Plasma Oscillations in Porous Samples

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Abstract: The influence of the shape of a sample on the type of uniform dipole collective electrons oscillations is discussed. In samples of a bulk shape uniform bulk dipole oscillations cannot exist. They exist in samples of a thin slab shape only. However in essentially porous materials the electrostatic energy of the oscillation in a sample is considerably larger, thus leading to stronger restoring force and higher frequency of the oscillation. When this frequency exceeds the Langmuir frequency, the oscillation becomes of a bulk type.

Keywords: Pores; Langmuir Oscillation; Mie Oscillation; Depolarization Factors

1. Introduction

Collective oscillations are the most prominent features of the excitation spectrum of all many particle systems, from macroscopic bodies such as metal samples, to clusters, molecules, atoms and nuclei.

Collective oscillations determine to a large extent the cross-sections of interaction of all the above-mentioned objects with electromagnetic radiation and fast charged particles. For macroscopic bodies (solids, liquids and gases) they present the density oscillations, or acoustic waves, which are known best of all. The frequency of acoustic waves, \( \omega_s \), is known to be proportional to the wave-vector, \( k \).

It has long since been known, however, that in the macroscopic body of a subsystem, formed by light charged unbound particles with infinite range Coulombic repulsive interactions, ordinary density or acoustic waves cannot exist. Instead, so-called plasma or Langmuir oscillations take place [1, 2], with a completely different relationship between the frequency, \( \omega_p \), and the wave-vector, \( k \), from that of the frequency of acoustic waves. For small \( k \) it has the following form [3]:

\[
\omega_p^2 \approx \omega_{p0}^2 + \alpha k^2,
\]

where the so-called Langmuir or plasma frequency is presented by the following relation:

\[
\omega_{p0}^2 = 4\pi^2 n/\varepsilon m.
\]

In Eqs. (1) and (2) \( \alpha \) is a constant, \( e \) and \( m \) are the value of the charge and the mass of the particle, \( n \) is the number of the particles per unit volume and \( \varepsilon \) is the dielectric constant of a conductor lattice (without the contribution of collective electrons). For metals it is usually assumed that \( \varepsilon = 1 \).

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Langmuir oscillation is the simplest mode of a bulk uniform plasma oscillation in a conductor. It influences many physical properties of a sample, e.g., optical properties. These properties are often important for ceramic sintered materials, in particular for materials for electronics.

Plasma oscillations exist, as follows from the name, in plasmas and in electron gasses or liquids of metals and semiconductors [3, 4]. In metals the corresponding frequency, $\omega_p$, weakly depends on temperature, $T$, only via the coefficient $\alpha$ and $\omega_{p0}$, for which both are functions of the charged particle density, $n$, varying with temperature due to thermal expansion only. For semiconductors $n$ can increase exponentially with temperature, $T$, thus leading to significant dependence of $\alpha$ and $\omega_{p0}$ on $T$.

Eq. (1) was derived for a thin slab of a conductor [5] and for the infinite conductive media [6]. Hence it is valid for bulk samples of arbitrary shape when the wavelength, $\lambda$, is much shorter than the size of a sample, $a$ ($1 \ll ak$). In this case the infinite media approximation is reasonable. For long enough wavelengths the frequency, $\omega_p$, according to Eq. (1) is almost constant.

It is worthwhile to emphasize that collective frequencies, presented by Eqs. (1) and (2), do not include Planck’s constant. Therefore the values of the frequencies can be understood in the frame of the classical approach (see, e.g. [6]). The quantum picture is important when we are interested in discrete quantum levels of oscillations. The oscillation frequencies are the same in quantum and classical approaches (compare results in [4] and [6]). The classical approach cannot give discrete quantum levels. However, two types of motion should be distinguished, surface and bulk oscillations. Surface oscillations are never accompanied by a variation of the electron density, while some bulk oscillations are density oscillations.

