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PERSPECTIVE

Toward a novel theoretical approach for determining the nature of electronic excitations in quasi-two-dimensional systems

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Abstract

The discovery of quasi-two-dimensional (Q2D) crystals has started a new era of materials science. Novel materials, atomically thin and mechanically, thermally and chemically stable, with a large variety of electronic properties are available and they can be assembled in ultrathin flexible devices. Understanding collective electronic excitations (plasmons) in Q2D systems is mandatory for engineering applications in plasmonics. In view of recent developments in the emerging field of graphene-based plasmonics, the correspondence between the theoretically calculated quantities and the observables experimentally measured in Q2D crystals is still unsatisfactory. Motivated by recent Nazarov's findings (Nazarov 2015 *New J. Phys.* **17** 073018), here we discuss some crucial issues of current theoretical approaches as well as the computational methods applied to two-dimensional materials with special emphasis to cover their peculiarities, range of application and pitfalls.

1. Perspective

In the last ten years, a variety of theoretical methods and experimental approaches has been intensively applied to graphene. In particular, the application capabilities of graphene-based plasmonic devices have stimulated research on plasmon modes in graphene and two-dimensional (2D) materials 'beyond graphene' [2–5].

The collective electronic excitation of 2D Dirac fermions (Dirac plasmon) forms a dispersive feature at 0–1 eV, with the characteristic $\sqrt{q}$ dependence [6–15], where q is the momentum. Such excitation, arising from intraband transitions involving electronic states in the Dirac cone, is observed only for doped graphene, where the doping may arise from gating potentials [1], the adsorption or the intercalation of chemical species [16], or just charge transfer from the metal substrate [17].

Although technological efforts have mainly focused in the spectral range from terahertz [18] to the visible [19], several potential applications of plasmon modes in the ultraviolet (UV) part of the electromagnetic spectrum exist. A possible advantage of UV plasmons is the matching of their high energy with the electronic transition energy of many organic molecules, thus paving the way for UV plasmonics [20], UV imaging, DNA sensing [21], UV absorbers [22], and metamaterials with UV plasmonic resonances [23].

Apart from these intriguing characteristics, the comprehension of UV plasmons has fundamental importance also for the detailed understanding of the elementary excitations of graphene, determined by the π and σ valence electrons lying outside the Dirac cone. Plasmon spectra of free-standing monolayer graphene were first obtained in [24], where the authors identified two distinct structures, attributed to the so-called π and $\pi+\sigma$ plasmons. They observed that these two plasmonic modes were red-shifted as compared to the corresponding features in the bulk graphite [25–27], due to the reduction of macroscopic screening when going from graphite to graphene [28]. However, the plasmonic nature of these electronic excitations for the case of graphene is highly debated. Recently, it has been suggested [29] that the previously accepted attribution should be revised and that the π and $\pi+\sigma$ plasmons are indeed single-particle $\pi\to\pi^*$ and $\sigma\to\sigma^*$ excitations, respectively, with a characteristic q^2 dependence of the energy. This affirmation is motivated by the finding that in graphene the value of the real part of the dielectric function ε_1 does not go through zero for either the $\pi\to\pi^*$ or the $\sigma\to\pi^*$

transition, and, moreover, the imaginary part ε_2 is not small in these energy regions to allow a plasmon excitation.

Similar debate has concerned the study of the dispersion relation of high-energy plasmons in free-standing monolayer and multilayer graphene. The early theoretical and experimental measurements observed linear dispersion of π plasmon in graphene [30–33], which differs from the q^2 dispersion observed in graphite [25, 26, 28, 34]. The reported linear dispersion has been correlated to transitions from the linearly dispersing Dirac cone and this claim was quickly widely accepted [35, 36]. Recently, the correlation of the reported linear dispersion of the π plasmon to the linear Dirac cone has been questioned. Strong evidence for 2D plasmon character of π and σ electron excitations has been demonstrated by means of energy loss spectroscopy (EELS) experiments, showing the $\sqrt{q}$ dependent dispersion [37]. Even taking into account possible uncertainties arising from experimental difficulties in EELS measurements for low q values, it is evident that this apparent controversy deserves to be analyzed and resolved.

This debate has been promptly solved by a theoretical study by Nazarov in this issue of *New J. Phys.* [1]. The starting point of Nazarov is to consider electronic excitations in quasi-two-dimensional (Q2D) samples, i.e. atomically thin crystals. Such systems represent real 2D films which are periodic and infinite in two-dimensions $(x. y)$ but they have finite thickness in the z direction (perpendicular to the layer). They notably differ from both bulk (three-dimensional, 3D) and zero-thickness 2D crystals. Both 3D and 2D systems are usually treated by introducing the well-known dielectric function $\varepsilon(\mathbf{q}, \omega)$. However, considering that the total (external plus induced) scalar potentials of the electric field $\varphi^{\text{tot}}(\mathbf{q}, \omega)$ depend on the z coordinate, even when φ^{ext} is uniform in z direction, the definition of $\varepsilon(\mathbf{q}, \omega)$ is not straightforwardly transferable to the Q2D case. Therefore, the dielectric function (and the related quantities as energy-loss function, conductivity, etc) of a Q2D crystal should be re-defined in accordance to the system's structure. In particular, Nazarov re-examines the problem of the correspondence between the theoretically calculated quantities and the observables in the measurements on Q2D crystals, finding that the energy-loss function $-\mathrm{Im}\,\frac{1}{\varepsilon(\mathbf{q}, \omega)}$, conventionally used for the interpretation of the EELS data, is not the right quantity to be compared with EELS experiments. Instead, in reflection EELS, the quantity, better characterizing the inelastic electron scattering, is the EELS-related energy-loss function, which is shown to be qualitatively and quantitatively different in the case of Q2D systems. Consequently, the use of an appropriate dielectric function proper of real 2D crystals with a finite z dimension is not straightforward to compare EELS measurements (both in reflection and transmission mode) with the so-called loss function.

