the latter being near the Brillouin zone boundary.

In order to recover information about $\alpha^*$, we need to determine the density-density re-
response function $\chi$,

$$\chi(x_1, x_2, t_1, t_2) = -\frac{i}{\hbar} \sum_m b_m \langle m | [\rho(x_1, t_1), \rho(x_2, t_2)] | m \rangle \theta(t_1 - t_2),$$

which describes the general charge dynamics of the system. The measured intensity in an IXS experiment at a given momentum and energy is proportional to the dynamic structure factor

$$S(q, \omega) = \sum_{n,m} p_m |\langle n | \rho(q_1) | m \rangle|^2 \delta(E - E_n + E_m),$$

where $|n\rangle$ and $|m\rangle$ are the many-body electron states and $p_m = e^{-\beta E_m}/Z$ is the Boltzmann factor. The dynamic structure factor is related to the density-density response function via the quantum-mechanical version of the fluctuation-dissipation theorem,

$$S(q, \omega) = -\frac{1}{\pi} \frac{1}{1 - e^{-\beta \hbar \omega}} \text{Im} \chi(q, -q, \omega).$$

We note that $\chi$ is causal and satisfies the Kramers-Kronig relation

$$\text{Re} \chi(q, -q, \omega) = \frac{2}{\pi} \mathcal{P} \int_0^\infty d\omega' \omega' \frac{\text{Im} \chi(q, -q, \omega')}{(\omega')^2 - \omega^2},$$

and so after extrapolating for $\omega \to \infty$, interpolating the discrete points in $\omega$, and computing the integral, we have both the real and imaginary parts of $\chi$. Fig. 1a shows the resulting spectra for graphite, which we call $\text{Im} \chi_{3D}(q, \omega)$, in absolute units after normalizing to the $f$-sum rule (for a detailed description of this procedure, see Appendix A). Note that in each spectrum we see the onset of particle-hole excitations near $\hbar v_f q$, which implies that we are indeed probing the $\pi$ electrons. The peak at $\omega \approx 8$ eV is the well-known $\pi$-plasmon, which is not a free carrier plasmon at all, but arises from the Van Hove singularity at the top of the band $^2$.

To determine $\alpha^*$, we must first convert our measured $\chi_{3D}(q, \omega)$ for graphite to the equivalent quantity for graphene, which we will call $\chi_{2D}(q, \omega)$. Following the same procedure used in our previous study $^1$, we apply the expression

$$\chi_{2D}(q, \omega) = \frac{\chi_{3D}}{1 - V(q)[1 - F(q)] \chi_{3D}},$$

which describes the response of an isolated, single layer. This expression assumes (1) that the primary interaction between layers in graphite is electrostatic, with interlayer hopping. 

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Footnotes:

1. Reference to previous study

2. Reference to Van Hove singularity
FIG. 1. (a) Measured and theoretical $\chi_{3D}(q, \omega)$. Both calculated spectra are for infinite multilayer graphene both with and without interlayer hopping ($\gamma_{1,3} \neq 0$ and $\gamma_{1,3} = 0$, respectively). (b) Measured and theoretical $\chi_{2D}(q, \omega)$. Red and green spectra are $\chi_{2D}$ that use $\kappa = 2.4$, whereas the orange spectrum uses $\kappa(q)$ for graphene. In both (a) and (b), the vertical line denotes $\hbar v_F q$ for the given $q$, and the calculated spectra have been multiplied by an arbitrary constant to facilitate visual comparisons of plasmon dispersion. The error bars are derived from both Poisson counting and our fitting parameters, and are discussed in greater detail in App. A.

