TDDFT for extended systems I: Plasmons

Carsten A. Ullrich
University of Missouri

Rutgers University, August 9, 2019
► classical plasma oscillations
► experimental observation of plasmons
► The homogeneous electron gas: how to calculate plasmons
► Plasmons in TDDFT
► Plasmon damping
► Nanoscale systems and plasmonics
Classical bulk motion of charge in a solid

A slab of electrons moving back and forth on top of a slab of neutralizing positive charge: plasma oscillations.
Classical bulk motion of charge in a solid

Total charge on one side: \( enA \delta \)

Uniform electric field caused by surface charge: \( E = 4\pi en \delta \)

Total force on all electrons: \( F = enVE = -4\pi n^2 e^2 V \delta \)

Set force equal to total mass times acceleration: \( F = M \ddot{\delta} \)

\[-4\pi n^2 e^2 V \delta = mnV \ddot{\delta} \quad \Rightarrow \quad \ddot{\delta} = -\frac{4\pi ne^2}{m} \delta \]

Plasma frequency: \( \omega_{pl}^2 = \frac{4\pi ne^2}{m} \)
### Table 2  Volume plasmon energies, in eV

<table>
<thead>
<tr>
<th>Material</th>
<th>Observed</th>
<th>Calculated</th>
<th>$\hbar\omega_p$</th>
<th>$\hbar\tilde{\omega}_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>7.12</td>
<td>8.02</td>
<td>7.96</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>5.71</td>
<td>5.95</td>
<td>5.58</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>3.72</td>
<td>4.29</td>
<td>3.86</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>10.6</td>
<td>10.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>15.3</td>
<td>15.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Includes ionic background*
Plasmons are quantized excitations of collective longitudinal waves of the electron gas. They are not optically excited, but by scattering with electrons or photons.
Electron loss spectra

Figure 8  Energy loss spectra for electrons reflected from films of (a) aluminum and (b) magnesium, for primary electron energies of 2020 eV. The 12 loss peaks observed in Al are made up of combinations of 10.3 and 15.3 eV losses, where the 10.3 eV loss is due to surface plasmons and the 15.3 eV loss is due to volume plasmons. The ten loss peaks observed in Mg are made up of combinations of 7.1 eV surface plasmons and 10.6 eV volume plasmons. Surface plasmons are the subject of Problem 1. (After C. J. Powell and J. B. Swan.)
Electron loss spectra

at low momentum: surface and volume plasmon

at large momentum transfer:
- double scattering
- Landau damping

A. vom Felde, J. Sprösser-Prou, and J. Fink, PRB 40, 10181 (1989)
The history of plasmons

A Collective Description of Electron Interactions: II. Collective vs Individual Particle Aspects of the Interactions

David Pines
Randal Morgan Laboratory of Physics, University of Pennsylvania, Philadelphia, Pennsylvania

AND

David Bohm*
Palmer Physical Laboratory, Princeton University, Princeton, New Jersey

(Received September 28, 1951)

Plasmons: proposed by David Pines in 1952-55

David Pines 1924-2018
Excitations in finite and extended systems

\[
\chi(\mathbf{r}, \mathbf{r}', \omega) = \lim_{\eta \to 0^+} \left[ \sum_j \frac{\langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_j \rangle \langle \Psi_j | \hat{n}(\mathbf{r}') | \Psi_0 \rangle}{\omega - E_j + E_0 + i\eta} \right] + \text{c.c.} \left( \omega \to -\omega \right)
\]

The full many-body response function has poles at the exact excitation energies.

- Discrete single-particle excitations merge into a continuum (branch cut in frequency plane)
- New types of collective excitations appear off the real axis (finite lifetimes)
The homogeneous electron gas

Kohn-Sham response function:

\[
\chi_s(r, r', \omega) = \sum_{j,k} \left( f_k - f_j \right) \frac{\phi_j(r)\phi^*_k(r')\phi^*_j(r')\phi_k(r')}{\omega - (\varepsilon_j - \varepsilon_k) + i\eta}
\]

Homogeneous electron gas:

\[
\phi_k(r) = \frac{1}{\sqrt{V}} e^{ik \cdot r}
\]

Lindhard function:

\[
\chi_s(q, \omega) = 2\int \frac{d^3k}{(2\pi)^3} \left[ \frac{\theta(k_F - k)}{\omega - k \cdot q - q^2/2 + i\eta} - \frac{\theta(k_F - k)}{\omega + k \cdot q + q^2/2 + i\eta} \right]
\]