A further limitation for theoretical approaches to plasmon modes in 2D materials is usually represented by the use of the 3D super-cell methods for calculating excitations in 2D materials to artificially replicate the periodicity of the system in the z direction, by choosing the interlayer distance d large enough to prevent the interlayer interactions. Clearly, whatever large is the interlayer separation d, at sufficiently small q the interlayer interaction persists and thus the super-cell calculation cannot be rightly transferred in the case of single-layer thickness. Nazarov [1] develops an appropriate method to get rid of this spurious contributions. The correct procedure allows concluding that the uncritical use of results of the super-cell calculations applied to Q2D systems has led to the misinterpretation of the π and $\pi + \sigma$ peaks as single-particle interband transitions rather than plasmons [29].

As its practical application, Nazarov [1] calculates the dielectric function and the related excitation spectrum of single-layer graphene. By resolving the recent controversy in the interpretation of the π and $\pi + \sigma$ peaks as plasmons or single-particle interband transitions, Nazarov's results [1] conclusively demonstrate that prominent π and $\pi + \sigma$ collective excitations in graphene exist. They are also accompanied by interband transitions in a close energy range. Dispersing plasmon modes and non-dispersive single-particle interband transitions can be theoretically distinguished from each other by a momentum-resolved analysis.

The results obtained by Nazarov [1] are particularly suitable for describing the electronic excitations in Q2D crystals by correctly accounting the finite thickness of the investigated systems. These findings constitute an important milestone in the comprehension of collective electronics modes in low-dimensional systems. Nazarov's work [1] will facilitate the comparison between theoretical and experimental results, so as to improve the dialogue between experimentalists and theoreticians working on plasmons in Q2D systems.

References

[1] Nazarov V U 2015 Electronic excitations in quasi-2D crystals: what theoretical quantities are relevant to experiment? *New J. Phys.* **17** 073018

[2] Tassin P, Koschny T, Kafesaki M and Soukoulis C M 2012 A comparison of graphene, superconductors and metals as conductors for metamaterials and plasmonics *Nat. Photonics* **6** 259–64

[3] Stauber T and Gómez-Santos G 2012 Plasmons in layered structures including graphene *New J. Phys.* **14** 105018

[4] Stauber T 2014 Plasmonics in dirac systems: from graphene to topological insulators *J. Phys.: Condens. Matter* **26** 123201

[5] Low T, Roldán R, Wang H, Xia F, Avouris P, Moreno L M and Guinea F 2014 Plasmons and screening in monolayer and multilayer black phosphorus *Phys. Rev. Lett.* **113** 106802