Playing a secondary role, (2) that the layers are infinitely thin, and (3) that the electrons are distributed homogeneously within each layer. Here, $V(q) = 2\pi e^2/q$ is the 2D Coulomb interaction, and $F(q) = \sinh(qd)/(\cosh(qd) - \cos(qz_d))$ is a structure factor that relates the 2D Coulomb interaction to that of a layered 3D material. If the above assumptions are true, it implies that the polarization functions of graphene and graphite are (apart from units) the same:

$$\Pi_{3D}(k, \omega) = \Pi_{2D}(k, \omega)/d. \quad (6)$$
In this case the 2D response of graphene can be acquired from
\[ \chi_{2D}(q, \omega) = \frac{\Pi_{2D}(q, \omega)}{1 - V(q)\Pi_{2D}(q, \omega)}. \]  
(7)
The spectra for \( \text{Im} \chi_{2D} \) obtained in this manner are shown in Fig. 1b. The associated \( \Pi \)-functions are shown in Fig. 3 and discussed in more detail in Sec. IV.

When characterizing the screening properties of graphene, it is sometimes useful to discuss the dielectric function, \( \epsilon_{2D} \), which is defined as
\[ \epsilon_{2D}(q, \omega) = 1 - V(q)\Pi_{2D}(q, \omega). \]  
(8)
Written in terms of the other quantities, the screened, effective fine structure constant of graphene \( \alpha^* \) is defined as
\[ \alpha^*(q, \omega) = \frac{\alpha}{\epsilon_{2D}} = \alpha \cdot \left[ 1 + V(q)\chi_{2D}(q, \omega) \right]. \]  
(9)
\( \alpha^* \) can be thought of as the fine structure constant incorporating the lowest order screening correction in the GW approximation. Note that although Eq. 9 appears similar to an RPA expression for \( \epsilon(q, \omega) \), we have at no point assumed that only RPA polarization bubbles contribute to the scattering; indeed, the \( \chi \) we recover from experiment includes all screening processes including excitonic corrections beyond the RPA. The asymptotic behavior of both \( \chi(q, \omega = 0) \) and \( \alpha^*(q, \omega = 0) \) as \( q \to 0 \) are shown in Fig. 4 and shows whether \( \alpha^* \) is influenced by interlayer hopping, excitonic shifts, \( \sigma \)-band screening, or a combination thereof.

### III. RPA CALCULATION

In order to determine what role interlayer hopping plays in screening in graphene, we model the polarization function \( \Pi(q, \omega) \) in the RPA both with and without the interlayer hopping parameters \( \gamma_1 \) and \( \gamma_3 \) depicted in Fig. 2a. The RPA does not include bound excitons that would contribute to excitonic shifts, so any discrepancies we see between our experiment and the calculated RPA spectra are potentially due to such excitonic effects. We model \( \chi(q, \omega) \) of both graphene and graphite within the RPA. Fig. 2a shows the structure of ABA-stacked graphite along with the interlayer hopping parameters, \( \gamma_1 = 0.4 \) eV and \( \gamma_3 = 0.3 \) eV. For both graphene and graphite, we use the Lindhard response function, which
FIG. 2. (a) Crystal structure of ABA-stacked graphite with hopping potentials \( t, \gamma_1, \gamma_3 \) shown. (b) Brillouin zone of graphene.

is equivalent to the RPA, to directly compute the polarization function \( \Pi(q_\parallel, \omega) \) in the RPA,

\[
\Pi(q_\parallel, \omega) = \frac{g_s}{(2\pi)^d} \int_{BZ} d^2k \sum_{s,s' = \pm 1} f_{s,s'}(k,q_\parallel) \frac{n_F[E^s(k)] - n_F[E^{s'}(k+q)]}{E^s(k) - E^{s'}(k+q) + \omega + i\eta},
\]

where the integral is over the Brillouin zone, \( d \) is the dimensionality (either 2 or 3 for graphene or graphite, respectively), \( g_s \) is the spin degeneracy, \( E^{s/s'}(k) \) is the energy dispersion for the conduction \( (s = 1) \) and valence \( (s = -1) \) \( \pi \)-bands, \( \eta \) is a convergence factor, and \( f_{s,s'}(k,q_\parallel) \) is a function that describes the overlap between the electron and hole wavefunctions. We use the full \( \pi \)-band wavefunctions (as opposed to linearized bands) to compute the responses of graphene and graphite. The details of this calculation, including the evaluation of the function \( f_{s,s'} \), can be found in Appendix B.