Mie demonstrated long ago that in a bulk conductive sample of spherical shape dipole oscillations of collective electrons as a whole relative to the lattice of ions do not exist [7]. Instead, surface oscillation of a frequency $\sqrt{3}$ times smaller than $\omega_{p0}$ (Mie oscillation) exists in the bulk conductive samples of a spherical shape [7]. This occurs because oscillations with frequencies smaller than $\omega_{p0}$ cannot penetrate in the bulk of a conductive sample [5]. They decay in the surface layer of a sample [5]. The uniform (with wave-vector $k = 0$) dipole oscillation of collective electrons as a whole relative to the lattice of ions exists in thin slabs of conductive materials only [5] (Fig. 1). In samples of more bulky shapes the restoring force acting on the collective electrons is not strong enough to provide a frequency equal or larger than $\omega_{p0}$ [7].

![Fig. 1](image)

**Fig. 1** Uniform dipole oscillation of collective electrons as a whole relative to the lattice of ions in a thin slab of a conductive material. The gray color shows collective electrons.

Small elongation of the sphere leads to splitting of a single Mie frequency into two, with a small difference between them [8].

The problem of uniform (with wave-vector $k = 0$) surface collective oscillation in essentially long shaped objects (nanotubes) was discussed in [9]. It was shown that the frequency of such oscillations decreases with the increase in the length of a nanotube. This frequency is inversely proportional to the square root of the length of a nanotube [9].
2. Electrostatic Energy and Oscillation in a Conductive Ellipsoid

Let us consider an electrically neutral bulk conductive ellipsoid with axes $a$, $b$ and $c$. The volume of the ellipsoid is $V = 4\pi abc/3$, the total charge of the ions is $enV$ (here $e > 0$ is the value of the electron charge, $n$ is the number of collective electrons per unit volume of a sample). The electrostatic potential inside a uniformly charged ellipsoid (with total charge $enV$) was calculated in [10]:

$$\varphi(x,y,z) = (enV/C) + \left\{3enabcV/2\pi\left[(ab)^2 + (ac)^2 + (bc)^2\right]\right\}[1 - (x/a)^2 - (y/b)^2 - (z/c)^2], \quad (3)$$

where $C$ is the electrical capacity of the metallic ellipsoid in vacuum.

One can see that Eq. (3) satisfies the Poisson equation, $\Delta \varphi = -4\pi en/\varepsilon$ and all necessary boundary conditions.

Now let us model the charge of ions by a uniformly charged ellipsoid with the charge of the opposite in respect to the collective electrons charge sign (jelly model).

Now let us calculate the electrostatic field in a sample when the ellipsoid of collective electrons is shifted along the $x$-axis by a small shift $h$ relative to the ellipsoid of ions. The electrostatic potential produced by the shifted ellipsoid of collective electrons according to Eq. (3) is

$$\varphi_e(x,y,z) = -(enV/C) + \left\{3enabcV/2\pi\left[(ab)^2 + (ac)^2 + (bc)^2\right]\right\}[1 - (x/h)^2 - (y/b)^2 - (z/c)^2]. \quad (4)$$

The total electrostatic potential is the sum of the potentials, produced by the ions and collective electrons:

$$\varphi = \varphi_i + \varphi_e = 2\pi en(bc)^2 h(h - 2x)/\pi\left[(a^2b^2 + a^2c^2 + b^2c^2)\right]. \quad (5)$$

The electrostatic field is equal to minus gradient of $\varphi$. It only has a $x$ component:

$$E_i = 4\pi enh^2c^2/\pi\left[(a^2b^2 + a^2c^2 + b^2c^2)\right]. \quad (6)$$

This field acts on each of the collective electrons with restoring force $-eE_i$. Let us assume that the displacement of some current carrier is $h = h_0\sin\omega_0 t$. Then the Newton equation for the current carrier, $m\ddot{h}/\dot{t}^2 = -eE_i$ and Eq. (6) yield:

$$\omega_0 = \omega_0 \sqrt{(a^2b^2 + a^2c^2 + b^2c^2)^{1/2}}. \quad (7)$$
According to Eq. (7) the value of $\omega_a$ is smaller than that of $\omega_{p0}$. Hence such oscillations could not penetrate into the bulk of a sample. These oscillations exist in the surface layer only (Mie oscillation).

