Graphene and 2D Materials for Nanophotonics

Prof. Wasserman

The rise of graphene
A. K. Geim & K. S. Novoselov
Final Presentation

• 15 minutes: 12 minute presentation, 3 minutes questions
• General Outline
  – Topic
  – Motivation: why do people care about this? What is the potential application or what is the fundamental importance?
  – Background: What are the fundamental mechanisms, physics behind this topic?
  – Results: Demonstration of phenomenon/structure/devices
  – Discussion: strengths/weaknesses, applications
  – Conclusion
• Hints:
  – Do not pick a broad topic (i.e. “plasmonics”, “metamaterials”)
  – Try to find a phenomenon or particular application within a larger subfield of nanophotonics.
  – Focus on ~1-4 particular publications…but should not be a literature review.
  – Need some technical heft to the presentation (not just pictures)
Final Presentation

• Example: LSPR for water boiling
  – Slides 1-4. Discussion of LSPR
    • Show/derive governing equations
    • Give expressions for scattering/absorption
    • Maybe even do a back of the envelope calculation of energy absorbed per unit volume, etc.
  – Slides 5-7
    • Examples of LSRP
    • How do we make them?
    • What do their spectra look like?
    • How do we control spectra?
  – Slides 8-12
    • Results from LSPR for boiling water
  – Challenges/Opportunities/Future work
  – Conclusions
Summary

- Previous Lecture
  - Hyperbolic Metamaterials
  - Transformation Optics
  - Invisibility Cloaks

- Today’s Lecture
  - 2D Materials
    - Band-structure
    - Optical properties
    - Plasmonics
    - Nano-photonics
What are “2D” Materials?

- Though the most often cited 2D material (graphene) is only 1ML thick, we should define 2D materials as any material with thickness on the order of the electron wavelength (1ML to ~10nm).
  - By doing so, we allow our definition to include any material which confines charge to motion in only 2 dimensions!

- Well, why not a quantum well?
  - The answer is actually complicated…
  - In fact, much of the interesting physics associated with 2D materials was first demonstrated in semiconductor QWs
  - But….2D materials are a little different than QWs.

- How?
What are 2D Materials?

- 2D materials generally come from a bulk material whose atomic layers are held together by the Van der Waals force.
  - In other words, the bonds between atomic layers are very weak compared to ionic or covalent bonds.
  - This means one could, conceivably, pull a single monolayer from such a material and have it be free-standing
  - No dangling bonds for a single layer
  - Strong bonding in lateral direction
  - Thermodynamically stable (point of discussion…)
  - Means that these 2D materials have very different electronic, optical, and even mechanical properties from a detached QW…which will have all sorts of dangling bonds, stability issues, etc.

http://casiraghi.weebly.com/research.html
Graphene

- Theoretically, graphene was a reasonably well-studied, if abstract, concept.
- That is, until:
And then everyone pretty much lost their minds...

- Why?
- Well, for the most part, the gold rush was set off by the **electronic** properties of graphene

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**The rise of graphene**
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**Two-dimensional gas of massless Dirac fermions in graphene**
*Nature* 438, 197-200 (10 November 2005)
Band structure of graphene

- Zero band gap
- Near linear dispersion
  - Using our previous definition of effective mass, this means that charge carriers in graphene are effectively ‘massless’ particles!
- Offers room temperature observation of quantum electrodynamic (QED) phenomena!
- And perhaps most importantly, fabrication of graphene is as easy as Scotch tape!
  - Cannot underestimate this!!!

The rise of graphene
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Tuning Graphene

Gate-Variable Optical Transitions in Graphene

REPORTS

Figure 2. TEM images of a) B-doped graphene (SG), b) N-doped graphene (NG). Calculated scanning tunneling microscopy (STM) images of c) B- and d) N-doped bilayers. B- and N-doping results in depletion or addition of electronic charge on carbon atoms on the sublattices of the substituted dopant, which is evident in the weaker black (B) and white colors (N), respectively.

Tuning the Graphene Work Function by Electric Field Effect


Advanced Materials

Synthesis, Structure, and Properties of Boron- and Nitrogen-Doped Graphene


COMMUNICATION

COMMUNICATION

NANO LETTERS

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Mid-IR Photonics
Bandstructure of 2D Materials

Optical Properties

• With band-gaps that range from 6eV (hBN) to 0eV (graphene), offer an intriguing set of material systems for nanophotonic applications.

• There are two primary ways we can think of 2D materials.
  – The first is as a nano-scale optical material (essentially free standing QWs) that we can integrate into larger photonic cavities. Or alternatively…
  – An atomically-thin material system capable of supporting polaritonic modes at the nanoscale.