Once we obtain \( \Pi_{2D} \) for graphene and \( \Pi_{3D} \) for graphite, we compute \( \chi \) using an approximation to include the screening effects of higher-order bands. The dielectric function
\[ \epsilon_{2D}(q, \omega) = \kappa(q) - V(q, \omega)\Pi_{2D}(q, \omega), \]  

(11)

where

\[ \kappa(q) = \frac{\kappa_1 + 1 - (\kappa_1 - 1)e^{-qL}}{\kappa_1 + 1 + (\kappa_1 - 1)e^{-qL}\kappa_1} \]  

(12)

contains the dielectric effects of higher-order bands\(^{14,15}\). Here, \( \kappa_1 \approx 2.4 \) is the dielectric constant of graphite, \( L = d_m + (N_{\text{layer}} - 1)d \) is the height of a multilayer graphite system given a layer height of \( d_m \approx 2.8 \text{ Å} \). For graphene, \( \kappa(0) = 1 \) and \( \kappa(q \to 0) \approx 2.4 \), in keeping with the asymptotic behavior of the \( \sigma \)-electrons. Note that Eq. (11) differs from previous expressions\(^7\) in that we have the correct leading term in the expression for \( \epsilon_{2D} \). When considering the two distinct sub-bands of the \( \sigma \)- and \( \pi \)-electrons, the background dielectric function of the \( \sigma \)-electrons does not enter as a simple multiplicative correction to the Coulomb interaction \( V(q, \omega) \), but as an additive constant to the dielectric function of the \( \pi \)-electrons. A detailed justification for Eq. (11) may be found in Appendix C.

In the absence of interlayer hopping, our expression for \( \chi_{2D} \) in our full \( \pi \)-band RPA calculation differs from Eq. (7) in just the denominator,

\[ \chi_{2D}(q, \omega) = \frac{\Pi_{2D}(q, \omega)}{\kappa(q) - V(q)\Pi_{2D}(q, \omega)}, \]  

(13)

and the graphitic response function may be written as

\[ \chi_{3D}(q, \omega) = \frac{\Pi_{3D}(q, \omega)}{\kappa(q) - V(q)\tilde{F}(q)\Pi_{3D}(q, \omega)d}. \]  

(14)

All of our calculations use \( \theta = 0^\circ \) (see Fig. 2b), since the experimental data was found to be insensitive to this angle at the low momentum values studied. We performed calculations for both \( 30^\circ \) and \( 60^\circ \) directions as well, and the differences were also found to be within numerical uncertainty.

**IV. RESULTS AND DISCUSSION**

We are now in a position to evaluate the source of the anomalous screening we observed in our original study\(^\text{11}\). In particular, we wish to know whether this screening is due to the graphitic effects discussed recently\(^\text{11}\), i.e. the interlayer hopping parameters \( \gamma_1 \) and \( \gamma_3 \), background screening from the \( \sigma \)-bands, or excitonic effects as we claimed previously\(^\text{11}\).
In Fig. 1 we compare our experimental data to the RPA results for $\chi_{2D}$ and $\chi_{3D}$. The first thing to note is that RPA with the full $\pi$-bands does a poor job of predicting the energy of the $\pi$-plasmon at $\approx 8$ eV. We attempted to improve the agreement by adjusting the parameters $t$, $\gamma_{1,3}$, and $\kappa_1$, but any parameters that produced the correct plasmon dispersion were dramatically different from the commonly accepted values\(^{2,16}\) of $t = 3$ eV, $\gamma_1 = 0.4$ eV, $\gamma_3 = 0.3$ eV, and $\kappa_1 = 2.4$. Changes to these parameters also drastically distorted the qualitative shape of the $\pi \rightarrow \pi^*$ continuum. We thus show only the spectra calculated using the commonly accepted values for the hopping parameters and $\kappa_1$.

