Plasmonic Periodic Structures Composed by 2D Materials

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Outline

I. Introduction to Surface Plasmon Polaritons

II. Surface Plasmons in 2-Dimensional Materials

III. Periodic Structures Composed by 2D Materials

IV. Open Issues & Conclusion

Introduction to Surface Plasmon Polaritons

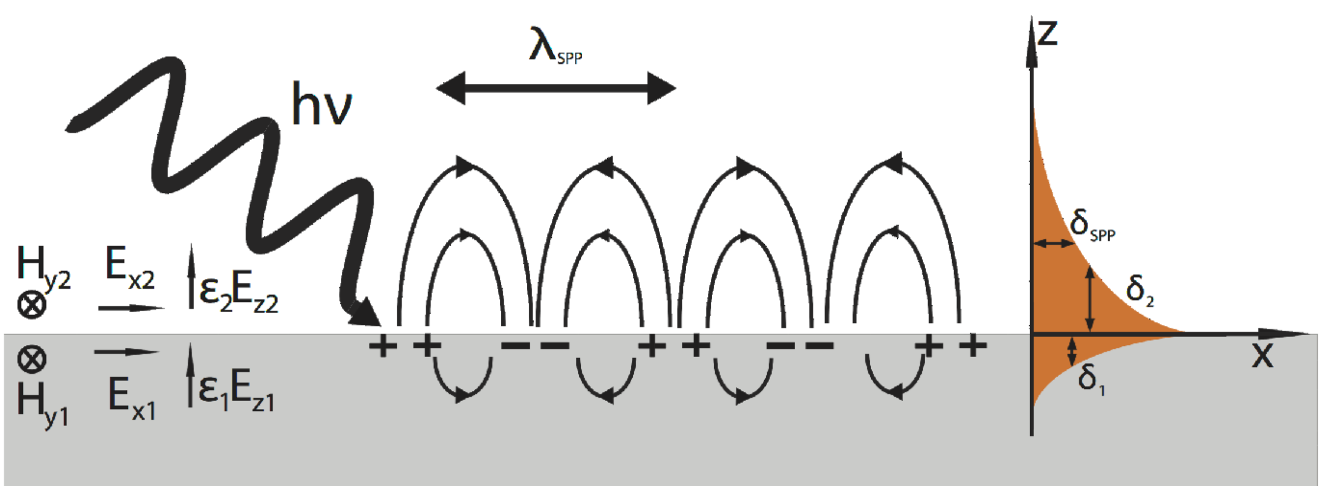
What are Surface Plasmons

The electrons in metals are free to move sustaining collective oscillations with normal modes.

Plasmon is the quantum of free electrons oscillation in a conducting media (plasma oscillation).

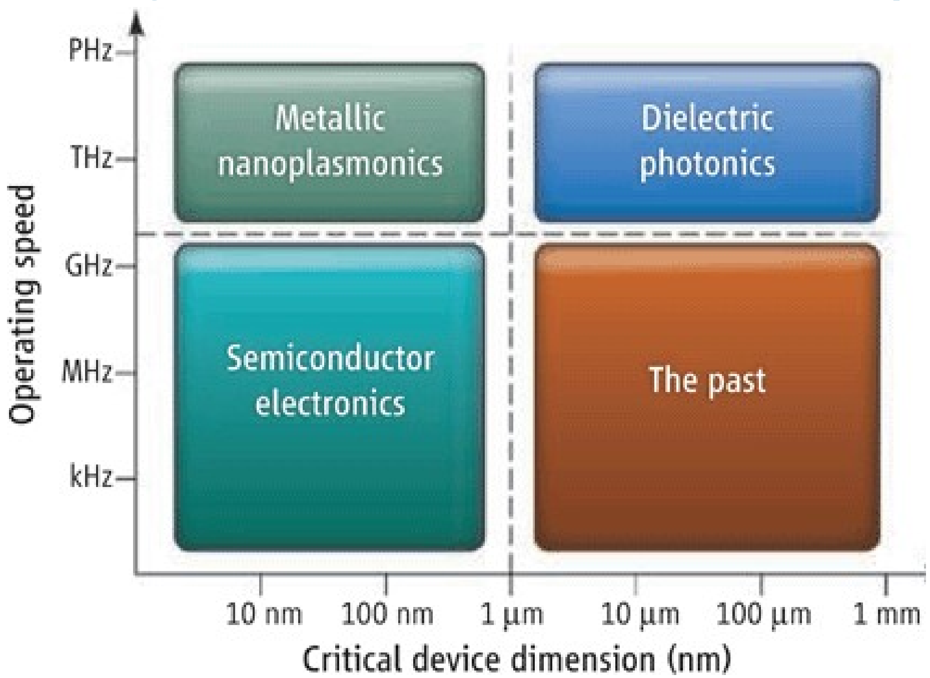
Plasmon Polariton is a quasi particle formed by the plasmon-photon coupling.

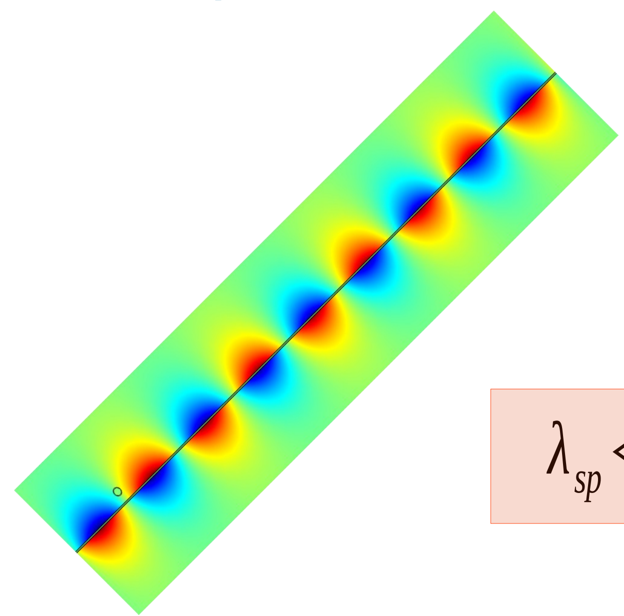
Surface Plasmon Polaritons are EM surface waves coupled to charge excitations at the surface of metal.



Plasmonics can:

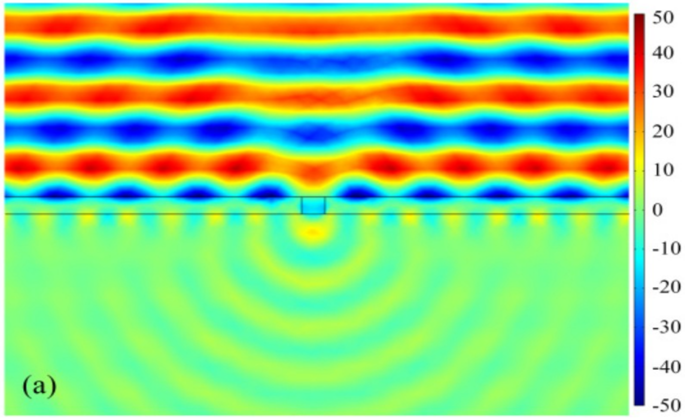
- Beat the diffraction limit (sub-wavelength optics).
- Strong localization of EM field (enhanced EM field, nonlinear optics).
- Built extremely small and ultrafast opto-electronic devices (integrated circuits, plasmonic laser).
- Control electromagnetic energy in subwavelength scales (nano-waveguides, nano-antennas).
- Be high sensitive in dielectric properties (detectors, lenses).



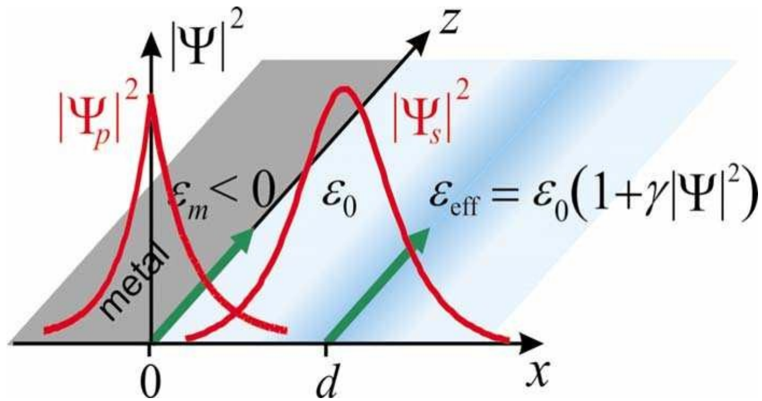


$$\lambda_{sp} \ll \lambda_{photon}$$

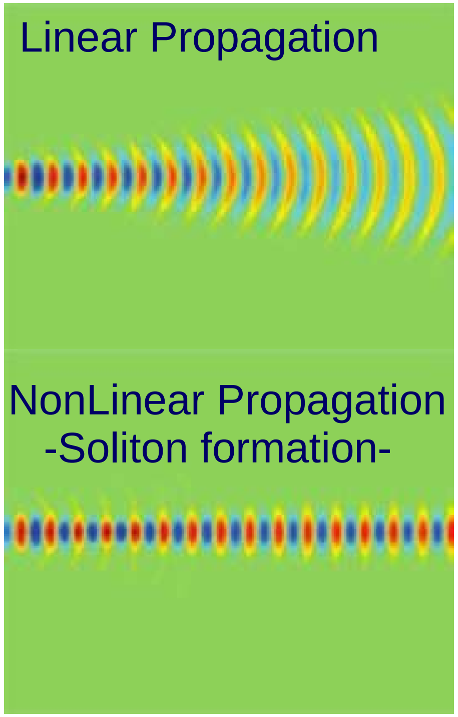
Applications I

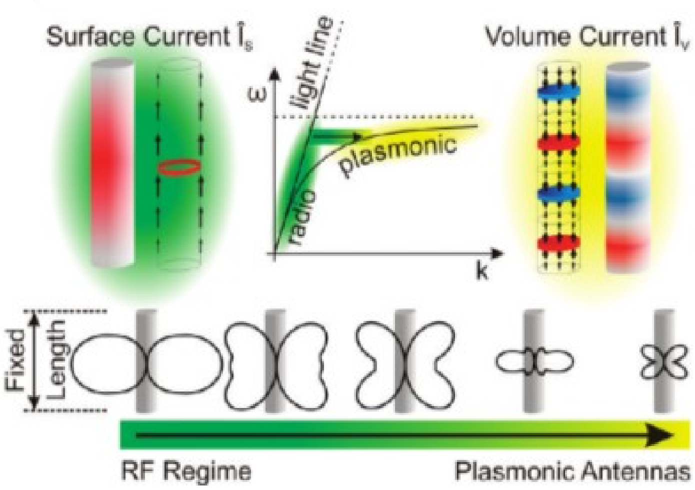


[1]**Subwavelength Optics:** 150nm slit fabricated in Ag film when illuminated by 488nm laser beam.

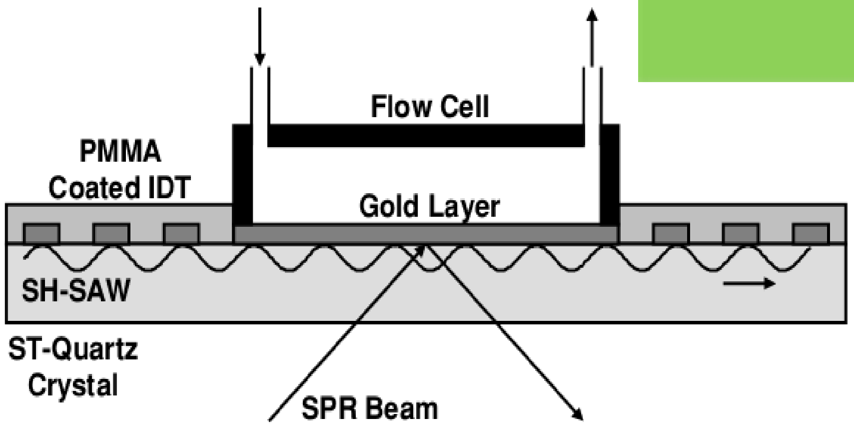


[2,3]**Nonlinear Optics:**
[2]Plasmon-soliton interaction **(Left).**
[3]SPP soliton formation **(Right).**





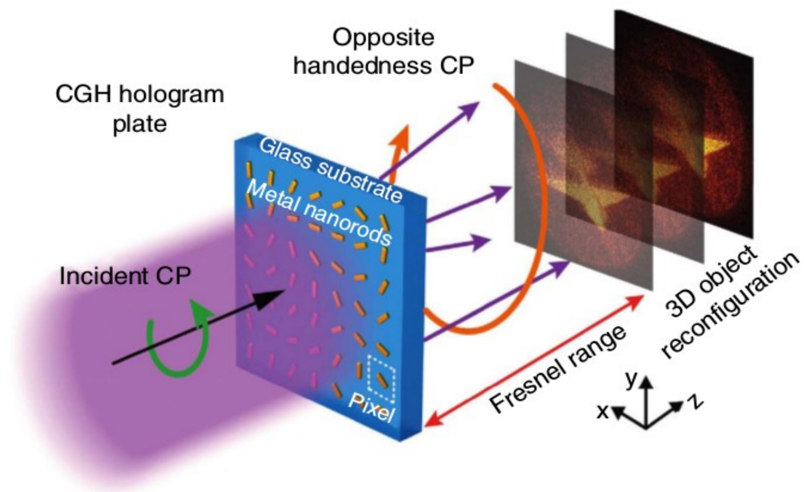
[4]**Plasmonics Nanoantennas:** Antennas with very short wavelength resonance.