The homogeneous electron gas

Full interacting response function from TDDFT:

\[ \chi(q, \omega) = \chi_s(q, \omega) + \chi_s(q, \omega)[v_q + f_{xc}(q, \omega)]\chi(q, \omega) \]

\[ \implies \chi(q, \omega) = \frac{\chi_s(q, \omega)}{1 - [v_q + f_{xc}(q, \omega)]\chi_s(q, \omega)} \]

What is the Fourier transform of the Coulomb interaction \( v_q \) in 3D, 2D and 1D?
The Coulomb interaction in real space is

\[ v(\mathbf{r} - \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|} \]

In q-space:

\[ v_q^{3D} = \frac{4\pi}{q^2} \quad v_q^{2D} = \frac{2\pi}{q} \]

This does not work in 1D: need regularized (“soft”) Coulomb interaction!

\[ v^{1D}(r - r') = \frac{1}{\sqrt{(r - r')^2 + \alpha^2}} \quad v_q^{1D} = 2K_0(\alpha q) \]
The homogeneous electron gas

Full interacting response function:

\[
\chi(q, \omega) = \frac{\chi_s(q, \omega)}{1 - [v_q + f_{xc}(q, \omega)]\chi_s(q, \omega)}
\]

Poles of the full response function:

Poles of the Lindhard function give the particle-hole continuum
In the ground state, all single-particle states inside the **Fermi sphere** are filled. A **particle-hole excitation** connects an occupied single-particle state inside the Fermi sphere with an empty state outside.

\[
\chi_s(q, \omega) = 2\int \frac{d^3k}{(2\pi)^3} \left[ \frac{\theta(k_F - k)}{\omega - k \cdot q - q^2/2 + i\eta} - \frac{\theta(k_F - k)}{\omega + k \cdot q + q^2/2 + i\eta} \right]
\]

Denominator vanishes for frequency range

\[
\frac{q^2}{2} - qk_F \leq \omega \leq \frac{q^2}{2} + qk_F
\]
Particle-hole continuum

Denominator vanishes for frequency range

\[
\frac{q^2}{2} - q k_F \leq \omega \leq \frac{q^2}{2} + q k_F
\]
The homogeneous electron gas

Full interacting response function:

\[
\chi(q, \omega) = \frac{\chi_s(q, \omega)}{1 - [v_q + f_{xc}(q, \omega)]\chi_s(q, \omega)}
\]

Poles of the full response function:

Vanishing denominator gives the plasmons

\[
[v_q + f_{xc}(q, \omega)]\chi_s(q, \omega) = 1
\]
Finding the plasmon dispersion

\[ [v_q + f_{xc}(q, \omega)]\chi_s(q, \omega) = 1 \]

► **Numerically solution**: for a given \( q \), find that \( \omega \) which solves this equation.

► **Analytic solution**: expand to second order in \( q \)

**Random Phase Approximation (RPA):**

\[ v_q \chi_s(q, \omega) - 1 = 0 \]

RPA dielectric function
Analytic plasmon dispersion

\[ \chi_s(q, \omega) = 2 \int \frac{d^3k}{(2\pi)^3} \left[ \frac{\theta(k_F - k)}{\omega - k \cdot q - q^2/2 + i\eta} - \frac{\theta(k_F - k)}{\omega + k \cdot q + q^2/2 + i\eta} \right] \]

\[ \chi_s(q, \omega) = \frac{1}{2\pi^2} \int_{0}^{k_F} k^2 dk \int_{0}^{\pi} \sin \theta d\theta \left[ \frac{1}{\omega - k \cdot q - q^2/2} - \frac{1}{\omega + k \cdot q + q^2/2} \right] \]

\[ = \frac{1}{\pi^2 \omega^2} \int_{0}^{k_F} k^2 dk \int_{0}^{\pi} \sin \theta d\theta [kq \cos \theta + q^2/2] + \mathcal{O}(q^4) \]

One finds

\[ \chi_s(q, \omega) = \frac{k_F^3}{3\pi^2} \frac{q^2}{\omega^2} \left[ 1 + \frac{3k_F^2 q^2}{5\omega^2} + \ldots \right] \]
Analytic plasmon dispersion

\[
\left[ \frac{4\pi}{q^2} + f_{xc}(q, \omega) \right] \chi_s(q, \omega) = 1
\]

\[
\chi_s(q, \omega) = \frac{k_F^3}{3\pi^2} \frac{q^2}{\omega^2} \left[ 1 + \frac{3k_F^2q^2}{5\omega^2} + \ldots \right]
\]

