Absence of surface plasma waves on hard-wall surfaces

Hai-Yao Deng

School of Physics and Astronomy, Cardiff University, 5 The Parade, Cardiff CF24 3AA, Wales, United Kingdom

It seems having been firmly established that surface plasma waves (SPWs) could exist on any metal surfaces, including those of the ideal hard-wall type frequently employed in \textit{ab initio} studies of the dielectric responses of metals. Here we show that the surface waves hosted on hard-wall surface are not SPWs. Though they possess the celebrated frequency $\omega_p/\sqrt{2}$ where $\omega_p$ is the volume plasma wave frequency, these waves are shown devoid of charges in the infinite wavelength limit. In contrast, SPWs are always associated with a finite density of charges localized on the surface. This finding corrects a historical mistake and calls for a reappraisal of innumerable work that interpret experimental data (e.g. electron energy loss spectroscopy) based on the hard-wall model and related models such as the specular reflection model.

Surface plasma waves (SPWs) are charge density waves propagating along the surface of metals\cite{1,2}. Nearly half a century ago, P. J. Feibelman claimed\cite{3} that, within the jellium model of metals, infinite-wavelength SPWs would possess a universal frequency that is insensitive to the particulars of the surface on which they are supported, amounting to $\omega_0 = \omega_p/\sqrt{2}$, where $\omega_p = \sqrt{4\pi n_0 e^2/m}$ with $e$ and $m$ being the charge and mass of an electron, respectively and $n_0$ the mean electron density of the bulk metal. So far as I am concerned, this notion has hardly been challenged\cite{4,5}. Indeed, many authors\cite{6,7} have seen wave modes with frequency $\omega_0$ in their wave equations irrespective of the underlying electron dynamics, and these modes have customarily been identified with SPWs.

The possibility of the above notion being at fault emerges from a hint in Feibelman’s own paper\cite{3}. As is clear from a statement made immediately after equation (5) in that paper, in reaching his conclusion Feibelman had relied on an ansatz assuming a constant electrostatic potential, which, however, entails the absence of charges. In other words, the mode extracted by Feibelman, though with frequency $\omega_0$, is unphysical and has nothing to do with the prototypical SPWs revealed by Ritchie in his original work\cite{8}. Actually, as is well known\cite{9}, SPWs possess a uniform layer of charges localized on the surface in the infinite wavelength limit. Another hint comes from a fact first pointed out by Forstmann and Gerhardt\cite{10} and recently revisited by the author\cite{11}, that in the hydrodynamic model, where the electrons are treated as a fluid, the usually assigned SPWs bear exactly the same feature as the waves found by Feibelman: they have frequency $\omega_0$ but carry no charges.

The chief purpose of the present work is to correct a historical mistake, that of the existence of SPWs on hard-wall surfaces. We show that the wave modes usually designated as SPWs in the infinite-barrier model\cite{12,13,14,15,16,17,18,19,20} (IBM) – which idealizes a surface as a hard wall that constitutes a node of the electronic wave functions – are also empty of charges in the infinite wavelength limit though with frequency $\omega_0$. Hence, these modes are again of the same type as those found by Feibelman and they are not SPWs. The significance of this result is multi-fold. Firstly, IBM seems to be the only analytically amenable quantum mechanical model and has been extensively used for studying surface effects in a plethora of physical and chemical processes\cite{17,18}, e.g. screening effects and image potentials\cite{21,22}, interactions of light and particles with surfaces\cite{23,24} (such as electron energy loss spectroscopy and differential reflectances), photoemission and chemical adsorption\cite{25}. Secondly, the classical limit of IBM corresponds to another popular model, viz. the so-called specular reflection model\cite{26,27}, which has also seen wide applications. Finally, the result might stimulate further research to deepen our understanding of the fundamental properties of SPWs from a fresh perspective, and help solving some of the problems encountered in the applications of SPWs\cite{28,29}.