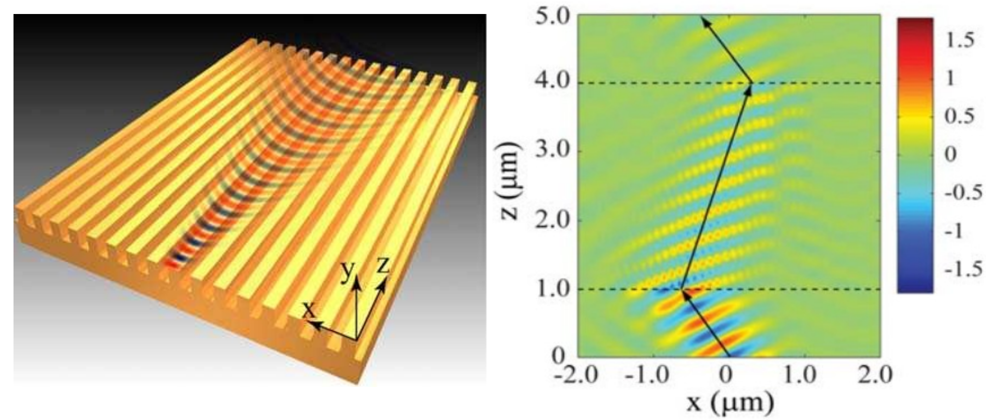
[5,6]**Biomolecules detectors:** SPPs with surface acoustic waves characterize biomolecules.

[1]V.A.G. Rivera *et al.,* inTech (2012)
[2]K. Y. Bliokh *et. al.*, Phys. Rev. A **79** (2009)
[3]A.R Davoyan *et. al.*, Opt. Express **17** (2009)
[4]J. Dorfmuller *et al.*, Nano Lett. **10** (2010)
[5]F. Bender *et al.*, Science and Technology **20** (2009)
[6] J.M. Friedt *et al.,* J. Appl. Phys. **95** (2004)

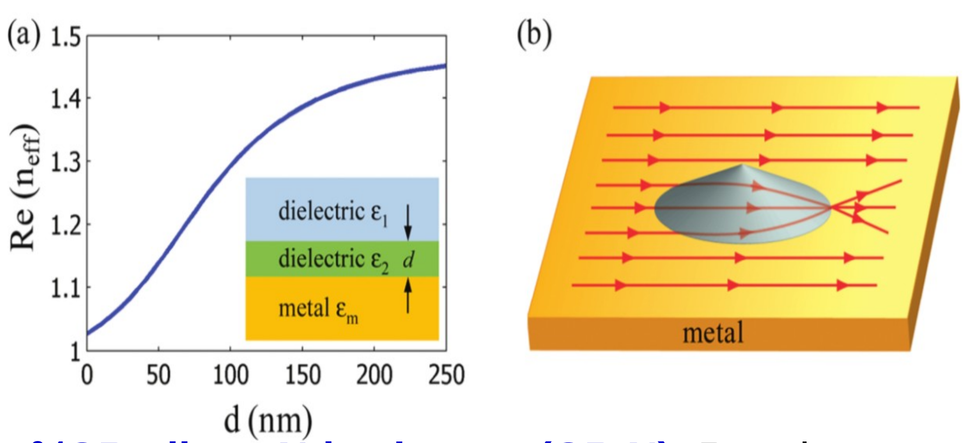
Applications II



[1]**Optical Holography:** Plasmonics meta-surfaces offers 3D optical holography.



[2]**Plasmonic Metamaterials:** Flat gold-air layers form a plasmonic metasurface providing (left) SPPs with hyperbolic phase fronts and (right) negative refraction.



[3,4]**GRadient INdex lenses (GRIN):** Regular dielectrics form plasmonics metaterials lenses.

- Plasmonic solar cells.
- Plasmonic nanolithography.
- Plasmonic waveguides.
- Integrated plasmonic circuits.
- Plasmonic laser.

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•
•

...a very promising and various scientific field...

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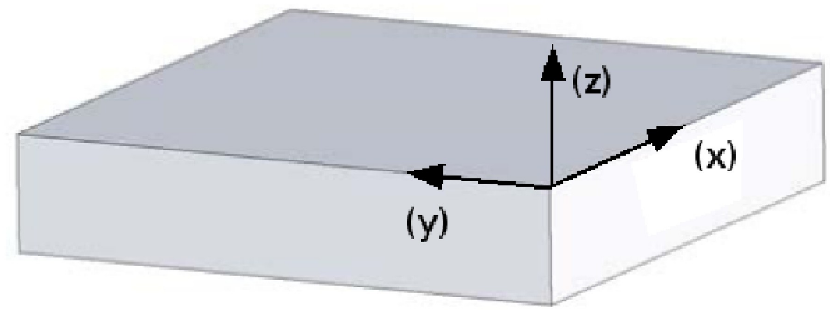
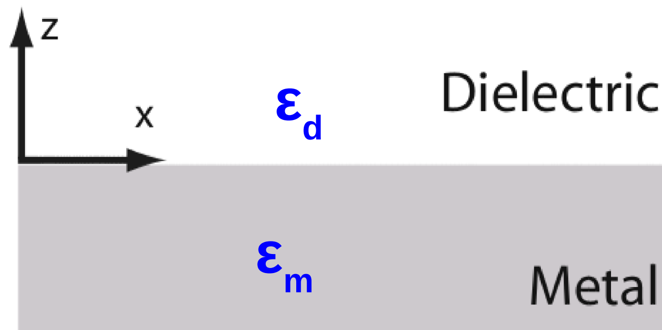
[1]L. Huang *et al.,* Nature Communications **4** (2013)
[2]Y. Liu *et. al.*, Appl. Phys. Lett. **14** (2013)
[3]Y. Liu *et. al.*, Nano Letters **10** (2010)
[4]T. Zentgra *et al.,* **10** Nat. Nanotechnology (2011)

Maxwell Equations

A metal-dielectric interface is located at z = 0



2D



Surface Waves

propagating — decaying

$$\begin{pmatrix} \vec{E} \\ \vec{B} \end{pmatrix}_{spp} \sim e^{iqx - k_{zj}|z|}$$

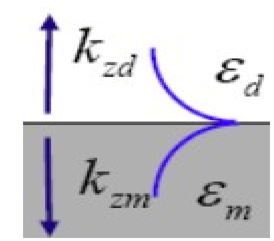
$j=(d,m)$

- q is the SPP wave number
- $k_{zj}^2 = q^2 - k_0^2 \varepsilon_j$
- Propagation along x direction
- Evanescent along z direction

Conditions

A) $\Re[\varepsilon_m] < 0$ → Metals, semimetals semiconductor

B) $k_{zj}^2 > 0 \Rightarrow q^2 > k_0^2 \varepsilon_j$ →



C) $\vec{E} = (E_x, 0, E_z)$, $\vec{H} = (0, H_y, 0)$ → TM polarization EM waves

Drude Metals

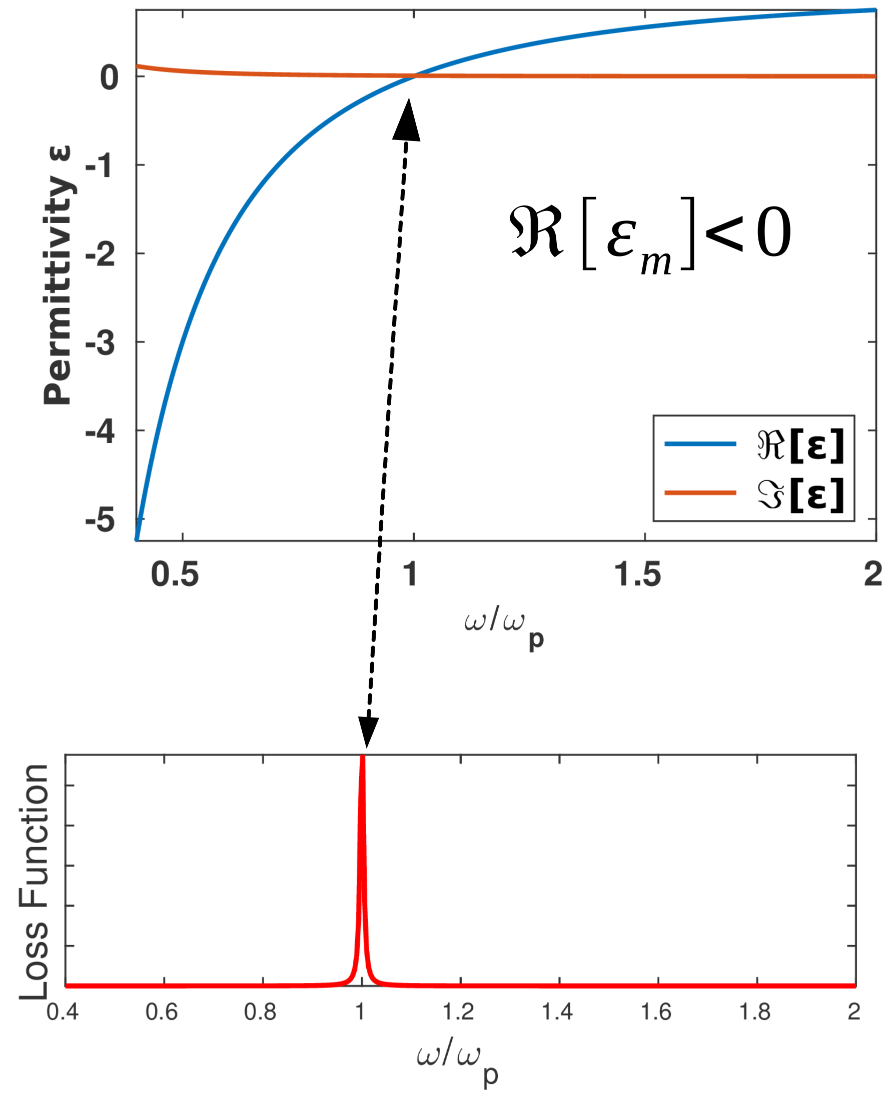
Drude model for metals:

$$\varepsilon_m(\omega) = \varepsilon_h - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega}$$

- ε_h : high frequency permittivity
- ω_p: plasma frequency
- Γ : metal losses (in freq. units)

SILVER

- $\varepsilon_h = 1$
- $\omega_p = 1.367\ 10^{16}$ Hz
- $\Gamma = 1.018\ 10^{14}$ Hz



Loss Function *L*(ω):

$$L = -\Im\left[\frac{1}{\varepsilon}\right] = \frac{\Im[\varepsilon]}{|\varepsilon|^2}$$

A useful quantity to determine SPP regime:

Maxima of *L* show plasmon resonance. SPPs are found before but near to a peak.