Second, there is significant discrepancy between the absolute magnitudes of the experimental and calculated $\chi$-functions; the calculated spectra in Fig. 1 have been multiplied by arbitrary constants between 0.15 and 1 in order to allow for visual comparison with the experimental data. This magnitude discrepancy is due to the presence of the $\sigma$-bands in the experimental spectra, which are included in the RPA calculations only approximately through use of Eq. 12. The $\sigma$-bands can manifest strongly in low energy part of the spectrum because $\chi$ is not a linear function of $\Pi(q,\omega)$. This magnitude problem is a known feature of the $\chi$-function\(^{10,17}\). Note, however, that as $q \rightarrow 0$, the multiplicative factor tends toward 1, which implies that the influence of the $\sigma$-bands decreases with decreasing momentum. This discrepancy in magnitude is absent in $\text{Im} \Pi(q,\omega)$ (Fig. 3), where the different contributions are additive and the low-energy spectrum does not depend on the details of the higher-energy bands.

In our original experiment, we proposed excitonic effects as a possible cause for the enhanced screening evident in our reduced $\alpha^*$. The signature of excitonic effects is a shift of spectral weight to lower-energy in the polarization function due to attractive interaction between the excited electron and hole, and may be significant even when a true exciton bound state does not form. In agreement with our original study, we see excitonic effects in Fig. 3 in the low energy part of the spectrum, with shifts of approximately 1 eV for the largest momenta (significant shifts are present for the $\pi$ plasmon at all momenta). As $q \rightarrow 0$, however, the shifts in the low-energy onset appear to become less pronounced, essentially disappearing for the lowest measured momentum transfer, $q = 0.212$ Å\(^{-1}\). We do, however, see in Fig. 1b that the magnitude discrepancy in $\chi(q,\omega)$ is present for all our measured momenta, which suggests that the $\sigma$-bands play a role in screening even at momenta as low as $q = 0.212$ Å\(^{-1}\), or equivalently, a distance of greater than ten lattice parameters.
FIG. 3. ImΠ(q, ω) from experiment and calculation. Note that the intensity discrepancy seen in χ is no longer seen here.
Asymptotic behavior of $\chi(q,0)$

\[ -\chi(q,0)/q = \frac{\alpha^*}{\epsilon^2_D} \]

- $\chi_2D(q,0)/qd$ MLG $\gamma_1,3 \neq 0$
- $\chi_3D(q,0)/q$ MLG $\gamma_1,3 \neq 0$
- $\chi_2D(q,0)/qd$ MLG $\gamma_1,3 = 0$
- $\chi_3D(q,0)/q$ MLG $\gamma_1,3 = 0$

\[ M_{\text{Momentum (Å}^{-1})} \]

Effective $|\alpha^*|$ for experiment and calculation

\[ \text{New experiment} \]
\[ \text{Original experiment} \]
\[ \alpha/\epsilon^2_D (\text{SLG}) \]
\[ \alpha/\epsilon^2_D (\text{MLG } \gamma_1,3 = 0) \]
\[ \alpha/\epsilon^2_D (\text{MLG } \gamma_1,3 \neq 0) \]

FIG. 4. (a) Asymptotic behavior of experimental and calculated $-\chi(q,0)$. (b) Comparison of experimental and calculated $\alpha^*(q,0)$.

Of particular interest is the static ($\omega = 0$) value of $\alpha^*$ as $q \to 0$, which determines the strength of the Coulomb interaction in certain low-energy, finite-wave-vector experiments such as STM. Figs. 4a and 4b show our results for experimental and calculated values of $\chi(q,0)$ and $\alpha^*(q,0)$, respectively. We display the RPA results for three different cases: (1) single-layer graphene (SLG), (2) infinite multi-layer graphene (MLG) without interlayer hopping, and (3) infinite MLG with interlayer hopping (graphite). MLG without interlayer hopping still includes the background dielectric constant $\kappa$, so results for MLG without interlayer hopping can be thought of as those of a single graphene sheet embedded in graphite which couples to the other layers through only the Coulomb interaction and higher-order bands.