• Let’s start with the latter, and in particular, graphene
  – Graphene is a highly conductive material (like an atomically-thin metal, but it is also electrically tunable!
  – So we should be able to support SPPs AND tune them dynamically!!!
Single-Interface SPP (TM)

Let’s look for solutions to the wave equations for a wave propagating at the interface between a dielectric \( \varepsilon_d > 0 \) and a metal \( \varepsilon_m < 0 \) at \( z=0 \).

Start with TM \( \mathbf{E}(x, y, z) = \mathbf{E}(z)e^{i\beta t} \)

\[
\begin{align*}
E_x &= -i \frac{1}{\omega \varepsilon_0 \varepsilon} \frac{\partial H_y}{\partial z} \\
E_z &= -\frac{\beta}{\omega \varepsilon_0 \varepsilon} H_y \\
\frac{\partial^2 H_y}{\partial z^2} + (k_0^2 \varepsilon - \beta^2)H_y &= 0
\end{align*}
\]

\[
\begin{align*}
&z > 0 \\
H_y(z) &= A_d e^{i\beta x} e^{-k_{zd}x} \\
E_x(z) &= -i A_d \frac{1}{\omega \varepsilon_0 \varepsilon_d} k_{zd} e^{i\beta x} e^{-k_{zd}x} \\
E_z(z) &= -A_d \frac{\beta}{\omega \varepsilon_0 \varepsilon_d} e^{i\beta x} e^{-k_{zd}x}
\end{align*}
\]

\[
\begin{align*}
&z < 0 \\
H_y(z) &= A_m e^{i\beta x} e^{k_{zm}x} \\
E_x(z) &= -i A_m \frac{1}{\omega \varepsilon_0 \varepsilon_m} k_{zm} e^{i\beta x} e^{k_{zm}x} \\
E_z(z) &= -A_m \frac{\beta}{\omega \varepsilon_0 \varepsilon_m} e^{i\beta x} e^{k_{zm}x}
\end{align*}
\]
Single-Interface SPP (TM) \( k_{zm}, k_{zd} \) are components of wavevector perpendicular to the surface.

\[
\begin{vmatrix}
1 \\
\frac{1}{k_{zm}}
\end{vmatrix} \begin{vmatrix}
1 \\
\frac{1}{k_{zd}}
\end{vmatrix}
\] Give the penetration depth into the metal, dielectric.

Continuity of \( H_y \) and \( \varepsilon_i H_z \) gives us:

\[
A_m = A_d \quad \frac{k_{zd}}{k_{zm}} = -\frac{\varepsilon_d}{\varepsilon_m}
\]

This tells us that the permittivity of the two materials must be opposite in sign!

\[
\frac{\partial^2 H_y}{\partial z^2} + (k_0^2 \varepsilon - \beta^2)H_y = 0
\]

\[
H_y(z) = Ae^{i\beta x} e^{-k_{zd}x}, z > 0
\]

\[
H_y(z) = Ae^{i\beta x} e^{k_{zm}x}, z < 0
\]

\[
k_{zd}^2 = (\beta^2 - k_0^2 \varepsilon_d)
\]

\[
k_{zm}^2 = (\beta^2 - k_0^2 \varepsilon_m)
\]

\[
\beta = k_0 \frac{\sqrt{\varepsilon_m \varepsilon_d}}{\varepsilon_m + \varepsilon_d} = \frac{\omega}{c} \frac{\sqrt{\varepsilon_m \varepsilon_d}}{\sqrt{\varepsilon_m + \varepsilon_d}}
\]

Surface plasmon dispersion relation.
Graphene plasmons

- The SPP is supported at the interface between a conducting ($\varepsilon_m < 0$) and dielectric ($\varepsilon_d < 0$) surface.
- Graphene is conducting, but what does it mean for an atomically-thin layer to have a permittivity?
  - This is a topic of some discussion
  - We will take the approach of writing the metal behavior in terms of conductivity.
  - We can assume we have a system equivalent to a LRSPP in order to understand the graphene plasmon

$$J_s = \sigma_s E_z (z = 0)$$
Graphene Plasmons (TM)

- Assume a wave that is decaying on both sides of the graphene, and a surface current on the graphene...

\[ E = E_{x,1} e^{iqx - \kappa_1 z} \hat{x} + E_{z,1} e^{iqx - \kappa_1 z} \hat{z}, \quad z > 0 \]
\[ H = H_{y,1} e^{iqx - \kappa_1 z} \hat{y}, \quad z > 0 \]
\[ E = E_{x,2} e^{iqx + \kappa_2 z} \hat{x} + E_{z,2} e^{iqx + \kappa_2 z} \hat{z}, \quad z < 0 \]
\[ H = H_{y,2} e^{iqx + \kappa_2 z} \hat{y}, \quad z < 0 \]