Dispersion Relation

Dispersion Relation q(ω):

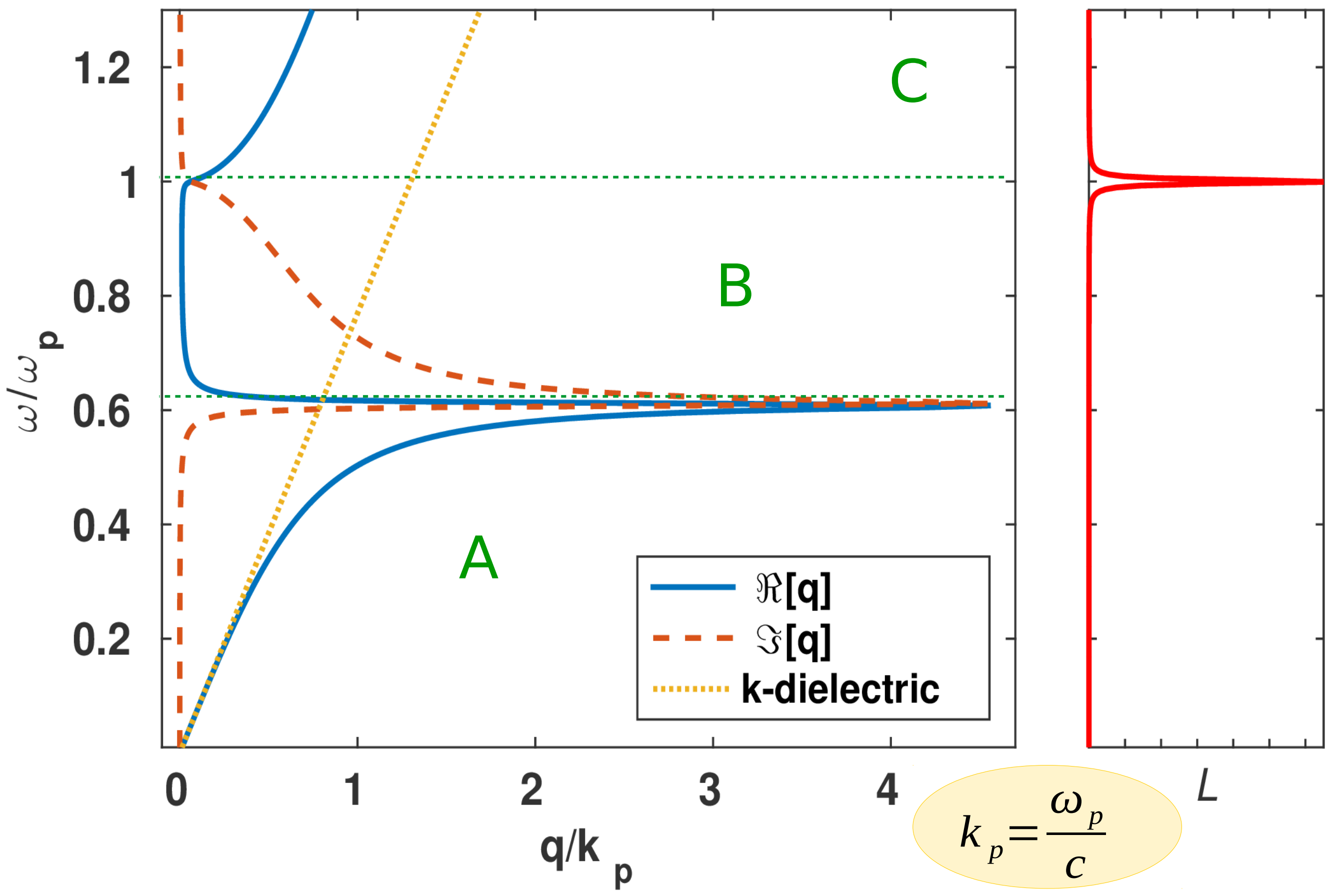
$$q(\omega)=k_0\sqrt{\frac{\varepsilon_d\varepsilon_m}{\varepsilon_d+\varepsilon_m}}$$

$$k_0=\frac{\omega}{c}=\frac{2\pi c}{\lambda_0}$$

SPP wavelength λ_{sp}:

$$\lambda_{sp}=\lambda_0\sqrt{\frac{\varepsilon_d+\varepsilon_m}{\varepsilon_d\varepsilon_m}}$$

SubWavelength
$\lambda_{sp}<\lambda_0$



$$k_p=\frac{\omega_p}{c}$$

A. Bound Modes

$$\varepsilon_m<-\varepsilon_d<0$$

q : Real
$k_{z:}$: Real

B. Quasi-Bound Modes

$$-\varepsilon_d<\varepsilon_m<0$$

q : Imaginary
$k_{z:}$: Imaginary

C. Radiative Modes

$$\varepsilon_m>0$$

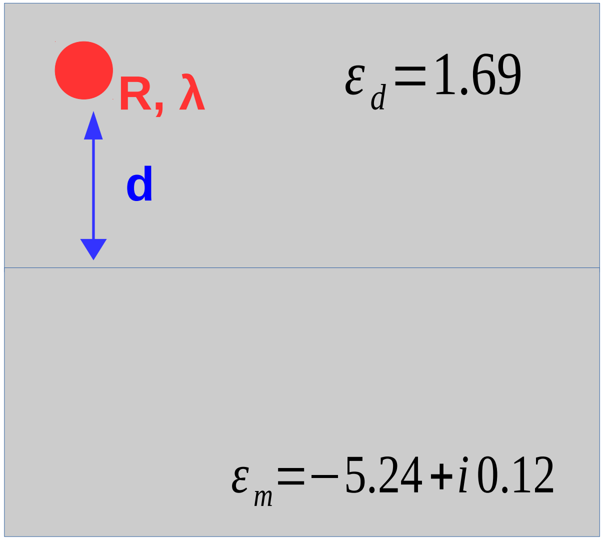
q : Real
$k_{z:}$: Imaginary

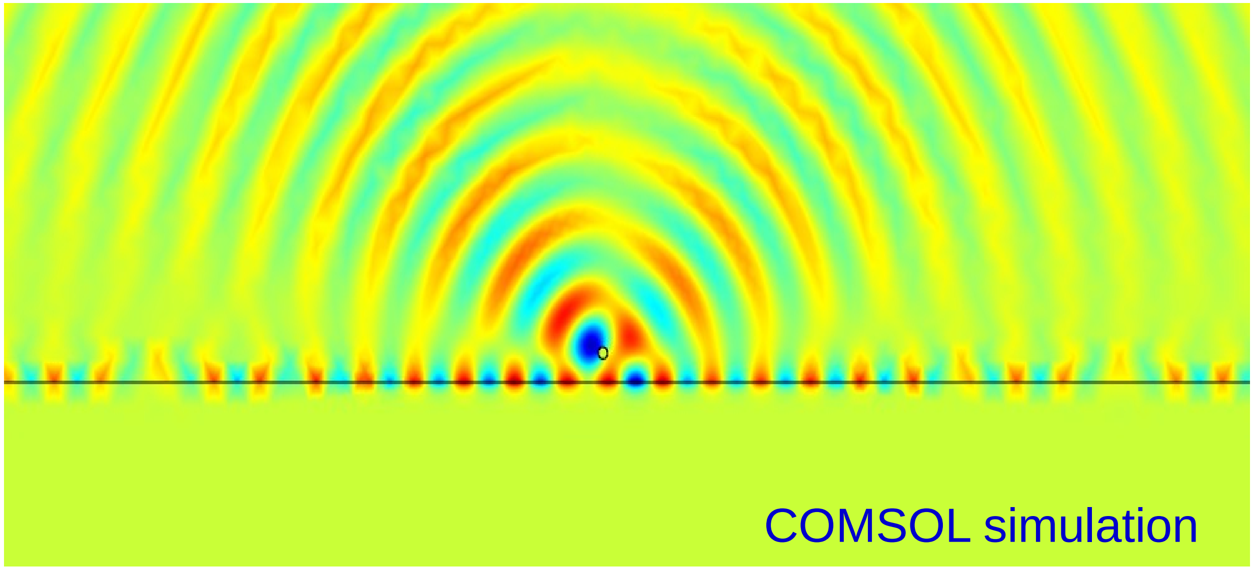
SPPs excitation

Near Field[1] method used for excitation of SPPs:

A point source with R=20nm located d=100nm above the metal surface acts as a point source since λ<<R.

Monochromatic TM EM source with λ=345nm.
Silica glass is used as dielectric with ε_d=1.69.
Silver is used as metal at f=870THz.





SubWavelength Optics

$$\frac{\lambda_0}{\lambda_{sp}} = 1.6$$

[1]SA Maier. Plasmonics: Fundamentals and applications. Plasmonics: Fundamentals and Applications (2007).

Lossy propagation

Metal's permittivity is a complex function

$$\varepsilon_m(\omega) = \varepsilon_{1m} + i\varepsilon_{2m}$$

→ METAL LOSSES

Drude Model

$$\varepsilon_m(\omega) = \varepsilon_h - \frac{\omega_p^2}{\omega^2 + \Gamma^2} + i\frac{\omega_p^2 \Gamma}{\omega^3 + \omega\Gamma^2}$$

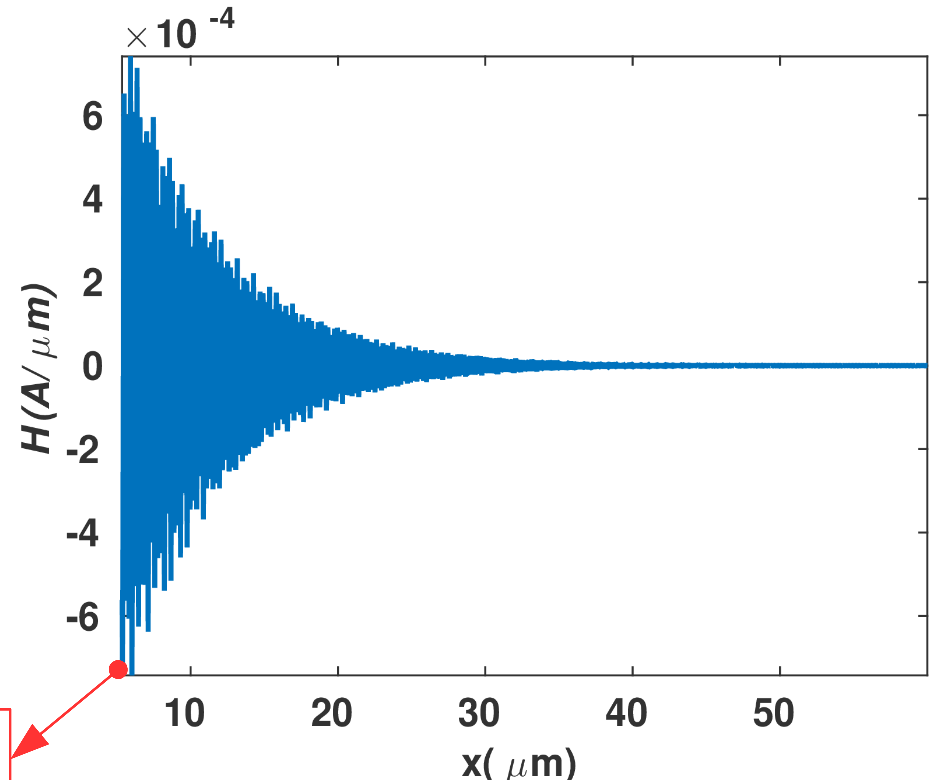
Resulting to complex q and lossy SPPs propagation

$$q(\omega) = q_1 + iq_2$$

Propagation length

The rate of change of the SPP EM energy attenuation

$$L_I = \frac{1}{\Im[q]}$$



Point Source x-location

SPPs in ultra-thin layers

Assume an ultra thin metallic film of thickness d → 0, sandwiched by two dielectrics with ε_1 and ε_2.

[1,2]Dispersion Relation q(ω):

$$q(\omega) = k_0 \frac{\varepsilon_1 + \varepsilon_2}{1 - \varepsilon_m}$$

$$k_0 = \frac{\omega}{c}$$

[1,2]A very good approximation near to plasmon resonance, where **$q \gg k_0$**

Case with same dielectrics ($\varepsilon_1 = \varepsilon_2 = \varepsilon_d$)

$$q(\omega) = k_0 \frac{2\varepsilon_d}{1 - \varepsilon_m}$$

These dispersion relations should be useful for studying plasmons in 2D materials.