Let us consider a metal slab of thickness $l$. The metal is treated by the jellium model. Our main interest rests with the large $l$ limit, where the two surfaces, located at $z = 0$ and $z = l$, respectively, of the slab are effectively decoupled. We shall work with units $\hbar = 1, e = 1, k_F = 1$ and $\omega_F = k_F^2/2m = 1$, where $h$ denotes the reduced Planck constant, $k_F = (3\pi^2 n_0)^{1/3}$ is the Fermi wavenumber and $\omega_F$ is the Fermi frequency (energy). With such units $\omega_p = \sqrt{8/3\pi} \approx 0.92$. In the IBM, the single-electron wave functions are given by

$$\psi_{k,j}(r,z) = \frac{e^{ikr}}{2\pi} \psi_j(z), \quad \psi_j(z) = \sqrt{\frac{2}{l}} \sin(k_2 z), \quad k = \frac{\pi j}{l}. \quad (1)$$

Here $r = (x,y)$, $k$ denotes the wave vector along the surface plane and $j$ is any positive integer. The full position vector is written as $x = (r,z)$.

Now we stimulate the system by a distribution of external charges with density $\rho(x,t)$. Polarization charges of density $\rho(x,t)$ are then induced. Due to the translational symmetry along the surfaces, we may assume without loss of generality that $\rho_{ext}(x,t) = \rho_{ext}(z)e^{i(q\cdot r-\omega t)}$, where $q$ denotes the wave vector and $\omega$ the frequency of the stimulus. In the regime of linear responses, one can then write $\rho(x,t) = \rho(z)e^{i(q\cdot r-\omega t)}$. Within the random phase approximation, $\rho(z)$ can be obtained as\cite{30,31}

$$\rho(z) = \int_0^\infty dz' S(z,z';q,\omega) V(z'), \quad (2)$$

where $S(z,z';q,\omega)$ is the linear density-density response function of a system of non-interacting electrons, and $V(z)e^{i(q\cdot r-\omega t)}$ denotes the electrostatic potential generated by all charges, i.e.

$$\left(\hat{a}^2 - q^2 \right) V(z) + 4\pi \left( \rho_{ext}(z) + \rho(z) \right) = 0,$$

or equivalently

$$V(z) = \frac{2\pi}{|q|} \int_{-\infty}^{\infty} \text{d}z' e^{i|q|z'_z} \left( \rho_{ext}(z') + \rho(z') \right). \quad (3)$$
Finally, the response function $S$ can be established by the Kubo-Greenwood formula, which gives

$$S(z, \bar{z}'; \mathbf{q}, \omega) = 2 \sum_{ij} \psi_i(z') \psi_j(z') \psi_i(z) \psi_j(z) F_q(k_i, k_j),$$

where the factor 2 accounts for spin degeneracy and

$$F_q(k_i, k_j) = \int \frac{d^2k}{4\pi^2} \frac{f(q_k + q_{k'}) - f(q_k - q_{k'})}{\omega + q_k + q_{k'} - \omega_k}.$$  \hspace{1cm} (5)

where $f(\omega)$ denotes the Fermi-Dirac function (zero temperature assumed throughout this work) $\omega_k = q^2 + k^2$, and $\bar{\omega}$ equals $\omega$ plus a positive infinitesimal imaginary part.

Equations (2) and (3) are closed and can be solved to determine the charge density responses of the system, including the behaviors of charge density waves. To this end, it proves convenient to expand $\rho(z)$ and $V(z)$ into a cosine series for $z$ lying in the slab. Since we are interested only in the large $l$ limit, it suffices to consider the external charges being outside the slab and and antisymmetric about its mid-plane $z = l/2$, in which case $\rho(z)$ and $V(z)$ are also antisymmetric about the mid-plane. Then they can be extended as

$$\left( \begin{array}{c} \rho(z) \\ V(z) \end{array} \right) = \sum_{n=0}^{\infty} \left( \begin{array}{c} \rho_n \\ V_n \end{array} \right) \cos(q_n z), \quad q_n = \frac{\pi}{l} (2n + 1),$$

for $0 \leq z \leq l$. Substituting this in Eq. (2) leads to

$$\rho_n = \sum_m S_{nm}(\mathbf{q}, \omega) V_m,$$

where the response matrix $S_{nm}$ is given by

$$S_{nm}(\mathbf{q}, \omega) = \frac{2}{\mathbf{q}^2} \int_0^l dz \int_0^l dz' \cos(q_n z) S(z, z'; \mathbf{q}, \omega) \cos(q_m z')$$

is the double cosine transform of $S$. Analogously, Eq. (3) can be converted into

$$V_n = \frac{4\pi q_n^2}{\mathbf{q}^2 + q_n^2} \left( \rho_n - 2(\sigma + \xi) \right)$$

where $\xi = \int_0^l dz \rho_{e,\omega}(z) e^{i\mathbf{q} \cdot (l-z)}$ and

$$\sigma = |\mathbf{q}| \sum_n \frac{\rho_n}{\mathbf{q}^2 + q_n^2}.$$ \hspace{1cm} (9)