As can be seen from Figs. 4a and 4b $\chi_{2D}(q,0)$ for SLG deviates from that of MLG for $q < \sim 1.5 \text{ Å}^{-1}$ due to the presence of the background dielectric constant $\kappa(q)$, which is unity for SLG but has the value 2.4 (in the limit of low $q$) for both MLG and graphite. From these plots one can also see that differences in $\chi_{2D}(q,0)$ for MLG due to interlayer hopping do not enter substantially into the RPA result until $q < \sim 0.2 \text{ Å}^{-1}$. This latter point suggests that graphitic effects, i.e., the influence of interlayer hopping, should not affect our measured
value for the effective fine structure constant, at least for the range of wave vectors studied.

It is also useful to examine the leading, power law behavior of \( \chi_{2D} \) and \( \chi_{3D} \) (Fig. 4a). Because \( \Pi_{2D} \propto q \) for \( q \to 0 \), we expect \( \chi_{3D} \propto q^2 \) and \( \chi_{2D} \propto q \) in the low momentum regime. As expected, Fig. 4a clearly shows that the ratio \( \chi_{3D}/q \) goes to zero linearly as \( q \to 0 \). \( \chi_{2D}/qd \) also clearly asymptotes to a non-zero constant, and we can estimate \( -\chi_{2D}/qd \approx 0.003 \) for \( q \to 0 \). That Eq. 5 recovers the correct asymptotic behavior for both \( \chi_{3D} \) and \( \chi_{2D} \) implies that we are properly correcting for dimensionality effects and deducing a true, two-dimensional quantity.

Finally, Fig. 4b compares the static \( \alpha^*(q,0) \) from our original experiment to the current data and RPA calculations. Our latest data gives a \( q \to 0 \) value for \( \alpha^* \) in the range of 0.25 to 0.35. This quantity is somewhat larger stated previously, but is within the error bars of our original study\( ^{11} \), and is still well below the RPA value, implying an asymptotic dielectric constant in the range 6.2 to 8.8. The mechanism behind this enhanced screening is a combination of excitonic shifts, which comprise a beyond-RPA contribution to screening, and screening from the \( \sigma \)-bands at finite \( q \). We note that both of these effects appear to fade as \( q \to 0 \), though \( \sigma \)-band screening is still significant even at length scales as large as 30 Å and should affect low-energy, local probes such as STM.

V. CONCLUSIONS

We presented significantly improved measurements of the fully momentum- and energy-dependent fine structure constant of graphene, \( \alpha^*(q,\omega) \), deduced from inelastic x-ray scattering measurements of graphite. We also performed full \( \pi \)-band RPA calculations with and without interlayer hopping. We found that graphitic effects from interlayer hopping have no significant effect on screening in the range of momenta we studied. We have shown from discrepancies in the absolute intensity of \( \chi_{2D} \) that screening from the \( \sigma \)-bands contributes even down to \( q = 0.212 \text{ Å}^{-1} \). We find an asymptotic value for \( \alpha^*(q,0) \) in the range 0.25 to 0.35 as \( q \to 0 \), which is well below the predicted RPA value. We attribute the anomalously large screening to a combination of excitonic effects and screening from deeper, \( \sigma \)-bonded electrons. Both of these effects appear to fade as \( q \to 0 \), and may become unimportant in the asymptotic limit, but will have a significant effect on local, low-energy measurements such as STM.
ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy grant DE-FG02-06ER46285. Use of the Advanced Photon Source supported by DEAC02-06CH11357.

Appendix A: Data Analysis

The measured spectra have background from the quasielastic line which must be subtracted out to recover the excitation spectrum of graphene. We use a pseudovoigt function, a linear combination of a Gaussian and a Lorentzian, to model the quasielastic lineshape:

\[
y = b + A \times \begin{cases} 
  ce^{-\frac{(x-x_0)^2}{2\sigma^2}} + (1-c)\frac{l^2}{(x-x_0)^2 + l^2}, & x < x_0 \\
  ce^{-\frac{(x-x_0)^2}{2(\sigma^2\eta^2)}} + (1-c)\frac{(l\eta)^2}{(x-x_0)^2 + (l\eta)^2}, & x \geq x_0
\end{cases}
\] (A1)