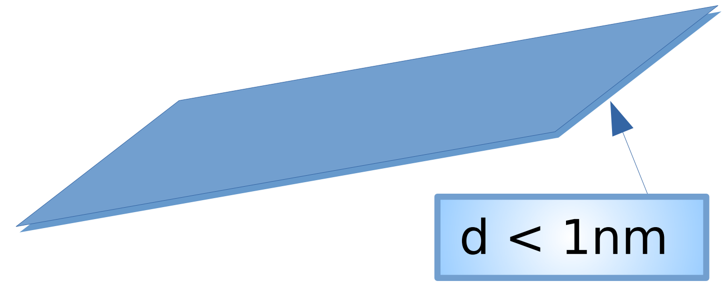
[1]M. Jablan *et al*. Proceeding of the IEEE, **101** 7 (2013)
[2]T. Low *et al*. Phys. Rev. Lett., **113** (2014)

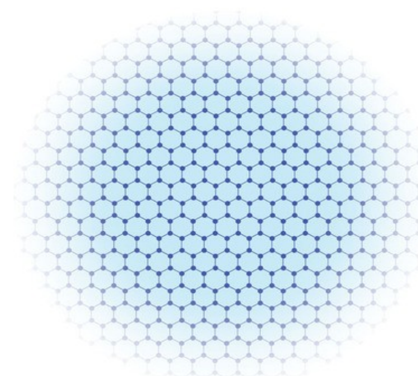
Surface Plasmons in 2-Dimensional Materials

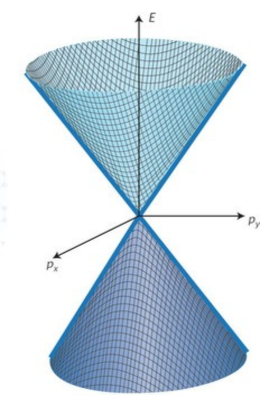
Two Dimensional Materials

The Flatland is real !!!

- **2D Materials** are crystalline materials consisting of few layers of atoms.
- In 2D materials the width *d* is much smaller than the other dimensions, the width is **less than 1nm!!!**
- The properties are dramatically changing when we are going from 3D to 2D.

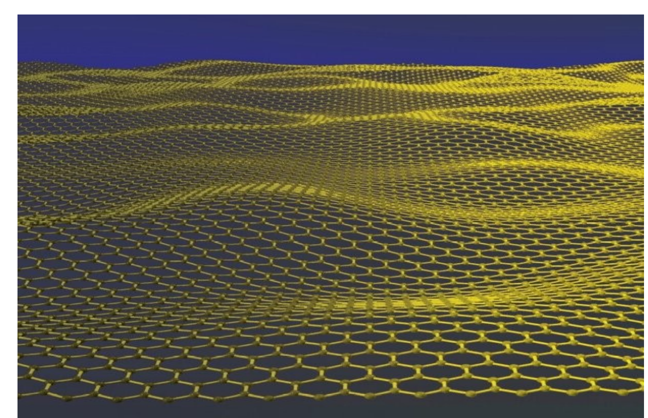






Graphene is an atomically thick **(d=0.32nm)** sheet honeycomb lattice of carbon atoms.

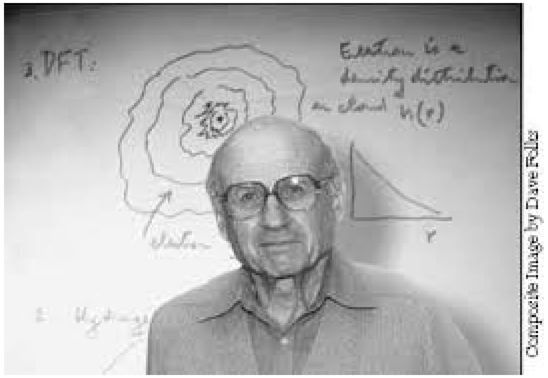
- ➔ It is hundreds of times stronger than steel.
- ➔ It has the largest thermal and electrical conductivity that is known.
- ➔ It supports plasmon modes with very short wavelength.



Ab initio Calculations

Permittivity ε is calculated by first principles, i.e. by solving quantum mechanics equations.

Density **F**unctional **T**heory (DFT) is a computational quantum mechanical modeling method for investigating the electronic structure.



Walter Kohn chemistry Nobel prize 1998

PHYSICAL REVIEW VOLUME 136, NUMBER 3B 9 NOVEMEBR 1964

Inhomogeneous Electron Gas*

P. Hohenberg†
École Normale Superieure, Paris, France
and
W. Kohn‡
École Normale Superieure, Paris, France and Faculté des Sciences, Orsay, France
and
University of California at San Diego, La Jolla, California

(Received 18 June 1964)

PHYSICAL REVIEW VOLUME 140, NUMBER 4A 15 NOVEMBER 1965

Self-Consistent Equations Including Exchange and Correlation Effects*

W. Kohn and L. J. Sham
University of California, San Diego, La Jolla, California

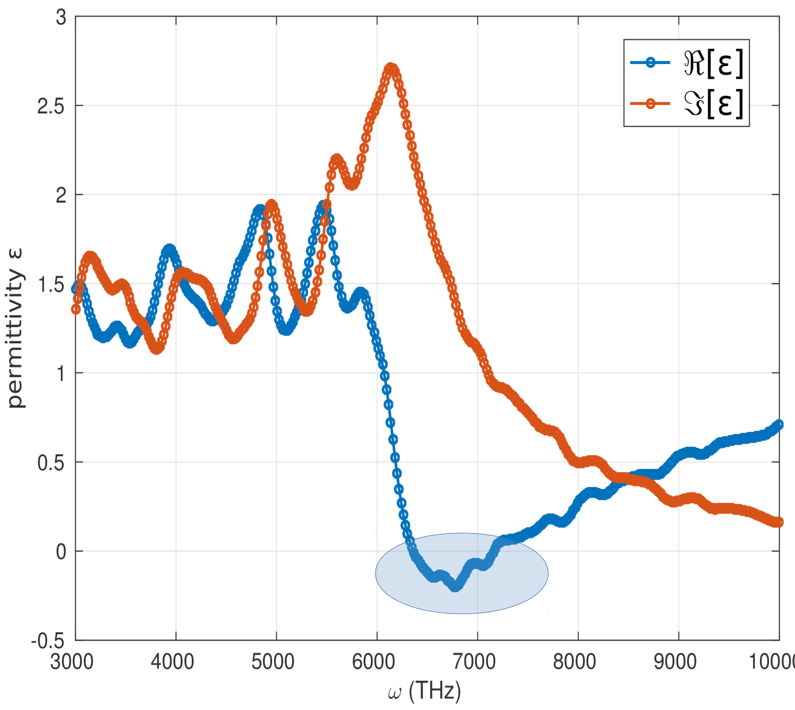
(Received 21 June 1965)

Graphene

Undoped Graphene has negative permittivity for a small regime, so we expect to support surface plasmons.

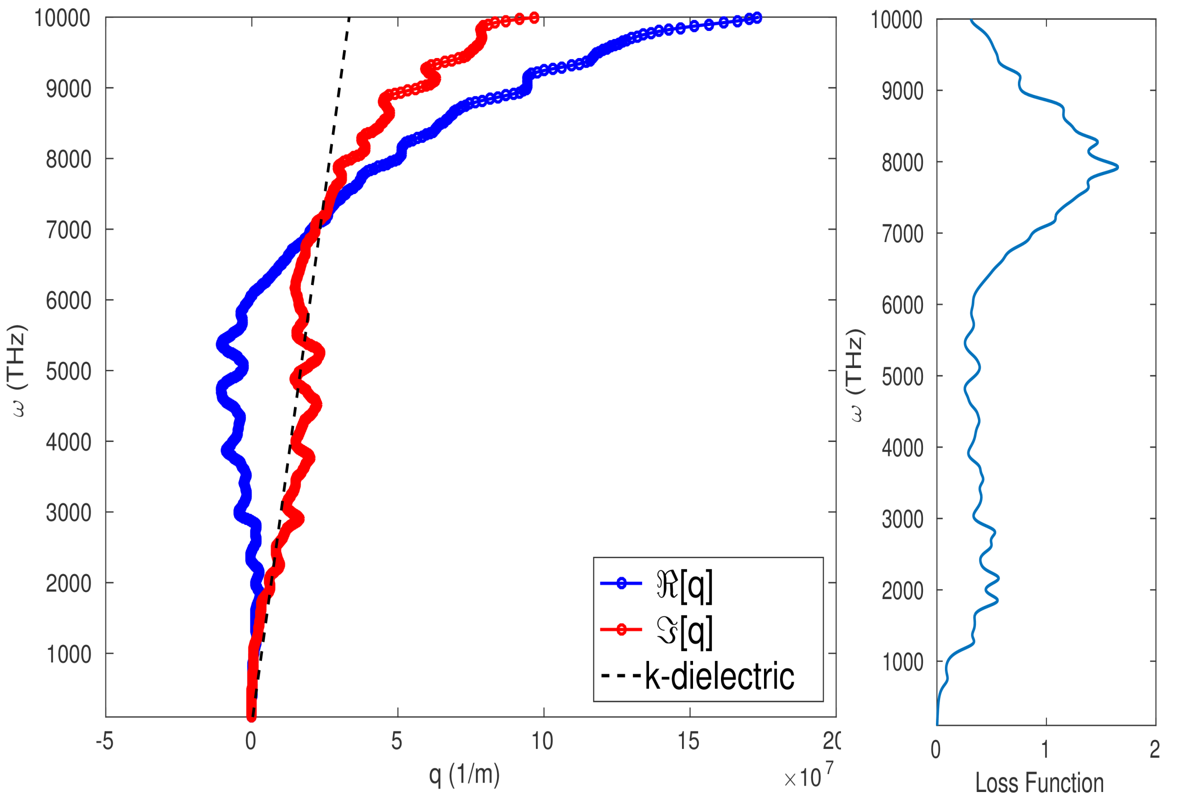
Air is used as enviroment $\varepsilon_1=\varepsilon_2=1$

Graphene permittivity obtained by DFT



A small negative ε regime, with high losses (Im[ε]).

Dispersion Relation q(ω) and Loss function:

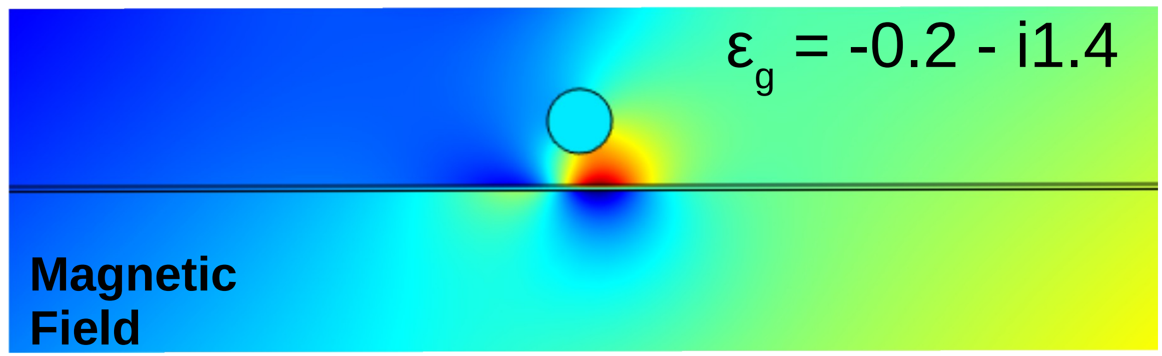


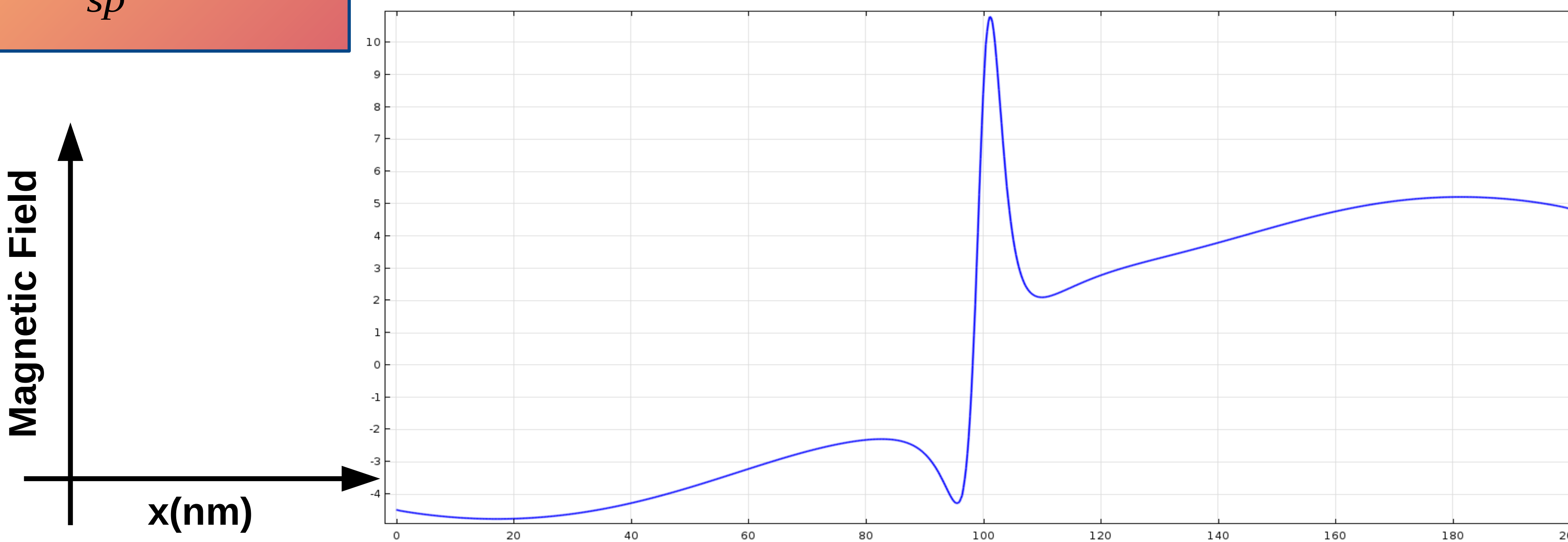
SPPs in Graphene

- COMSOL simulation for SPP propagation.
- Point source of ω=6770THz and λ=278nm.
- SSP is generated but cannot propagate for long due to high losses.
- It could be applied as a photo-sensor for high frequencies.