One may easily show that

$$V(0) = \frac{2\pi}{|\mathbf{q}|} \left[ \sigma \left( 1 + e^{-i\mathbf{q} \cdot \mathbf{r}} \right) - \xi \left( 1 - e^{-i\mathbf{q} \cdot \mathbf{r}} \right) \right].$$ \hspace{1cm} (10)

Equations (7) - (9) form the basis for the analysis to be conducted in what follows.

A few remarks are made on some useful properties of $S$. Direct calculation shows that $S_{nm}$ can be split into a diagonal part and a non-diagonal one, i.e. $S_{nm} = \delta_{nm} D_n - A_{nm}$, where $\delta_{nm}$ denotes the Kronecker symbol and

$$D_n(\mathbf{q}, \omega) = \frac{1}{l} \sum_{j=0}^{\infty} F_q \left( q_n + \frac{\pi j}{l} \right),$$

$$A_{nm} = \frac{1}{l} \left[ F_q \left( \frac{q_m + q_n}{2} \right) - F_q \left( \frac{q_m - q_n}{2} \right) + F_q \left( \frac{q_m - q_n}{2} \right) - F_q \left( \frac{q_m + q_n}{2} \right) \right].$$ \hspace{1cm} (12)

Further, one may show that, in consistency with the fact that $S(0, z'; \mathbf{q}, \omega) \equiv 0$, $\sum_n S_{nm} \equiv 0$, or equivalently

$$D_n \equiv \sum_m A_{nm},$$ \hspace{1cm} (13)

which ensures that no charges can exist on the surface, i.e. $\rho(0) = \sum_n \rho_n \equiv 0$, a feature inherent to the IBM. In the limit $l \to \infty$, the sum in Eq. (11) becomes an integral and $D(\mathbf{Q}, \omega) := D_n(\mathbf{q}, \omega)$ determines the dielectric responses of an infinite system, where $\mathbf{Q} = (q, q)$ with $q$ renamed $q$. Actually, $e(\mathbf{Q}, \omega) = 1 - 4\pi D(\mathbf{Q}, \omega)/Q^2$ gives the dielectric function for the infinite system. For $k_\perp |\mathbf{q}| \ll \omega$, one finds that $4\pi D(\mathbf{Q}, \omega) \approx (\omega_p/\bar{\omega})^2 Q^2$, yielding the Drude formula $\epsilon \approx \epsilon_0 = 1 - \omega_p^2/\bar{\omega}^2$. Finally, we may note that $A$ scales as $l^{-1}$ whereas $D$ becomes independent of $l$ as $l$ increases.
Using Eq. (7) to eliminate $\rho_n$ from Eq. (8), we obtain
\[
\sum_n \Gamma_{nm} V_m = 8\pi (\sigma + \xi) l^{-1} \left(1 + e^{-|q|}\right),
\]
where the matrix $\Gamma$ is defined by
\[
\Gamma_{nm} = 4\pi S_{nm} - \Delta_{nm}, \quad \Delta_{nm} = (q^2 + q_n^2) \delta_{nm}.
\]
Together with the expression of $\sigma$, Eq. (9), the above equation can be solved to yield
\[
V_n = -\frac{8\xi}{\tilde{W}(q, \omega)} 2\pi \sum_m (\Gamma^{-1})_{nm},
\]
where $\Gamma^{-1}$ denotes the matrix inverse of $\Gamma$ and
\[
\tilde{W}(q, \omega) = 1 - 4l^{-1}|q| \sum_{n,m} (\Gamma^{-1})_{nm}.
\]

With $V_n$ given by Eq. (16), $\rho_n$ can then be obtained from Eq. (7) for the charge density. The expression of $\rho_n$ is the same as that of $V_n$, except that $\Gamma^{-1}$ is replaced with $\Sigma \Gamma^{-1}$.