To order \(q^2\), one finds

\[
\omega(q) = \omega_{pl} \left[ 1 + \left( \frac{3k_F^2}{10\omega_{pl}^2} + \frac{1}{8\pi} f_{xc}(0, \omega_{pl}) \right)q^2 \right]
\]
Plasmon dispersion

\[ \omega = F_k \, \omega_{pl} \]

\[ k_F = 1 \]
Plasmon dispersion

\[ r_s = 4 \]

\[ \frac{\Omega}{\varepsilon_F} \]

Re \( \Omega \)

Im \( \Omega \)

K. Tatarczyk, A. Schindlmayr, and M. Scheffler, PRB 63, 235106 (2001)
Plasmons in different dimensions

Bulk plasmon:

\[ \omega(q) = \omega_p + \alpha q^2 + \ldots \]

2D plasmon:

\[ \omega(q) = \beta \sqrt{q} + \ldots \]

Intersubband plasmons:

\[ \omega(q) = (\varepsilon_2 - \varepsilon_1) \pm \Delta_{Hxc}^{c,s} + \ldots \]
Suggested exercises

1. Derive the small-q plasmon dispersions of an electron gas in 3D, 2D, and 1D

2. Obtain plasmons starting from the Casida equation in TDDFT. In other words, show that, for an electron gas,

\[
\begin{pmatrix}
A & K \\
K^* & A^*
\end{pmatrix}
\begin{pmatrix} X \\ Y \end{pmatrix} = \Omega
\begin{pmatrix} -1 & 0 \\
0 & 1
\end{pmatrix}
\begin{pmatrix} X \\ Y \end{pmatrix} \iff \left[ \frac{4\pi}{q^2} + f_{xc}^{\text{adia}}(q) \right] \chi_s(q, \omega) = 1
\]

3. Convince yourself that the Tamm-Dancoff approximation fails completely for plasmons.

4. Write a simple code to calculate the full plasmon dispersions.
Excitations in nanostructures

**Vertical** excitations: no momentum change, \( k_\parallel = 0 \)

**Nonvertical** excitations: finite momentum transfer, \( k_\parallel > 0 \)
Inter- versus intrasubband dynamics

Intersubband plasmon: perpendicular to the plane

Intrasubband plasmon (charge/spin-density wave): within the plane
Intersubband plasmon dispersions

- Charge plasmon
- Spin plasmon

40 nm GaAs/AlGaAs quantum well

\( \omega \) (meV) vs. \( k_x \) (Å\(^{-1}\))
Large Exchange Interactions in the Electron Gas of GaAs Quantum Wells

A. Pinczuk, S. Schmitt-Rink, G. Danan, J. P. Valladares, L. N. Pfeiffer, and K. W. West

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

"depolarized" spin plasmons

"polarized" charge plasmons
2D-3D crossover

ALDA/GGA: crossover from quasi-2D to 3D is fine, but from quasi-2D to strictly 2D is problematic

S. Karimi and C. A. Ullrich, PRB 90, 245304 (2014)
Plasmon damping: adiabatic xc kernel

$$\chi_s(q, \omega) = \left[ \frac{4\pi}{q^2} + f_{xc}^{adia}(q) \right]$$

**Adiabatic xc kernel:** $\omega$ is real outside the particle-hole continuum

- **Infinite plasmon lifetime**
- **Plasmon decays into individual particle-hole excitations (Landau damping)**

**How does TDDFT do this?** $f_{xc}(q, \omega)$
Intrinsic plasmon damping mechanism

- Plasmon has energy and momentum different from any single p-h pair → plasmon is robust

- But, can find two p-h pairs at right energy, and combined right total momentum → (weak) decay channel, requires Coulomb correlation beyond ALDA
The VK-functional of current-TDDFT

\[ A_{xc,1}^{VK}(r, \omega) = A_{xc,1}^{ALDA}(r, \omega) - \frac{1}{i\omega n_0(r)} \nabla \cdot \vec{\sigma}_{xc}(r, \omega) \]

xc viscoelastic stress tensor:

\[ \sigma_{xc,\mu \nu}(\omega) = \eta_{xc} \left( \nabla_\nu u_{1,\mu} + \nabla_\mu u_{1,\nu} - \frac{2}{3} \nabla \cdot u_1 \delta_{\mu \nu} \right) + \zeta_{xc} \nabla \cdot u_1 \delta_{\mu \nu} \]

\[ u(r, \omega) = j(r, \omega) / n_0(r) \quad \text{velocity field} \]