Subwavelength

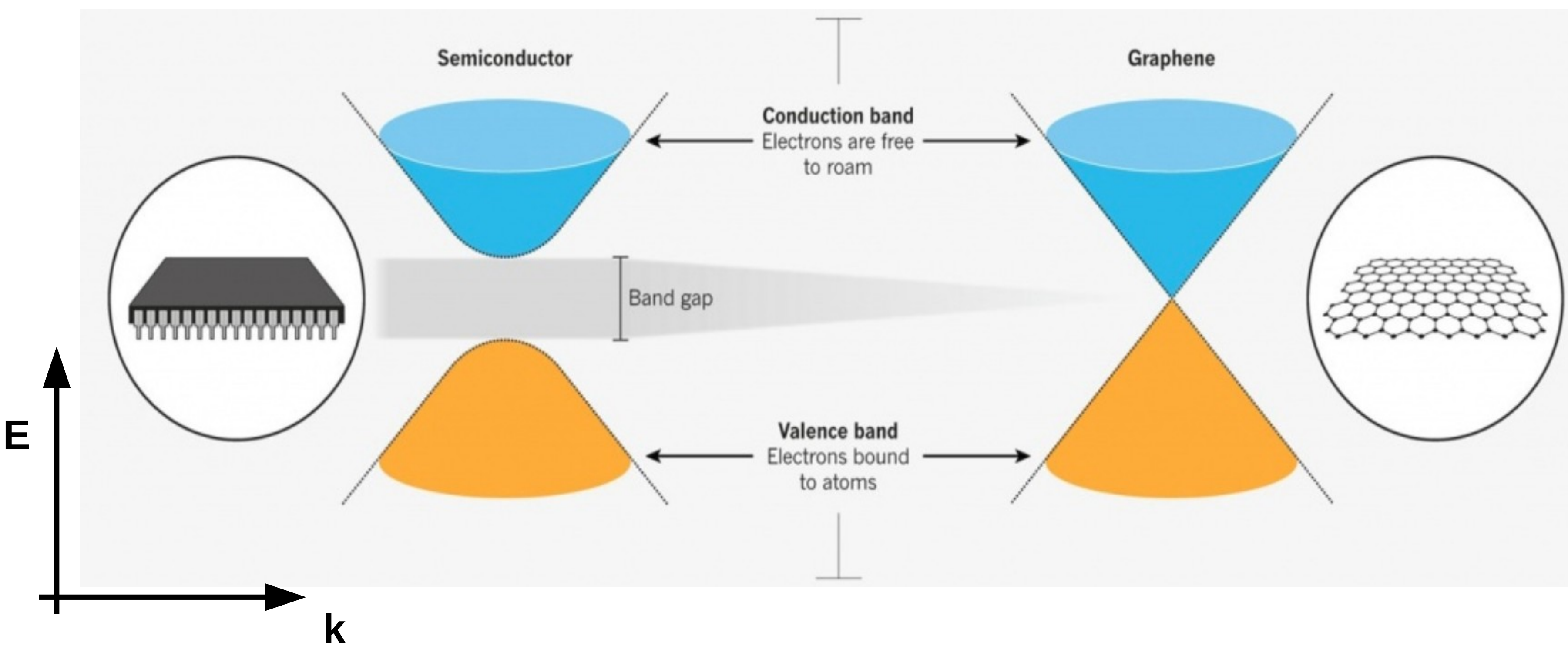
$$\frac{\lambda_0}{\lambda_{sp}} \sim 20$$





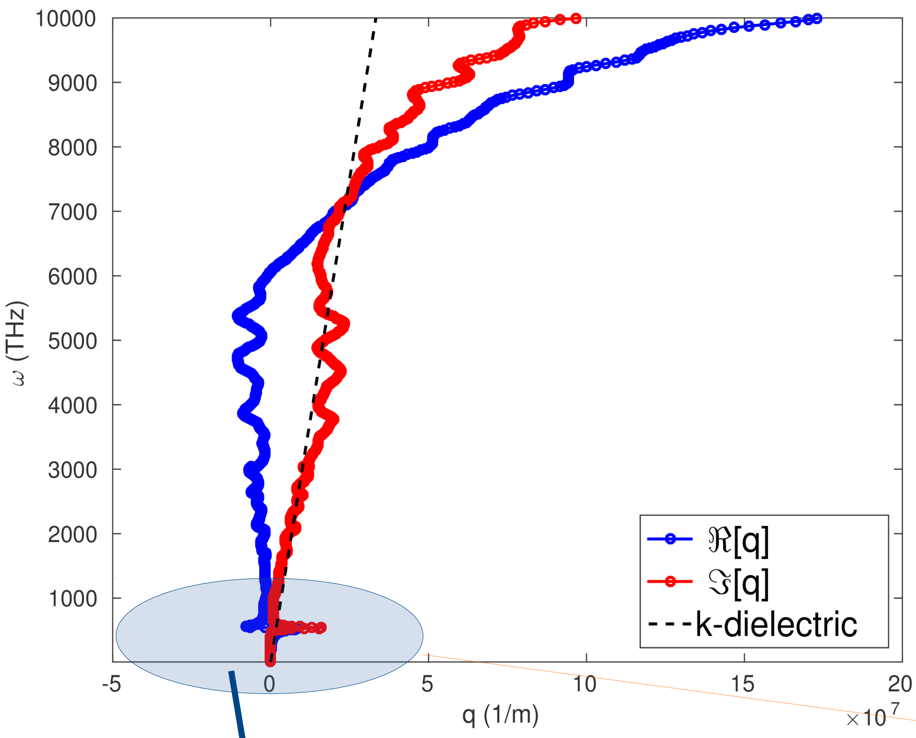
Doping materials

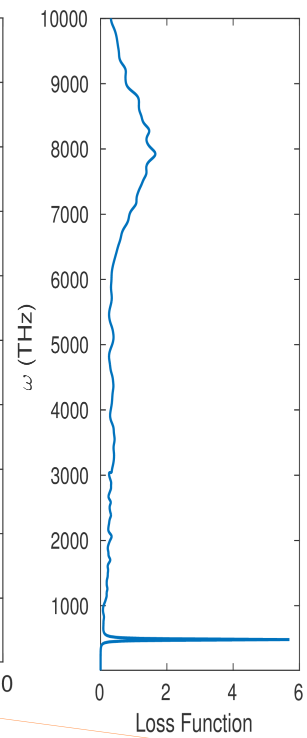
- With **doping** we **add** electrons to the conduction band or **remove** from the valence band. As a result, **the conductivity** of the material is increased, because more electrons can move free.
- The doping can be performed by **chemical** reactions or by applying external **voltage.**
- The amount of doping **controls the plasmon resonace frequency.** More doping leads to higher plasmon frequency and vice versa.
- It is a way to use semi-conductors for plasmonics.

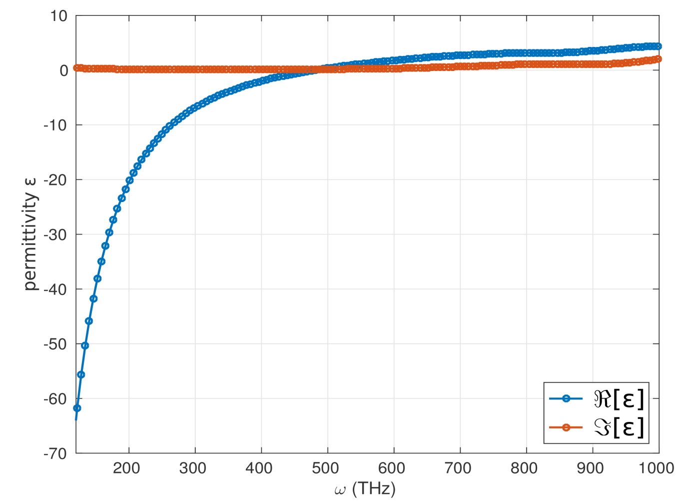


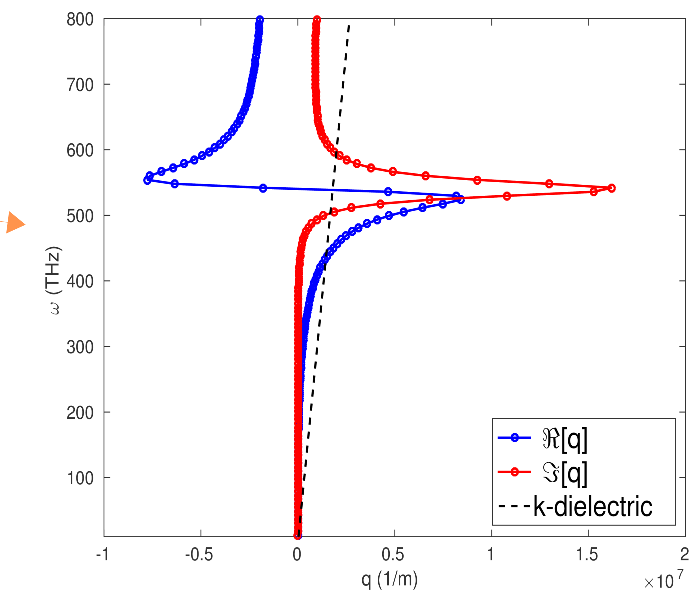
Doped Graphene

Doped graphene shows a new plasmon resonance, at lower frequency (THz regime).







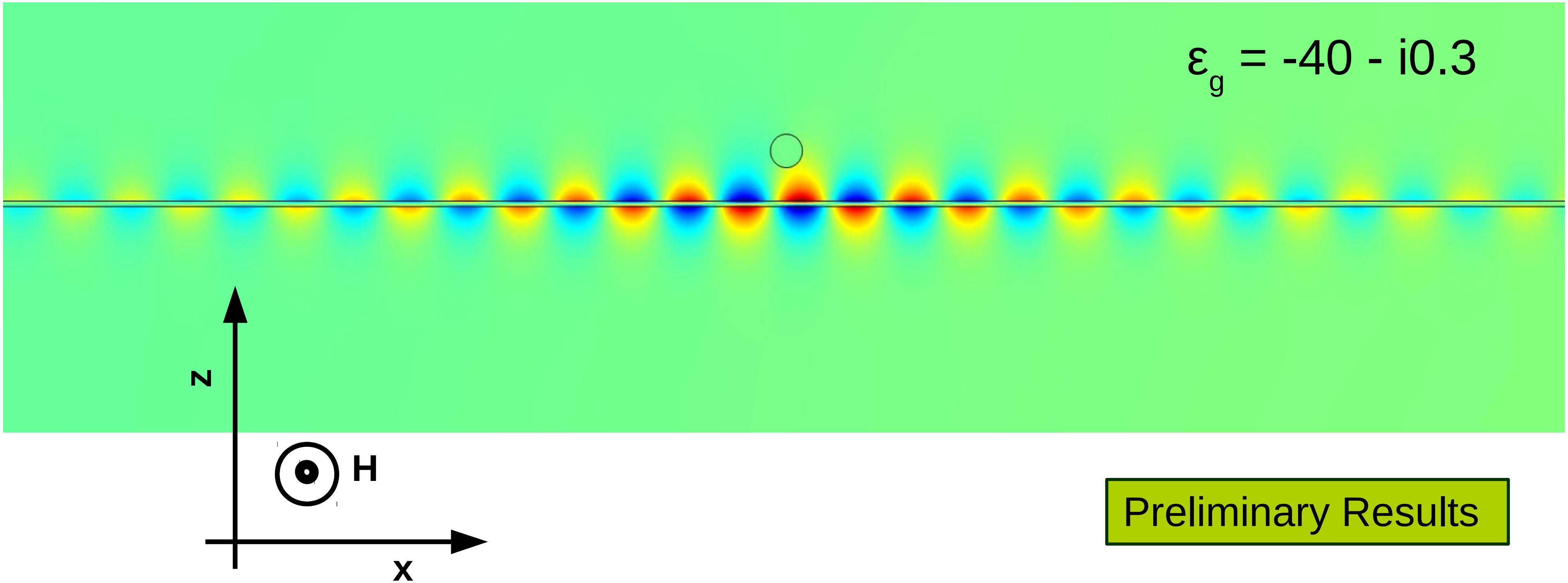


- New plasmon resonance at lower frequency.
- The new plasmon resonance frequency can be tuned by the amount of doping.