Here, \(\sigma\) is the Gaussian width, \(l = \sqrt{2\log 2}\sigma\) is the Lorentzian width, \(c\) is a relative amplitude between the Guassian and Lorentzian, \(x_0\) is the center of the lineshape, and \(b\) and \(A\) are overall background and amplitude factors, respectively. The parameter \(\eta\) is an asymmetry factor that allow the left- and right-hand sides of the lineshape to be different, which is a feature in the experiment due to energy-dependent background scattering from the sample chamber itself. In particular, the Lorentzian width \(l\) is defined this way to best approximate a voigt function, which is a convolution of a Gaussian and Lorentzian. In our experiments, background measurements on lithium fluoride, a large band gap material, show \(b\) to be 0, so that is not a free parameter in our fits. To estimate the error produced by fitting the elastic line and subtracting, we repeat the fit with different constraints and initial parameters and treat all of the subsequent subtractions as reasonable fits. Figs. 5a and 5c shows subtractions for two different momentum transfers of \(q = 0.212\) \(\text{Å}^{-1}\) and \(q = 0.282\) \(\text{Å}^{-1}\), respectively.

The crucial step is converting from our measured spectra, which is only proportional to \(S(q,\omega)\), to \(\text{Im}\chi(q,\omega)\) in absolute units. To do this, we normalize our data to the \(f\)-sum rule over the entire momentum range. Fig. 1a shows the results of normalization. Because our experiment only measured energy-loss spectra for -4–15 eV, we must normalize and patch our data to the data from\(^\text{[1]}\) to have enough energy points to perform a Kramers-Kronig integration. This is complicated by the fact that our \(q\) are not the same as the \(q\) from\(^\text{[1]}\). To overcome this \(q\) mismatch, we linearly interpolate the data from\(^\text{[1]}\) to match our \(q\) transfers. To properly normalize and patch our spectra to the previous spectra, we first
FIG. 5. (a) and (c) energy-loss spectra for $q = 0.212$ Å$^{-1}$ and $q = 0.282$ Å$^{-1}$, respectively, with elastic line fit and subtraction, along with corresponding sum-rule normalizations in (b) and (d), respectively.

Note that in $\text{Ref.}$, the proportionality between the measured spectra and $S(q, \omega)$ (and thus, $\chi(q, \omega)$), is determined by fitting the spectra to the $f$-sum rule. In our new experiment, for each separate beam time, we take our spectra, with the exception of the $q = 0.212$ Å$^{-1}$, and fit to the spectra of $\text{Ref.}$, finding a multiplicative factor for each momentum transfer, and then take the average of these multiplicative factors. This is because the multiplicative factor is determined predominantly by incident beam features including intensity, angular divergence, and energy resolution, as well as sample thickness, which are features that are either constant or mostly constant throughout a single beamtime but may be different from one beamtime to the next. For $q = 0.212$ Å$^{-1}$ we take the average multiplicative factor for the $q = 0.352$ Å$^{-1}$ and $q = 0.563$ Å$^{-1}$ spectra (the other two momentum transfers from that beamtime) and define that its multiplicative factor rather than directly fitting to the old data; this is because the lowest momentum value from the old data is $q = 0.238$ Å$^{-1}$, so interpolation below it is unreliable. Figs. 5b and 5d show our final normalized $\text{Im } \chi$ spectra for $q = 0.212$ Å$^{-1}$ and $q = 0.282$ Å$^{-1}$, respectively, in absolute units.
In particular, this method of normalization fits the π-plasmon intensities well, which is ideal given that π-plasmon is the strongest contribution to the Kramers-Kronig integral in the energy range we measure. Unfortunately, this method also introduces discontinuities at the patch location in energy (~15 eV), which can be seen in the spectra in Fig. 5d, but we simply include this as an error in the value of \( \chi(q, \omega) \). Indeed, the spectra in Fig. 1 represent the average values of \( \chi \) after elastic line subtraction and intensity normalization, and the error bars are a sum in quadrature of the maximum positive or negative deviation from the mean and a 5% estimate of the variance of the sum-rule normalization.