[6] Langer T, Förster D F, Busse C, Michely T, Pfnür H and Tegenkamp C 2011 Sheet plasmons in modulated graphene on Ir(111) *New J. Phys.* **13** 053006
[7] Politano A, Marino A R and Chiarello G 2012 Effects of a humid environment on the sheet plasmon resonance in epitaxial graphene *Phys. Rev.* B **86** 085420
[8] Fei Z *et al* 2011 Infrared nanoscopy of Dirac plasmons at the graphene–SiO_2 interface *Nano Lett.* **11** 4701–5
[9] Das Sarma S and Hwang E H 2009 Collective modes of the massless Dirac plasma *Phys. Rev. Lett.* **102** 206412
[10] Liu Y, Willis R F, Emtsev K V and Seyller T 2008 Plasmon dispersion and damping in electrically isolated two-dimensional charge sheets *Phys. Rev.* B **78** 201403
[11] Politano A and Chiarello G 2014 Plasmon modes in graphene: status and prospect *Nanoscale* **6** 10927–40
[12] Stern F 1967 Polarizability of a two-dimensional electron gas *Phys. Rev. Lett.* **18** 546–8
[13] Gerber J A, Berweger S, O'Callahan B T and Raschke M B 2014 Phase-resolved surface plasmon interferometry of graphene *Phys. Rev. Lett.* **113** 055502
[14] Alonso-González P *et al* 2014 Controlling graphene plasmons with resonant metal antennas and spatial conductivity patterns *Science* **344** 1369–73
[15] Luo X, Qiu T, Lu W and Ni Z 2013 Plasmons in graphene: recent progress and applications *Mater. Sci. Eng.* R **74** 351–76
[16] Shin S Y, Kim N D, Kim J G, Kim K S, Noh D Y and Chung J W 2011 Control of the π plasmon in a single layer graphene by charge doping *Appl. Phys. Lett.* **99** 082110
[17] Politano A, Marino A R, Formoso V, Farías D, Miranda R and Chiarello G 2011 Evidence for acoustic-like plasmons on epitaxial graphene on Pt(111) *Phys. Rev.* B **84** 033401
[18] Koppens F H L, Mueller T, Avouris P, Ferrari A C, Vitiello M S and Polini M 2014 Photodetectors based on graphene, other two-dimensional materials and hybrid systems *Nat. Nanotechnology* **9** 780–93
[19] García de Abajo F J 2014 Graphene plasmonics: challenges and opportunities *ACS Photonics* **1** 135–52
[20] McMahon J M, Schatz G C and Gray S K 2013 Plasmonics in the ultraviolet with the poor metals Al, Ga, In, Sn, Tl, Pb, and Bi *Phys. Chem. Chem. Phys.* **15** 5415–23
[21] Taguchi A, Saito Y, Watanabe K, Yijian S and Kawata S 2012 Tailoring plasmon resonances in the deep-ultraviolet by size-tunable fabrication of aluminum nanostructures *Appl. Phys. Lett.* **101** 081110
[22] Kesim Y E, Battal E and Okyay A K 2014 Plasmonic materials based on ZnO films and their potential for developing broadband middle-infrared absorbers *AIP Adv.* **4** 077106
[23] Ou J-Y, So J-K, Adamo G, Sulaev A, Wang L and Zheludev N I 2014 Ultraviolet and visible range plasmonics in the topological insulator $Bi_{1.5}Sb_{0.5}Te_{1.8}Se_{1.2}$ *Nat. Commun.* **5** 5139
[24] Eberlein T, Bangert U, Nair R R, Jones R, Gass M, Bleloch A L, Novoselov K S, Geim A and Briddon P R 2008 Plasmon spectroscopy of free-standing graphene films *Phys. Rev.* B **77** 233406
[25] Zeppenfeld K 1971 Nichtsenkrechte interbandübergänge in graphit durch unelastische elektronenstreuung *Z. Phys.* **243** 229–43
[26] Büchner U 1977 Wave-vector dependence of the electron energy losses of boron nitride and graphite *Phys. Status Solidi* B **81** 227–34
[27] Marinopoulos A G, Reining L, Olevano V, Rubio A, Pichler T, Liu X, Knupfer M and Fink J 2002 Anisotropy and interplane interactions in the dielectric response of graphite *Phys. Rev. Lett.* **89** 076402
[28] Marinopoulos A G, Reining L, Rubio A and Olevano V 2004 *Ab initio* study of the optical absorption and wave-vector-dependent dielectric response of graphite *Phys. Rev.* B **69** 245419
[29] Nelson F J, Idrobo J-C, Fite J D, Mišković Z L, Pennycook S J, Pantelides S T, Lee J U and Diebold A C 2014 Electronic excitations in graphene in the 1–50 eV range: the π and $\pi + \sigma$ peaks are not plasmons *Nano Lett.* **14** 3827–31
[30] Kramberger C *et al* 2008 Linear plasmon dispersion in single-wall carbon nanotubes and the collective excitation spectrum of graphene *Phys. Rev. Lett.* **100** 196803
[31] Yan J, Thygesen K S and Jacobsen K W 2011 Nonlocal screening of plasmons in graphene by semiconducting and metallic substrates: first-principles calculations *Phys. Rev. Lett.* **106** 146803
[32] Kinyanjui M K, Kramberger C, Pichler T, Meyer J C, Wachsmuth P, Benner G and Kaiser U 2012 Direct probe of linearly dispersing 2D interband plasmons in a free-standing graphene monolayer *Europhys. Lett.* **97** 57005
[33] Lu J, Loh K P, Huang H, Chen W and Wee A T S 2009 Plasmon dispersion on epitaxial graphene studied using high-resolution electron energy-loss spectroscopy *Phys. Rev.* B **80** 113410
[34] Kramberger C, Einarsson E, Huotari S, Thurakitseree T, Maruyama S, Knupfer M and Pichler T 2010 Interband and plasma excitations in single-walled carbon nanotubes and graphite in inelastic x-ray and electron scattering *Phys. Rev.* B **81** 205410
[35] Wachsmuth P, Hambach R, Kinyanjui M K, Guzzo M, Benner G and Kaiser U 2013 High-energy collective electronic excitations in free-standing single-layer graphene *Phys. Rev.* B **88** 075433
[36] Despoja V, Novko D, Dekanić K, Šunjić M and Marušić L 2013 Two-dimensional and π plasmon spectra in pristine and doped graphene *Phys. Rev.* B **87** 075447
[37] Liou S C, Shie C S, Chen C H, Breitwieser R, Pai W W, Guo G Y and Chu M W 2015 π plasmon dispersion in free-standing graphene by momentum-resolved electron energy-loss spectroscopy *Phys. Rev.* B **91** 045418