Preliminary Results

SPPs in Doped Graphene

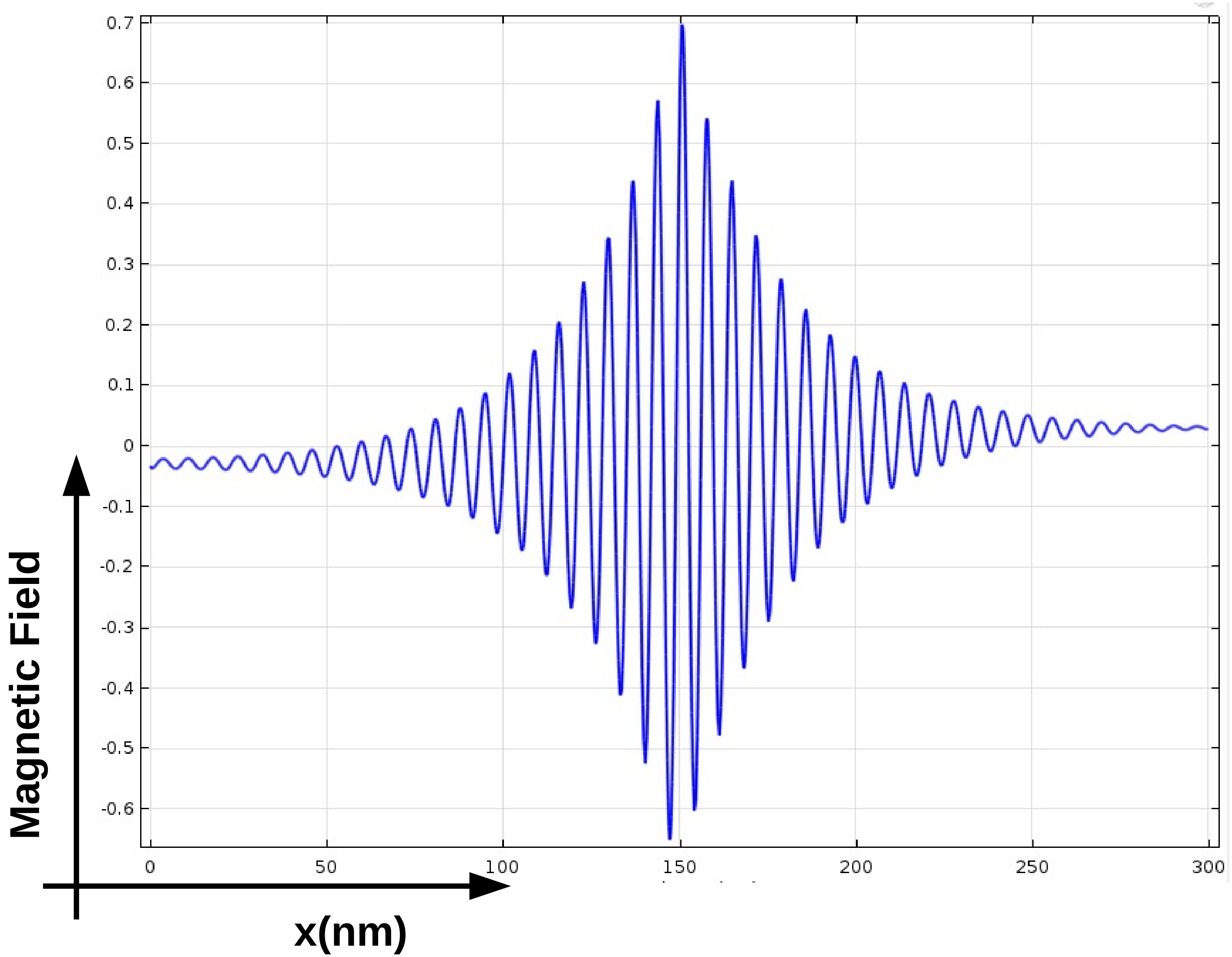
- COMSOL simulation for SPP propagation.
- The doped graphene layer of thickness d=0.33nm surrounded by air.
- A point EM source is located 3nm above the graphene layer. The source is monochromatic with ω=300THz and λ=6.3μm.
- The magnetic field is illustrated showing the SPP propagation



Preliminary Results

Graphene and subwavelength optics

- COMSOL simulation for SPP propagation.
- Magnetic field on the graphene surface.



Extreme small wavelength!

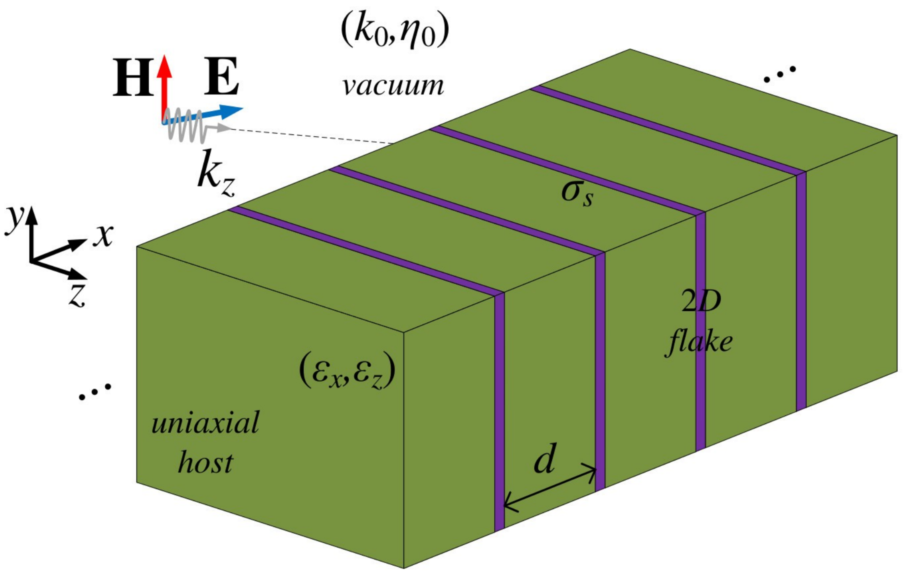
$$\frac{\lambda_0}{\lambda_{sp}} = 900$$

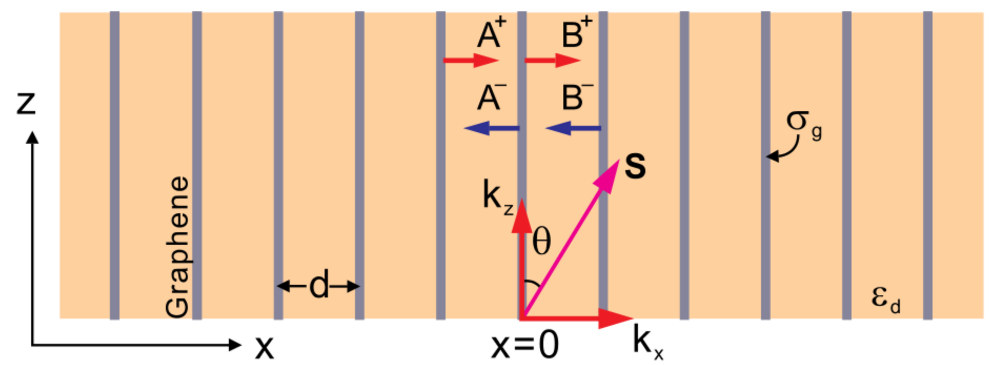
Preliminary Results

Periodic Structures Composed by 2D Materials

Multilayer of 2D Plasmonic Media

Graphene monolayer sheets are extended in (y,z) plane and arranged periodically along x.

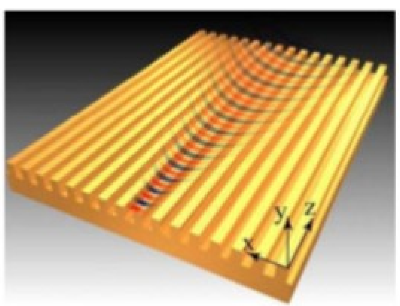


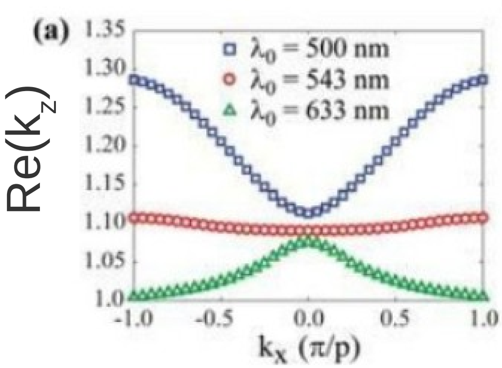


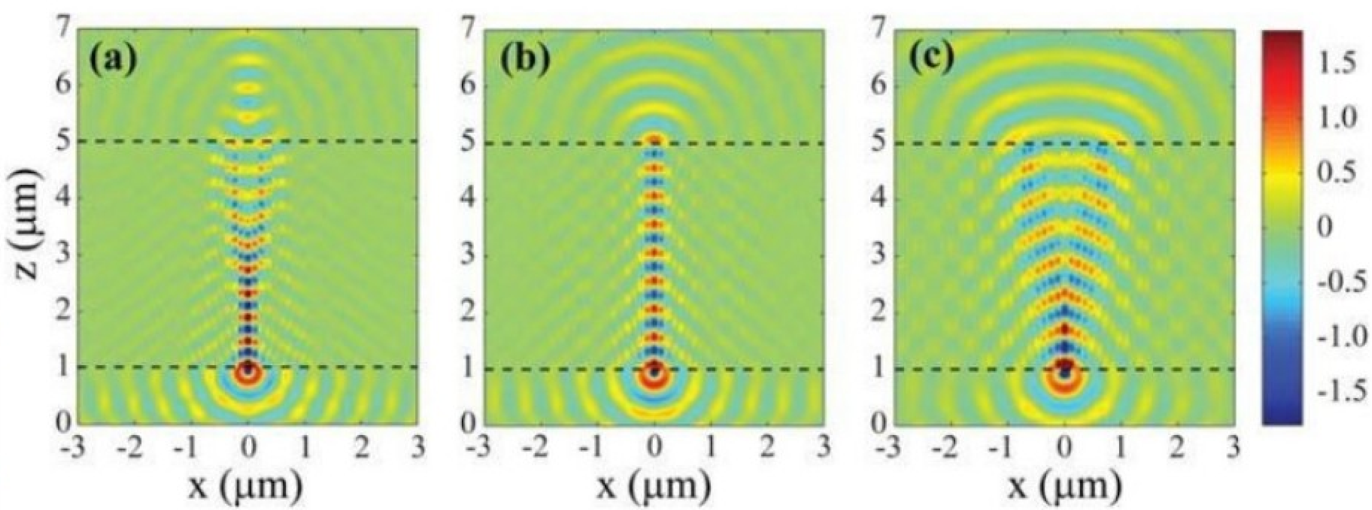
- The interlayer distance called period d.
- Anisotropic uniaxial dielectric as host media $\varepsilon_z = \varepsilon_y \neq \varepsilon_x$.
- The 2D flakes are characterized by the surface conductivity σ_s.
- Surface Plasmon wavenumber k_z.
- Bloch wave number k_x.

Plasmonic Properties & Diffraction Relation

- The allowed SPs modes comprise bands on (k_x, k_z) plane.
- We are looking for the diffraction relation $k_z(k_x)$.
- The curvature of the band determines the SP propagation $(v_g \sim \frac{\partial k_z}{\partial k_x})$.
  - Hyberbolic Band: Negative/Anomalous Refraction.
  - Linear Band: Non-dispersive SPs Propagation.
  - Elliptical Band: Dispersive Propagation.