G. Vignale and W. Kohn, PRL 77, 2037 (1996)

Gives correct description of plasmon damping, but tends to overdamp as soon as the plasmon is less "hydrodynamic". Not recommended for excitations in atoms and molecules.
In general, excitations in (simple) metals very well described by ALDA. Time-dependent Hartree (=RPA) already gives the dominant contribution. $f_{xc}$ typically gives some (minor) corrections (damping!). This is also the case for 2DEGs in doped semiconductor heterostructures.
Two-plasmon excitations

Na dynamic structure factor (exp. via IXS)

Two-plasmon excitation requires $\omega$-dependent xc kernel

M. Panholzer, M. Gatti and L. Reining, PRL 120, 166402 (2018)
Plasmons in doped graphene

- Low loss, good tunability, good material properties
- Topological materials (transition metal dichalcogenides, MoS$_2$): strong spin-orbit coupling, valley effects
- TDDFT: standard xc functionals don’t work (Dirac Fermions)


Grigorenko, Polini & Novoselov, Nature Photonics 6, 749 (2012)
K. Thygesen, 2D Materials 4, 022004 (2017)
Surface plasmons (“Mie plasmon”) in metal clusters are very well reproduced within ALDA.

Plasmonics: mainly using classical electrodynamics, not quantum response, but TDDFT becoming more and more widely used.

Yabana and Bertsch, PRB 54, 4484 (1996)

Oscillation of a uniformly charged sphere against neutralizing background.

A standard result from electrostatics: conducting sphere in a uniform electric field:

Surface charge density:

\[ \sigma = \frac{3}{4\pi} E_0 \cos \theta \]
Displacing two charged spheres, we find
\[
\sigma = en d \cos \theta
\]

This surface charge is identical to what one gets in an electric field, so
\[
\sigma = \frac{3}{4\pi} E_0 \cos \theta = en d \cos \theta
\]

Total force on all electrons:
\[
F = enV E_0 = -\frac{4\pi}{3} n^2 e^2 V d
\]

Set force equal to total mass times times acceleration:
\[
F = mnV \ddot{d}
\]

\[
\ddot{d} = -\frac{4\pi n e^2}{3m} d
\]

\[
\omega_{\text{sphere}}^2 = \frac{4\pi n e^2}{3m} = \frac{\omega_p^2}{3}
\]
Rayleigh scattering: \( \lambda \gg d \)

Rayleigh scattering intensity:
\[
I \sim I_0 \frac{1 + \cos^2 \theta}{\lambda^4}
\]
(Explains why sky is blue)

Rayleigh-Gans-Debye scattering: \( \lambda \ll d \)

Mie scattering: \( \lambda \approx d \)  

Metal nanoparticles: \( \bigcirc \)

Diameter \( d \): 1 – 100 nm

Gustav Mie  
1869-1957
Absorption changes with particle size and refractive index of the medium.

Localization of optical fields: nanoplasmonics

(a) Scattering cross section of a gold nanotriangle ($55 \times 50 \times 8$ nm, $n_b = 1.34$). The panels (b) and (c) show the electric field at the resonance energy of 792 nm at the particle surface and on the outside, respectively. (Also see Fig. 3.7.)

A. Trügler, PhD thesis (2011)
Hot spots arise from the multiplication of the SP enhancement factors, constructive interference of SP fields from different particles, and additional enhancement due to sharp tips and small gaps.

M.I. Stockman, Physics Today (2011)
Nanoplasmonics with TDDFT: local E-fields

A. Varas, P. Garcia-Gonzalez, J. Feist, F.J. Garcia-Vidal & A. Rubio,
Nanophotonics 5, 409 (2016)
Summary

► TDDFT is very good for collective plasmon excitations in metallic systems (mostly small corrections to RPA)

► There is a lot of activity applying TDDFT to nanoplasmonics (beyond linear response!)

► Challenges for TDDFT:
  ● plasmon damping, multiple plasmons, satellites (nonadiabatic xc effects)
  ● collective spin modes (no RPA, purely xc, hence very sensitive to choice of functional)
  ● Plasmons in graphene and topological 2D materials
  ● Coupling of plasmons to other excitations (polaritons, plexcitons...)

E. B. Guidez and C. M. Aikens, Nanoscale 6, 11512 (2014)