Appendix B: RPA

The Hamiltonian of ABA(Bernal)-stacked graphite (shown in Fig. 2a), including nearest-neighbor interlayer hopping, can be written as

\[
H = -t \sum_{L,\langle i,j \rangle} \left[ a_{i,l}^\dagger b_{j,l} + b_{j,l}^\dagger a_{i,l} \right] \\
- \gamma_1 \left[ \sum_{l_{\text{even}},\langle j,j' \rangle} \left[ a_{j,l}^\dagger b_{j',l+1} + b_{j',l+1}^\dagger a_{j,l} \right] \right] \\
+ \sum_{l_{\text{odd}},\langle j,j' \rangle} \left[ b_{j,l}^\dagger a_{j',l+1} + a_{j',l+1}^\dagger b_{j,l} \right] \\
- \gamma_3 \left[ \sum_{l_{\text{even}},\langle\langle j,j' \rangle\rangle} \left[ b_{j,l}^\dagger a_{j',l+1} + a_{j',l+1}^\dagger b_{j,l} \right] \right] \\
+ \sum_{l_{\text{odd}},\langle\langle j,j' \rangle\rangle} \left[ a_{j,l}^\dagger b_{j',l+1} + b_{j',l+1}^\dagger a_{j,l} \right] 
\]

\[ \text{(B1)} \]

where the sum is taken over nearest neighbors \( \langle i, j \rangle \) and the layers \( l, t = 3 \text{ eV} \) is the in-plane hopping parameter, \( \gamma_1 = 0.4 \text{ eV} \) is the vertical hopping between the A and B sublattice points (indicated by the double brackets), and \( \gamma_3 = 0.3 \text{ eV} \) is the nearest A and B interlayer coupling (indicated by the triple brackets). Single layer graphene can be described by the first sum in Eq. \[ \text{B1} \] For graphene, the wavefunctions can be computed explicitly, and we can write the overlap function as

\[
f_{s,s'}(k, q_\parallel) = \left| \frac{\phi^*(k) \phi(k + q)}{\phi(k)} \right|^2 + s \cdot s' \]

\[ \text{(B2)} \]
where

\[
\phi(k) = e^{-ik_x a} + 2e^{-ik_x a/2} \cos\left(\frac{\sqrt{3}}{2} k_y a\right),
\]

(B3)

and \(a = 1.42\) Å is the in-plane carbon-carbon distance. It is straightforward to numerically integrate Eq. 10 to recover the polarization of graphene. Using a convergence factor of \(\eta = 0.01\) eV we can recover calculated \(\Pi\) functions that very closely resemble those in[2].

For graphite, we have four symmetry-inequivalent sublattices, the A and B sublattices in the odd-numbered layers and the corresponding sublattices in the even-numbered layers, leading to four basis functions rather than the two of graphene. There is no simple analytic expression for these wavefunctions, so to perform the integral in Eq. 10 we simply find the eigenfunctions of the graphite Hamiltonian, and use those to compute the corresponding energies and overlap functions \(f\). It is again straightforward to numerically integrate Eq. 10 over the 3D Brillouin zone of graphite to obtain \(\Pi_{3D}(q, \omega)\).

Appendix C: Dielectric function

We treat the electrons from the \(\pi\)-bands and \(\sigma\)-bands as two separate fermionic species. In general, we can write the Hamiltonian for such a system as

\[
H = H_0 + H_I + H_U,
\]

(C1)

where

\[
H_0 = \sum_{k\sigma} E_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_{k\sigma} E_k g_{k\sigma}^\dagger g_{k\sigma}
\]

(C2)

describes the non-interacting Hamiltonian for the fermionic operators of the \(\pi\)- and \(\sigma\)-electrons, \(g(g^\dagger)\) and \(c(c^\dagger)\), respectively.