Y. Liu et. al. Appl. Phys. Lett. **103** (2013)

Maxwell Equations (MEs)

Assuming EM waves harmonic in time with TM polarization.

Maxwell Equations can be written:

$$-\mathrm{i}\frac{\partial}{\partial z}\mathbf{\Psi} = \mathcal{M}\cdot\mathbf{\Psi} \Leftrightarrow$$

$$-\mathrm{i}\frac{\partial}{\partial z}\begin{pmatrix} E_x \\ H_y \end{pmatrix} = k_0\eta_0 \begin{pmatrix} 0 & 1+\frac{1}{k_0^2}\frac{\partial}{\partial_x}\frac{1}{\varepsilon_z}\frac{\partial}{\partial_x} \\ \frac{\varepsilon_x}{\eta_0^2} & 0 \end{pmatrix}\begin{pmatrix} E_x \\ H_y \end{pmatrix}.$$

with tangential component: $$E_z = \frac{\mathrm{i}\eta_0}{k_0\varepsilon_z}\frac{\partial H_y}{\partial x}$$

$k_0 = \omega / c$ is the free space wavenumber

$\eta_0 = \sqrt{\mu_0 / \varepsilon_0}$ is the free space impedance

Eigenvalue Problem

Assuming EM waves propagate along z

$$\mathbf{\Psi}(x,z) = \mathbf{\Psi}(x)e^{\mathrm{i}k_z z},$$

We obtain an Eigenvalue problem

$$k_z \mathbf{\Psi} = \mathcal{M}\mathbf{\Psi}$$

Where the asking eigenvalue k_z is the SPPs wavenumber.

Because of the periodicity, the allowable $k_z(k_x)$ are expected to be arranged in bands.

Y. Liu et. al. Phys. Rev. Lett. **99** (2007)

O. Peleg et. al. Phys. Rev. Lett. **102** (2009)

Eigenvalue Problem & Bloch SPs Waves

- Graphene is inserted as Boundary Condition in MEs.

$$J_s = \sigma_g E_z$$

- Solve the eigenvalue problem in between two adjacent dielectric slabs separated by graphene monolayer at $x = 0$.

$$H_y^- e^{\mathrm{i}k_z z} \text{ for } -d < x < 0 \qquad H_y^+ e^{\mathrm{i}k_z z} \text{ for } 0 < x < d$$

- Matching conditions at $x = 0$
  - Discontinuity of Mangetic Field: $H_y^+ - H_y^- = J_s = \sigma_g E_z$
  - Continuous Tangential Electric Field: $\partial_x H_y^+ = \partial_x H_y^-$
- Periodic Boundary Conditions
  - Bloch Theorem: $H_y^+(x) = H_y^-(x - d) e^{\mathrm{i}k_x d}$
  - Bloch wavenumber: $k_x = 2\pi n/(Nd)$ (n integer from 0 to N)
  - Because of the periodicity, the linear eigenmodes are Bloch waves and they are arranged in bands.

Dispersion Relation

- Dispersion Relation $k_z(k_x)$:

$$\cos(k_x d) = \cosh(\kappa d) - \frac{\xi\kappa}{2}\sinh(\kappa d)$$

where $\kappa = \sqrt{\frac{\varepsilon_z}{\varepsilon_x}(k_z^2 - k_0^2\varepsilon_x)}$.

- Investigating at first Brillouin zone viz. $k_x d = (-\pi, \pi)$.
- Plasmonic Thickness

$$\xi = -\frac{\mathrm{i}\sigma_g \eta_0}{k_0 \varepsilon_z}$$

The decay length of SPs in dielecric is $\xi/2$. Subsequently:

- Weak SPP coupling regime: $d > \xi$.
- Strong SPP coupling regime: $d < \xi$.

Analytical Investigation of Diffraction Relation

- Assume very dense grid: $\kappa d << 1$
- Around Brilloun center: $k_x \sim 0$.
  Taylor expansion up to second order terms of d and k_x

$$\frac{k_z^2}{\varepsilon_x} + \frac{d}{(d-\xi)\varepsilon_z} k_x^2 = k_0^2.$$

- The sign of $\xi - d$ determines the behavior of the band, reflecting the strong and weak SPs coupling regime.
  - $\xi > d$ Hyperbolic Band (Strong SPs Coupling).
  - $\xi < d$ Elliptic Band (Weak SPs Coupling).
- Around critical period $d \sim \xi$
  - $d = \xi$ is a pole.
  - Linear Dispersion Relation.

$$k_z^2 \simeq \frac{\varepsilon_x d}{\varepsilon_z(\xi - d)} k_x^2$$

Dirac Point

- Make the choice ξ=d and replace to Dispersion Relation.
- We have Saddle Point at $\left(k_x, k_z\right) = \left(0, k_0\sqrt{\varepsilon_x}\right)$
- Two Bands coexist

Saddle Point + Linear Dispersion = Dirac Point

Spatial harmonics travel with the same velocity.

Non-Dispersive EM waves propagation.

ENZ Metamaterials

Effective anisotropic medium with effective permittivity

$$\varepsilon_{x,eff} = \varepsilon_x \quad , \quad \varepsilon_{z,eff} = \varepsilon_z + \mathrm{i}\frac{\eta_0 \sigma_s}{k_0 d} = \varepsilon_z \frac{d - \xi}{d}.$$

Epsilon Near Zero (ENZ) plasmonic metamaterial

$$d = \xi \quad \Rightarrow \quad \varepsilon_{z,eff} = 0$$

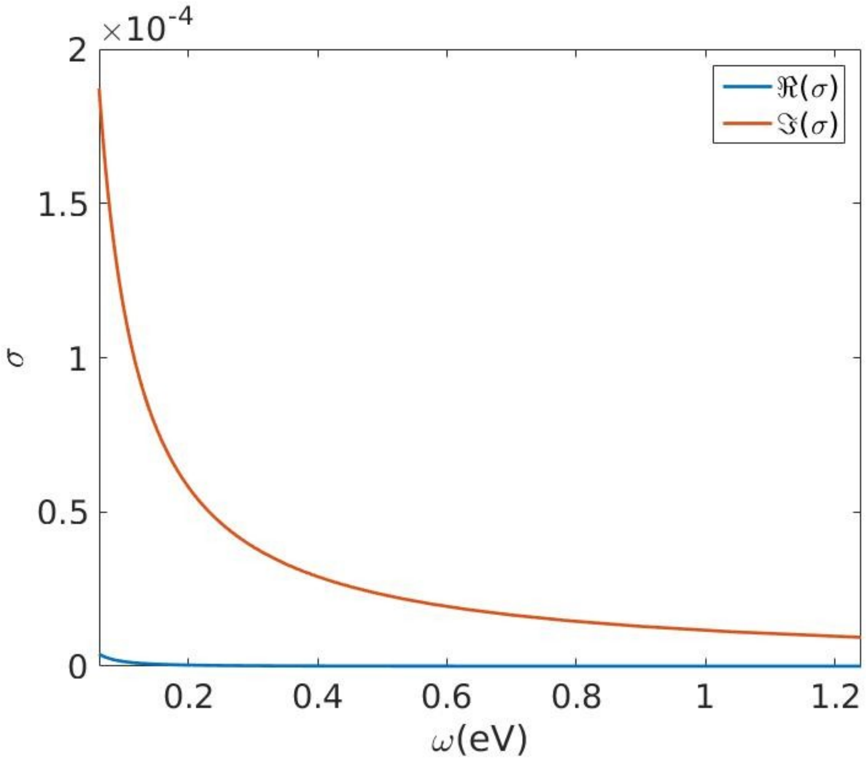
Two different concepts are brought together.

Dirac Point leads to **ENZ** metamaterial

Surface Conductivity of Graphene

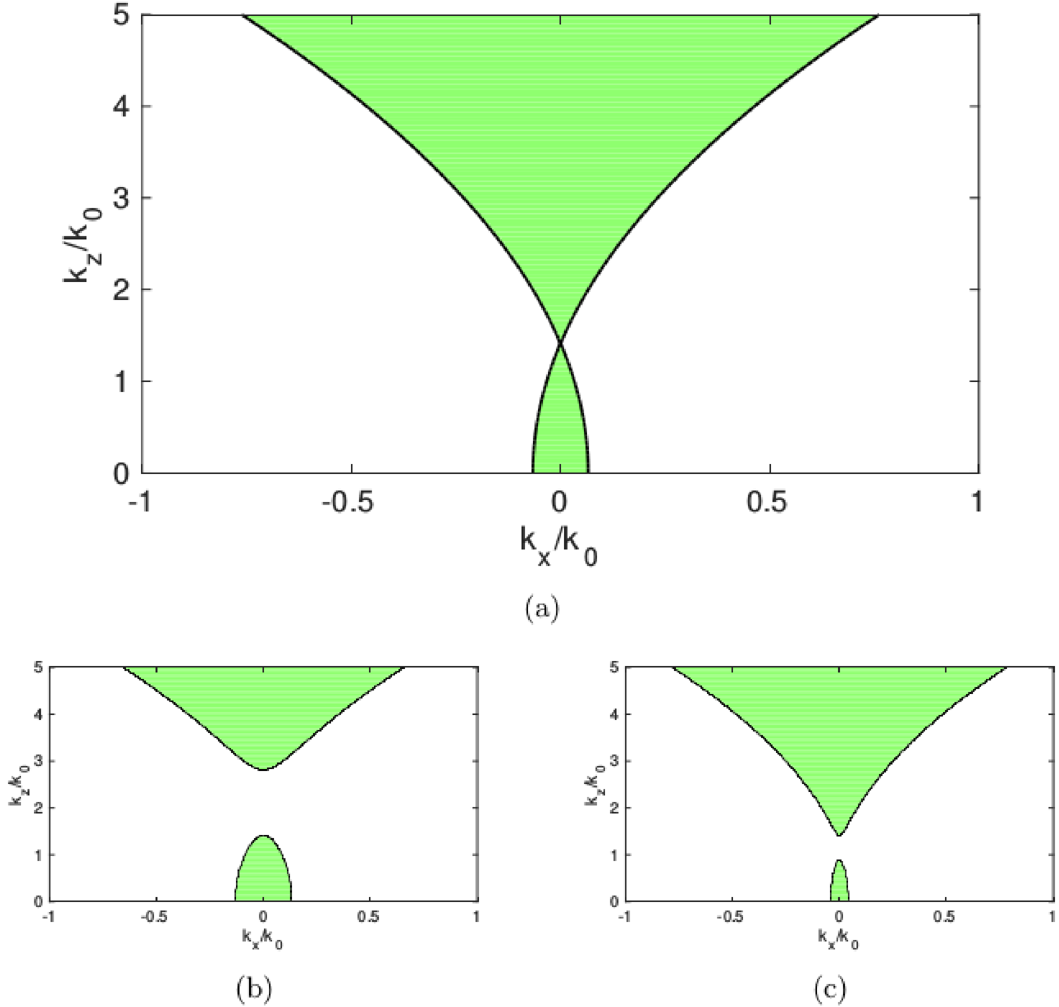
In THz regime the surface conductivity of Graphene can be approximated by Drude model.

$$\sigma_g(\omega) = \frac{ie^2 \mu_c}{\pi \hbar (\omega + i/\tau)}$$



- chemical potential: $\mu_c = 0.15eV$
- momentum relaxation time: $\tau = 0.5ps$
- angular frequency: $\hbar\omega = (0.06eV \ to \ 1.24eV)$
- photon wavelength in vacuum: $\lambda = (1\mu m \ to \ 20\mu m)$

Plasmonic Bands



Host dielectric is built by several layers of MoS_2.

Anisotropic dielectric with:

$\varepsilon_x=2$ & $\varepsilon_z=13$

Figure 4: Dispersion relation of the real part of equation (3) for a periodic structure composed by bulk MoS_2 and graphene flakes. (a) Dirac Point at $d = \Re[\xi]$ (b) Band gap for 0.1% deviation ($d = 1.001\Re[\xi]$) (c) Band gap for 0.02% deviation ($d = 0.9997\Re[\xi]$).

Band Gap

- A band gap opens destroying the Dirac Point.
- Extremely sensitive to condition $\xi = d$.
- Imperfections on surface of regular dielectrics are about 10% complete destroying the Dirac Point.
- Bulk material built by 2D materials, like MoS_2, restricts the defects in atomic scales (<1%).