- Boundary conditions...
\[ E_{x,1} = E_{x,2}, \quad H_{y,1} - H_{y,2} = J_s, \quad E_{z,1} = E_{z,2} \]

- Maxwell’s Equations...
\[ \frac{\partial E_x}{\partial z} - \frac{\partial E_z}{\partial x} = i \omega \mu_0 H_y \]
\[ - \frac{\partial H_y}{\partial z} = -i \omega \varepsilon_0 \varepsilon E_x \]
\[ - \frac{\partial H_y}{\partial x} = -i \omega \varepsilon_0 \varepsilon E_z \]
Graphene Plasmons (TE)

- Assume a wave that is decaying on both sides of the graphene, and a surface current on the graphene...

  $$J_s = \sigma_s E_z$$

- Boundary conditions...

  $$E_{y,1} = E_{y,2} \quad H_{x,1} - H_{x,2} = J_s \quad H_{z,1} = H_{z,2}$$

- Maxwell’s Equations...

  $$H_x, H_z, E_y \neq 0$$

  $$- \frac{\partial E_y}{\partial z} = i \omega \mu_0 H_x$$

  $$- \frac{\partial E_y}{\partial x} = i \omega \mu_0 H_z$$

  $$\frac{\partial H_x}{\partial z} - \frac{\partial H_z}{\partial x} = -i \omega \varepsilon_0 \varepsilon E_y$$
Graphene Conductivity

- Graphene conductivity is not as straightforward as a simple metal.
  - i) Interband transitions
  - ii) Intraband (Drude) transitions
- We can then write conductivity using the “Random Phase Approximation” (RPA)

\[
\sigma(\omega) = \sigma(\omega, k_\parallel = 0) = \frac{-e^2}{\pi \hbar^2} \frac{i}{\omega + i/\tau} \int_{-\infty}^{+\infty} dE \left[ |E| \frac{\partial f_E}{\partial E} + \frac{(E/|E|)}{1 - 4E^2/[\hbar^2(\omega + i/\tau)^2]} f_E \right]
\]

- \( f_E \) is Fermi distribution, approximate to \( T=0 \)
- “non-local” approximation \( k_\parallel = 0 \)
- For \( \hbar \omega < E_F \), Drude term dominates

\[
\sigma(\omega) = \frac{e^2}{\pi \hbar^2} \frac{iE_F}{\omega + i/\tau} = \frac{iv}{\omega + i/\tau}, \quad v = \frac{e^2E_F}{\pi \hbar^2}
\]
Graphene Plasmons (TM)

- Now we have everything we need to solve for plasmons
- Plug into boundary conditions, Maxwell’s equations:
  
  \begin{align*}
  -\kappa_1 E_{1,x} - iq E_{1,z} &= i\omega \mu_0 H_{1,y} \\
  \kappa_1 \mu_0 H_{1,y} &= -i\omega c^2 \epsilon_1 E_{1,x} \\
  q\mu_0 H_{1,y} &= -\omega c^2 \epsilon_1 E_{1,z} \\
  \kappa_2 E_{2,x} - iq E_{2,z} &= i\omega \mu_0 H_{2,y} \\
  -\kappa_2 \mu_0 H_{2,y} &= -i\omega c^2 \epsilon_2 E_{2,x} \\
  q\mu_0 H_{2,y} &= -\omega c^2 \epsilon_2 E_{2,z}
  \end{align*}

\[ \kappa_1^2 = q^2 - \omega^2 \epsilon_1/c^2 \quad \kappa_2^2 = q^2 - \omega^2 \epsilon_2/c^2 \]

\[ E_{1,x} = E_{2,x} \quad H_{1,y} = -\frac{\kappa_2 \epsilon_1}{\kappa_1 \epsilon_2} H_{2,y} \]

\[ \mu_0 H_{1,y} = \mu_0 H_{2,y} - \sigma E_{1,x} \]
Graphene Plasmons (TM)

• Finally, we get the graphene plasmon dispersion relation

\[ 1 + \frac{\kappa_1 \epsilon_2}{\kappa_2 \epsilon_1} + i\sigma(\omega) \frac{\kappa_1}{\omega \epsilon_0 \epsilon_1} = 0 \]