\[
H_I = \sum_q V(q) \hat{\rho}_\pi(-q) \hat{\rho}_\pi(q) + 2 \sum_q V(q) \hat{\rho}_\pi(-q) \hat{\rho}_\sigma(q)
\]

\[
+ \sum_q V(q) \hat{\rho}_\sigma(-q) \hat{\rho}_\sigma(q),
\]

(C3)

is the Coulomb interaction energy, with

\[
\hat{\rho}_\pi(q) = \sum_{k\sigma} c_{k+q,\sigma}^\dagger c_{k\sigma} \quad , \quad \hat{\rho}_\sigma(q) = \sum_{k\sigma} g_{k+q,\sigma}^\dagger g_{k\sigma}
\]

(C4)
the particle densities and $V(q) = 2\pi e^2 / q$, and

$$H_U = \sum_q [U_s(q)\hat{\rho}_s(q) + U_\pi(q)\hat{\rho}_\pi(q)]$$  \hspace{1cm} (C5)$$

is an external potential with couples to the density. A standard calculation\textsuperscript{19} lets us write the equations of motion for this system in matrix form as

$$\begin{pmatrix} \langle \hat{\rho}_s(q, i\omega) \rangle \\ \langle \hat{\rho}_\pi(q, i\omega) \rangle \end{pmatrix} = \frac{1}{\epsilon(q, i\omega)} M \begin{pmatrix} U_s(q)\Pi_s(q, i\omega) \\ U_\pi(q)\Pi_\pi(q, i\omega) \end{pmatrix}$$  \hspace{1cm} (C6)$$

where

$$M = \begin{pmatrix} 1 - V(q)\Pi_\pi(q, i\omega) & V(q)\Pi_s(q, i\omega) \\ V(q)\Pi_\pi(q, i\omega) & 1 - V(q)\Pi_s(q, i\omega) \end{pmatrix}$$  \hspace{1cm} (C7)$$

and

$$\epsilon(q, i\omega) = \det M$$

$$=1 - V(q)\Pi_\pi(q, i\omega) - V(q)\Pi_s(q, i\omega)$$

$$- [V^2(q) - V(q) V(q)]\Pi_\pi(q, i\omega) \Pi_s(q, i\omega)$$  \hspace{1cm} (C8)$$

is the dielectric function of the system, where $\Pi_\pi$ and $\Pi_\sigma$ are the polarization functions of the $\pi$- and $\sigma$-electrons, respectively. Simplifying, we have

$$\epsilon(q, i\omega) = 1 - V(q)\Pi_\pi(q, i\omega) - V(q)\Pi_s(q, i\omega)$$

$$= \kappa_s(q) - V(q)\Pi_\pi(q, i\omega),$$  \hspace{1cm} (C9)$$

where we have defined

$$\kappa_s(q) = 1 - V(q)\Pi_s(q, i\omega)$$  \hspace{1cm} (C10)$$

as the background dielectric constant due to the $\sigma$-electrons. In this way we recover Eq. \textsuperscript{11} for the total dielectric function of graphene and graphite.

\begin{flushleft}
\textsuperscript{1} J. P. Reed \textit{et al.}, Science \textbf{330}, 805 (2010).
\end{flushleft}

\begin{flushleft}
\textsuperscript{2} A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, Rev. Mod. Phys. \textbf{81}, 109 (2009).
\end{flushleft}

\begin{flushleft}
\textsuperscript{3} S. Das Sarma, S. Adam, E. H. Hwang, and E. Rossi, Rev. Mod. Phys. \textbf{83}, 407 (2011)
\end{flushleft}
In particular, the value of $\alpha^* \approx 0.3$ in Ref. 7 is not directly comparable with this value, as in that paper $\alpha^* = \alpha/\epsilon_{3D}$, where $\epsilon_{3D}$ as $1 - V(q)/\kappa(q)F(q)\Pi_{3D}(q,\omega)d$, which differs from our definition from Eq. 8. Since we are interested in the 2D response derived from graphite, Eq. 8 is the more relevant quantity.

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18. D. Pines, *Elementary Excitations in Solids* (Westview Press, 1999).