When $a = b = c = R$ (spherical sample) Eq. (7) yields $\sqrt{3}$ times smaller value of $\omega_a$ than that of $\omega_{p0}$ (Mie frequency). When $a$ is essentially smaller than $b$ and $c$ Eq. (7) yields $\omega_a \approx \omega_{p0}$ like in the case of a thin slab. For $a$ essentially larger than $b = c$ $\omega_a \approx (b/a\sqrt{2})\omega_{p0}$, that is in this case $\omega_a$ is inversely proportional to the length of a long axis, $a$. In general Eq. (7) describes 3 frequencies of the oscillations along the axes of a sample, $\omega_a$, $\omega_b$, and $\omega_c$. They could be obtained from Eq. (7) by cycling of $a$, $b$, and $c$. It is worthwhile to mention that

$$\omega_a^2 + \omega_b^2 + \omega_c^2 = \omega_{p0}^2.$$  

For a spherical sample they are all equal, $\omega_a^2 = \omega_b^2 = \omega_c^2 = (1/3)\omega_{p0}^2$.

3. Electrostatic Energy and Dipole Oscillation in a Porous Metallic Ellipsoid

Samples containing pores or inclusions are inhomogeneous. Inhomogeneity leads to the increase in the electrostatic energy of a sample, as a rule. Larger electrostatic energy causes a greater restoring force and higher frequency of oscillations. When the frequency of the oscillation becomes equal to or larger than $\omega_{p0}$, the oscillation penetrates into the bulk of a sample. Here we shall consider the simplest model of a metallic sample to describe the mentioned phenomenon.

Fig. 3 Uniform dipole shift of collective electrons as a whole relative to the lattice of the ions in the porous ellipsoid of a conductive material. The gray color shows collective electrons.

Let us assume that as a result of the shift of collective electrons no charge arises on the surface of pores. That is, we assume that the collective electrons are glued to the pore surface. But we assume also that the cloud of collective electrons of a sample is shifted relative to the ion lattice (Fig. 3). To calculate the electrostatic energy in the model considered let us use some trick, used by the author in [11], when the electrostatic field in the interior of a fullerene molecule was calculated. Let us imagine that we fill the interior of pores with positive and negative electric charges of the same density as in the bulk of a sample, $\pm e$. This does not change the real electrostatic potential and the energy of a system. Let us assume also that the dielectric constant of the lattice is equal to 1 throughout the sample as it is usually accepted for metallic materials. Then after introducing imaginary positive and negative electric charges the problem looks exactly like that in the previous section. Let us place a charged ellipsoid of the collective electrons in the potential of a charged ellipsoid of the ions, described by Eq. (3), not exactly coaxially but shifted by a small distance $h$ along the $x$-axis (Fig. 2). Then the part of the interaction energy depending on $h$ could be calculated quite easily and it reads as follows:
Let us assume as before that \( h = h_0 \sin \omega_\theta t \). Then the time-averaged value of the interaction energy is as follows:

\[
\langle U \rangle = \frac{\pi (enbc)^2}{(ab)^2 + (ac)^2 + (bc)^2} V h_0^2. \tag{10}
\]

The time-averaged value of the kinetic energy of the oscillating really existing collective electrons is

\[
\langle K \rangle = 0.25nm(1 - f) V h_0^2. \tag{11}
\]

Here \( f \) is the volume fraction of pores in a sample of a total volume \( V \).

To calculate the frequency of the oscillation let us use the virial theorem [12]. The virial theorem states that \( 2 \langle K \rangle = q \langle U \rangle \) for the motion with potential energy described by the uniform function of coordinates of the \( q \) degree [12]. As for the linear harmonic oscillation \( q = 2 \) [see Eq. (9)], the time-averaged values of the kinetic and potential energies of the oscillations for a linear harmonic oscillator are equal, which yields

\[
\omega_k = \omega_{b_d} bc [(ac^2 + b^2 c^2 + b^2 c^2)(1 - f)]^{1/2} \tag{12}
\]

with \( \varepsilon = 1 \) in Eq. (2) for \( \omega_{b_d} \).