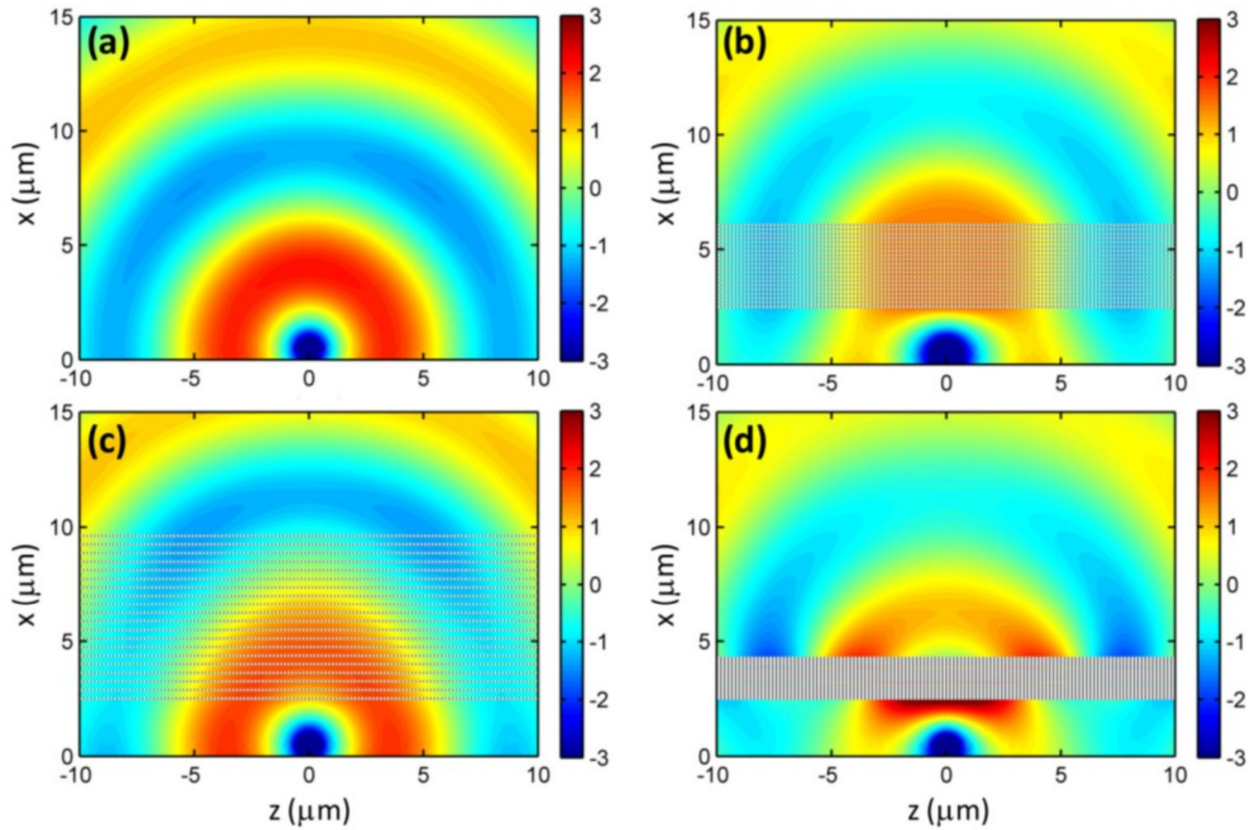
- **MoS_2** is another 2D media acts as anisotropic dielectric.
- After few layers MoS_2 permittivity saturates in:

$$\varepsilon_x = 2 \quad \& \quad \varepsilon_z = 13$$

- In THz and optical frequencies the permittivity is constant.

Propagation Close to Dirac Point

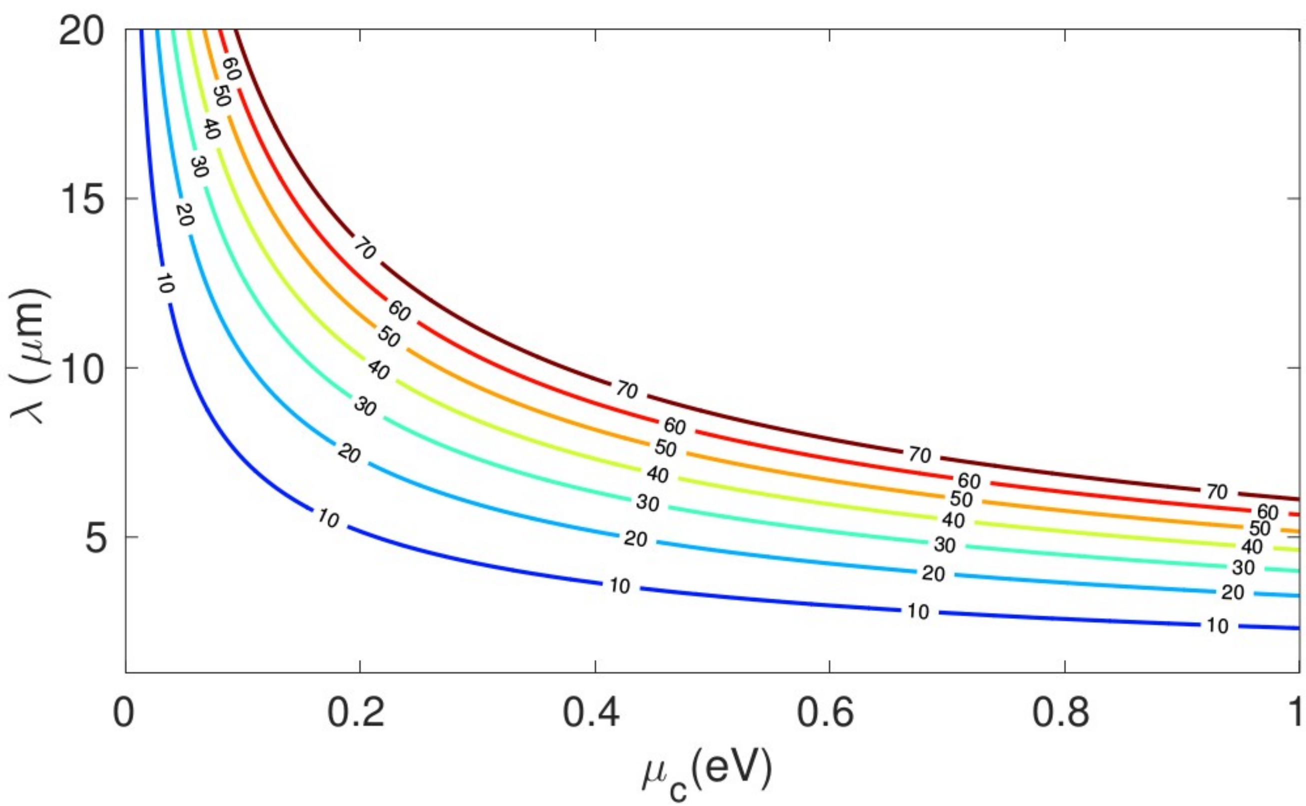
a) No graphene structure: The phase front is identical in all directions.
b) d=ξ: The phase does not change in normal direction.
c) d>ξ: The phase propagates faster in the normal direction.
d) d<ξ: The structure behaves as bulk metal. The transmitted light excites surface states on the upper surface, which are SPs on the effective metal



B. Wang et. al. J. Appl. Phys. **115** 213102 (8pp) 2014.

Dynamical Tuning of ξ

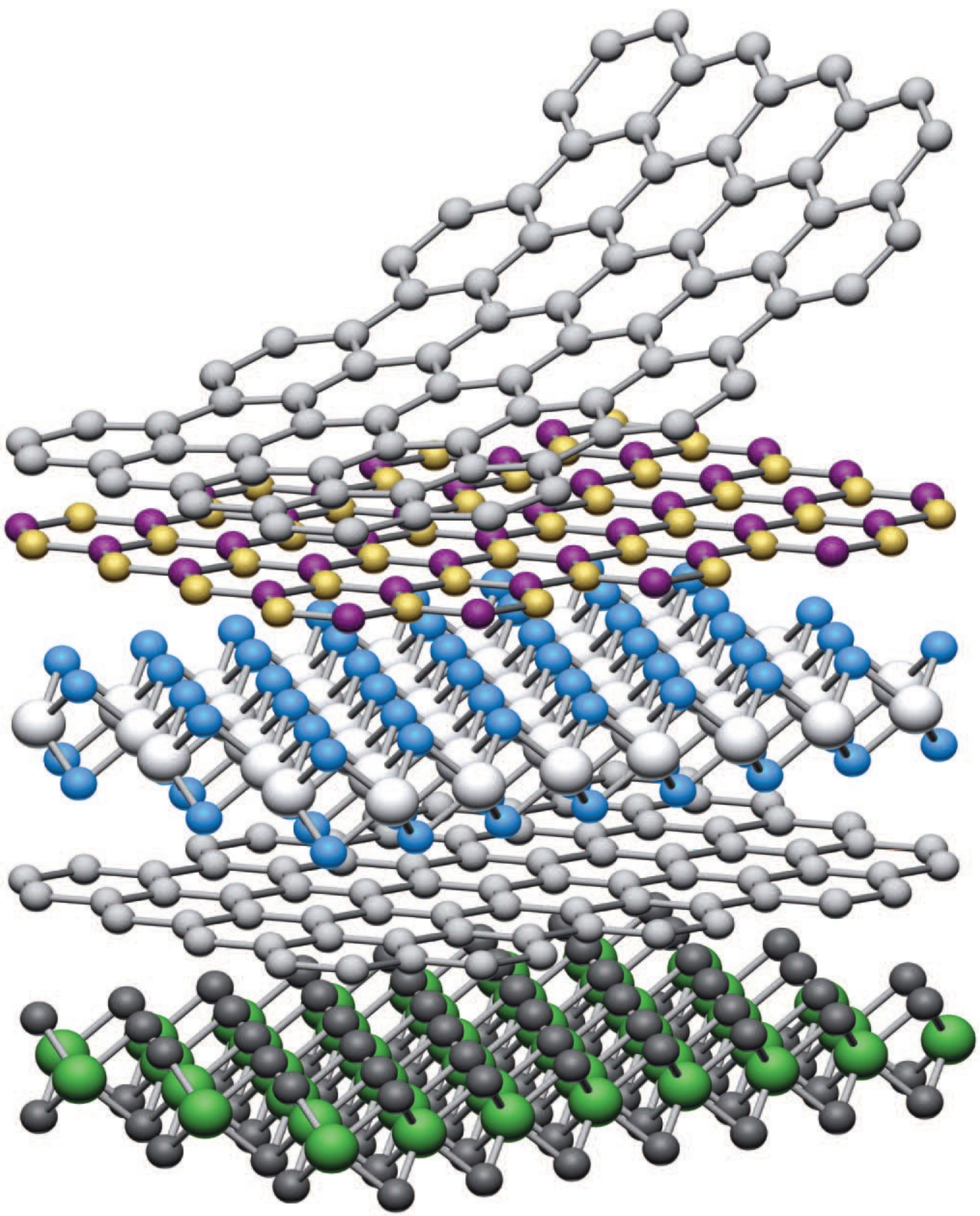
- The plasmonic thickness ξ can be dynamically tuned by:
  - Operation wavelength (or frequency).
  - Doping amount (μ_c) of graphene.
- A structure can be built with arbitrary d and then dynamically we can control the dispersion relation.



Lines indicate ξ calculated in nm.

Open Issues

Heterostructures of 2D materials



Geim *et. al.*, Nature **499**, 419–425 (2013)

A very promising field is the **heterostructures** of 2D materials

<u>...Future Goals...</u>

Find a heterostructure which...

- supports SPPs and has low losses
- supports SPPs on optical frequencies
- SPP with even shorter wavelength

Conclusion

- Surface Plasmon Polaritons (SPPs).
  - ➔ Dispersion relation and SPP wavelength.
  - ➔ SPPs provide nano-scale exploration.
- Two Dimensional Materials, Graphene.
  - ➔ Graphene supports plasmons at high frequencies.
  - ➔ Doped Graphene shows new plasmonic resonance.
  - ➔ Even smaller SPP wavelength.
- Periodic Structures composed by 2D Materials.
  - ➔ Analytical derivation of Dispersion Relation.
  - ➔ Control the kind of band (Elliptical, Hyperbolic & Linear)
  - ➔ Photonic Dirac Point & ENZ metamaterial.
  - ➔ Extreme sensitive bandgap and the role of MoS_2.

Collaborators

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- Prof. Efthimios Kaxiras, Harvard University.
- Prof. Costas Valagiannopoulos, Nazarbayev University.
- Dr. Sharmila Shirodkar, Harvard University.

Thank you…

QCN CRETE CENTER FOR QUANTUM COMPLEXITY AND NANOTECHNOLOGY

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