We can see that \( \sigma'' > 0 \) for this expression to be satisfied, which will be the case when \( \sigma \) is dominated by Drude contribution

\[ \frac{\epsilon_1}{\kappa_1} + \frac{\epsilon_2}{\kappa_2} + i\frac{\sigma(\omega)}{\omega \epsilon_0} = 0 \]

• Simplified: \( \epsilon_1 = \epsilon_2 = 1, \text{therefore } \kappa_1 = \kappa_2, \text{Drude term only} \)

\[ \frac{1}{\kappa_1} = \frac{e^2}{2\pi \epsilon_0 \hbar^2} \frac{E_F}{\omega^2 + i\omega/\tau} = \frac{\nu}{2\epsilon_0 (\omega^2 + i\omega/\tau)} \quad , \quad \nu = \frac{e^2 E_F}{\pi \hbar^2} \]

\[ \kappa_1^2 = q^2 - \omega^2 \epsilon_1/c^2 \]

\[ q^2 = \left[ \frac{2\epsilon_0 (\omega^2 + i\omega/\tau)}{i\nu} \right]^2 + \omega^2 \epsilon_1/c^2 \]
Graphene Plasmons (TE)

- For TE polarization, we can go through the same process and we get:
  \[ \kappa_1 + \kappa_2 - i\omega\mu_0\sigma(\omega) = 0 \]
  We can see that \( \sigma'' < 0 \) for this expression to be satisfied, which will be the case when \( \sigma \) is dominated by interband effects.

- Thus, TE polarized plasmons can be supported on graphene.
- But only where interband contribution to conductivity gives a negative imaginary component to the conductivity!
- In general, most applications you will see for graphene plasmons use TM polarized SPPs.
Graphene Plasmons (TM)

Graphene Plasmonics: A Platform for Strong Light–Matter Interactions
Frank H. L. Koppens,† Darrick E. Chang,† and F. Javier García de Abajo*†

NANO LETTERS

http://pubs.acs.org
Graphene Plasmons (TM)

\[ q^2 = \left[ \frac{2\epsilon_0(\omega^2 + i\omega/\tau)}{iv} \right]^2 + \omega^2\epsilon_1/c^2 \]
Graphene Plasmons

• If we look at the confinement factor for graphene plasmons it is MUCH larger than for traditional metals!!
• What is the primary implication of this?
  – $\lambda_{sp} \ll \lambda_o$, and therefore $k_{sp} \gg \lambda_o$.
• So to couple to the graphene plasmon we will need surface features $a \ll \lambda_o$!!
Graphene Nano-Ribbons

- Note scale on GNRs…
- ~5nm!
Gate Tunable Graphene Plasmons

Optical nano-imaging of gate-tunable graphene plasmons

Jianing Chen1,2,*, Michela Badioli1,*, Pablo Alonso-González1,*, Sukosin Thongrattanasiri1,*, Florian Hurkl1,2,*, Johann Osmond1,*, Marko Spasenović1,*, Alba Centeno1,*, Amala Pesquera1,*, Philippe Godignon1,*, Amalia Zurutuza Elorza1,*, Nicolas Camara1,*, F. Javier García de Abajo1,*, Rainer Hillenbrand2,3,6,8 & Frank H. L. Koppens1,6,8

LETTER

doi:10.1038/nature21254
Graphene Optical Properties

• Let's go back and take a closer look at a previous slide…

• You will notice that at energies above the Fermi Level, we see a constant real part of the conductivity!

\[ G = \frac{e^2}{4\hbar} \]

• Apply Fresnel Eqs. in thin film limit to show that

\[ \alpha = \frac{e^2}{4\pi\varepsilon_0 c\hbar} = \frac{1}{137} \]

\[ T = (1 + 2\pi G/4\pi\varepsilon_0 c)^{-2} = (1 + \pi\alpha/2)^{-2} = 97.7\%!! \]

\[ R \approx 0\% \]

\[ A \approx 2.3\%!!! \]
Graphene Optical Properties

• While 2.3% might not seem particularly impressive, it is important to note that this is pretty strong absorption for a film that is only 1 ML thick!

Fine Structure Constant Defines Visual Transparency of Graphene

R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, A. K. Geim
Graphene Optoelectronics

Two-dimensional material nanophotonics

Fengnian Xia¹, Han Wang², Di Xiao³, Madan Dubey⁴ and Ashwin Ramasubramaniam⁵
Summary

• Today’s Lecture
  – 2D Materials
    • Band-structure
    • Optical properties
    • Plasmonics
    • Nano-photonics

• Next Lecture
  – Nanoscale light-matter interaction
  – Purcell Effect
  – Emission enhancement