It should be mentioned also that like in the previous section three oscillations exist along the three axes of a sample, \( \omega_a, \omega_b \) and \( \omega_c \). Instead of Eq. (8) we have

\[
\omega_a^2 + \omega_b^2 + \omega_c^2 = \omega_{b_d}^2 / (1 - f). \tag{13}
\]

It follows from Eq. (13) that for a spherical sample \( a = b = c = R \) \( \omega_b \geq \omega_{b_d} \) at \( f \geq 2/3 \). So essentially porous samples could be penetrated by a uniform bulk dipole collective oscillation.

4. Oscillation in a Spherical Layer of Metallic Material

Let us consider a sample of a shape of a spherical layer \( R_0 \leq r \leq R \). Let us assume that the collective electrons are glued to the surface of the cavity (as in the previous section). This results in smaller displacements near the cavity surface, which leads to a smaller kinetic energy during the oscillation. Let us estimate the influence of this effect here. To estimate the kinetic energy let us assume that the displacements inside the electronic cloud, \( h \), are directed along the \( x \)-axis and (like in [11])

\[
h(r,t) = [(r - R_0)/(R - R_0)] h_0 \sin \omega t. \tag{14}
\]

At \( r = R_0 \) we have \( h = 0 \), and at \( r = R \) we have \( h = h_0 \sin \omega t \). The local velocity, \( v \), is directed along the \( x \)-axis also and,

\[
v(r,t) = \partial h(r,t)/\partial t = [(r - R_0)/(R - R_0)] \omega h_0 \cos \omega t. \tag{15}
\]

Time-averaged value of the kinetic energy is equal to the integral over the volume of the electronic cloud of half of the product of the density, \( nm \), and time-averaged value of \( v^2 \):

\[
\langle T \rangle = \pi nm \omega^2 (R^3 - R_0^3)(0.6R^2 + 0.3RR_0 + 0.1R_0^2)/(R^2 + RR_0 + R_0^2) h_0^2. \tag{16}
\]
To calculate the electrostatic energy of the shift let us use again the same trick, used by the author in [11]. Let us imagine that we fill the interior of the cavity with positive and negative electric charges of the same density, ±\(en\), as in the metallic spherical layer. This does not change the real electrostatic potential and the energy of a system. After introducing imaginary positive and negative electric charges the problem looks mainly like that in Section 2, and the part of the time-averaged interaction energy depending on \(h\) is described by Eq. (10) with \(a = b = c = R\) and \(V = 4\pi R^3/3\). This yields:

\[
\langle U \rangle = (2\pi en/3)^2 R^3 h_0^2.
\]

The time-averaged values of the kinetic and potential energies of the oscillations for a linear harmonic oscillator should be equal, according to the virial theorem (see Section 2), which yields

\[
\omega = [R^3/3(R - R_0)(0.6R^2 + 0.3RR_0 + 0.1R_0^2)]^{1/2}\omega_{p0}.
\]

At \(R_0 = 0.6R\) Eq. (18) yields \(\omega = 1.01\omega_{p0}\). Oscillations with frequencies larger than \(\omega_{p0}\) penetrate the bulk of a material.

So in a metallic sample of the shape of a spherical layer two types of uniform plasma oscillations exist: Mie surface oscillation with a frequency, \(\omega_{p0}/\sqrt{3}\) and penetrating bulk oscillation with a frequency higher than \(\omega_{p0}\). This could be used to design lasers, converting plasmons into phonons.

5. Discussion

The proposed approach allows calculation of frequencies of uniform dipole plasma oscillations in a sample of a shape of an arbitrary ellipsoid. This approach can be also used to calculate the depolarization factors of an arbitrary ellipsoid. Let us do it. Let us regard a case of \(e = 1\) (metallic sample). The total electrostatic field inside the ellipsoid, \(E_i\), is given by (see [5, 12])

\[
E_i = E_0 - E_d = E_0 - 4\pi N_d P_a,
\]

where \(E_0\) is external homogeneous electrostatic field directed along the \(x\)-axis, \(N_d\) is the corresponding depolarization factor and \(P_a\) is the density of the electric moment in a sample (it is assumed that the substance of the conductor is isotropic, hence the moment is directed along the \(x\)-axis). The density of the electric moment in a sample, \(P_a = enh\) [5]. This moment produces the depolarization electrostatic field in a sample, \(E_d = 4\pi N_d P_a = 4ehN_d h\) [5]. Comparing this value with the one, calculated above and given by Eq. (6) (for \(e = 1\)) yields

\[
N_d = b^2c^2/(a^2b^2 + a^2c^2 + b^2c^2).
\]

Two other depolarization factors can be obtained from Eq. (20) by cycling \(a, b\) and \(c\). As expected \(N_a + N_b + N_c = 1\). When \(a = b = c = R\) (spherical sample) Eq. (20) yields \(N_a = N_b = N_c = N = 1/3\). When \(a\) is essentially smaller than \(b\) and \(c\) Eq. (20) yields \(N_a = 1\), like in the case of a thin slab. For \(a\) essentially larger than \(b = c N_a \approx b^2/2a^2\), that is in this case \(N_a\) is inversely proportional to the square of the length of a long axis, \(a\).

The energy of the interaction of the ellipsoid with external homogeneous field is \(-enVE_d h\). The total energy of the system is as follows:

\[
U_i = \{2\pi enbc^2/[(ab)^2 + (ac)^2 + (bc)^2]\} Vh^2 - enVE_d h.
\]
The equilibrium value of the shift, $h_e$, corresponds to the minimum of $U$, on $h$:

$$h_e = [(a^2b^2 + a^2c^2 + b^2c^2)/b^2c^2](E_0/4\pi\varepsilon).$$  \hspace{1cm} (22)

The electrostatic field inside the ellipsoid, $E_i$, is given by Eq. (19). From $P_a = enh_e$, Eqs. (19) and (20) follows that $E_i = 0$. This proves that in our case the electrostatic field inside a metallic ellipsoid in an external field in equilibrium is zero as expected. The equilibrium value of the electric moment of the ellipsoid in an external homogeneous electrostatic field is as follows:

$$P_{ae} = enh_e = [a(a^2b^2 + a^2c^2 + b^2c^2)/3bc]E_0.$$  \hspace{1cm} (23)

This value could be measured experimentally.

The polarizability of the ellipsoid is

$$\alpha_e = P_{ae}/E_0 = [a(a^2b^2 + a^2c^2 + b^2c^2)/3bc].$$  \hspace{1cm} (24)

The presented approach allows calculation of the depolarization factors and polarizability of an arbitrary ellipsoid in the general case.

6. Conclusions

It was shown that not only thin slabs, but also essentially porous bulk samples of arbitrary shape could be penetrated by uniform bulk dipole oscillations. The physical reason for this phenomenon is a considerable increase in the electrostatic energy of the oscillation in a sample when inhomogeneities are introduced, thus leading to the increase in the restoring force and frequency of the uniform oscillation.

It was also shown that uniform plasma oscillation of a bulk type could be found in spherical metallic layers of a certain thickness. This result could be used to design lasers, converting plasmons into phonons.

7. References

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Резюме: Рассмотрено влияние формы образца на тип однородных дипольных колебаний коллективизированных электронов. В объёмных образцах однородные
объёмные дипольные колебания не могут существовать. Они существуют только в тонких пластинах. Однако в существенно пористых материалах электростатическая энергия колебаний существенно выше, что приводит к большей возвращающей силе и более высокой частоте колебаний. Когда частота колебаний превышает Лэнгмюровскую, объёмные однородные колебания становятся возможными.

Ключевые слова: Поры; колебания Лэнгмюра; колебания Ми; факторы деполяризации.

Содержание: Разматран је утицај облика узорка на тип униформних диполних колективних осцилација електрона. У блок-узорцима не могу постојати униформне групе диполне осцилације. Оне постоје у узорцима облика танке плоче. Међутим, у доминантно порозним материјалима електростатичка енергија осцилација у узорку је доста већа што доводи до јаче силе опоравка и веће фреквенције осцилација. Када је ова фреквенција већа од Лангмирове фреквенције, униформне осцилације групног типа су изводљиве.

Ключне речи: Поре, Ленгмирове осцилације, Миеве осцилације, фактори деполаризације.