Note that the expression of $V_n$ contains a pole where $\tilde{W} = 0$. The mode represented by this pole has been designated as the lowest energy mode in the literature. This designation seems justified as this mode does have the frequency $\omega_0 = \omega_p/\sqrt{2} \approx 0.65$ for $q \to 0$ in the semi-infinite limit $l \to \infty$. To see this, first note that in this limit $\alpha$, which scales as $l^{-1}$, gives higher order effects and is negligible in evaluating $\Gamma^{-1}$. With this approximation, $(\Gamma^{-1})_{nm} \approx \delta_{nm}/(4\pi D_n - (q^2 + q_n^2))$. Converting the sum in Eq. (17) into an integral, we find
\[
\tilde{W}(q, \omega) \approx 1 + \frac{2}{\pi} \int_0^\infty dq Q^2 e(Q, \omega).
\]

With $q \to 0$ the integral amounts to $\epsilon_0^{-1}$ and hence $\tilde{W} \approx 1 + \epsilon_0^{-1}$. Setting this equal to zero gives $1 + \epsilon_0 = 0$ and hence $\omega = \omega_p/\sqrt{2}$. We have also numerically solved the equation that $W(q, \omega) = 0$ and obtained the dispersion of the mode, which is displayed in Fig. 1(a). The dispersion is linear for small wavenumber, as is well known.

We proceed to examine the character of the mode. To this end, let us look at the self-sustained density waves in the absence of external stimuli (i.e. $\xi = 0$). Using Eq. (10), we rewrite Eq. (14) as
\[
\sum_{nm} \Gamma_{nm} V_m = 4l^{-1} |q| V(0),
\]
which is homogeneous (because $\xi = 0$) and serves as the wave equation. It admits of two types of solutions, depending on whether $V(0)$ vanishes or not. Those with $V(0) = 0$ must satisfy the secular equation $|\Gamma| = 0$ and they are extended modes, which closely resemble volume plasma waves. For the mode with $V(0) \neq 0$, for which we shall call $V_n$ by $\mathcal{V}_n$, one can invert the wave equation to get
\[
\mathcal{V}_n = 4l^{-1} |q| \sum_m (\Gamma^{-1})_{nm},
\]
which has been normalized so that $V(0) = 1$. Summing this over $n$ yields $\tilde{W}(q, \omega) = 0$, which corresponds exactly to the pole in Eq. (16). Thus, the mode represented by the pole is just the mode with $V(0) \neq 0$. Again using the approximation $(\Gamma^{-1})_{nm} \approx \delta_{nm}/(4\pi D_n - (q^2 + q_n^2))$, we get
\[
\mathcal{V}_n \approx 4l^{-1} \frac{|q|}{4\pi D_n - q^2/q_n^2}.
\]
In the limit $q \to 0$, this generally vanishes except for small $q_n$. If $q_n$ is also small, we can take $4\pi D_n \approx (\omega_p^2/\omega^2)(q^2 + q_n^2) = 2(q^2 + q_n^2)$ and then $\mathcal{V}_n \approx 4l^{-1} |q| q^2/q_n^2$. It follows that $V(z) = \sum_n \mathcal{V}_n \cos(q_n z) = \frac{\pi}{2} \int_0^\infty dq \cos(qz) |q| q^2 = 1$, where the semi-infinite limit has been taken to convert the sum into an integral.

We have thus seen that $V(z) = V(0)$ is a constant for the mode in the infinite-wavelength limit. Now we show that such a mode does not carry charges in this limit. This is self-evident from the laws of electrodynamics, but it is worth an explicit calculation. Actually, for this mode $\rho = \sum_n S_{nm} V_n = \mathcal{V}_0 S_{n0} \approx D_{00} \delta_{n0} - A_{n0}$. However, both $D_{00}$ and $A_{n0}$ vanish in the limit $l \to \infty$ and $q \to 0$ and hence $\rho_n$ also vanishes. To gain further insight, we have numerically evaluated $\rho(z)$ for this mode at various wavelengths. Typical results are shown in Fig. 2. It is interesting to observe that $\rho(z)$ well fits the following curve,
\[
\rho(z) \approx \rho_0 e^{-\nu z} \sin^2(z/\lambda).
\]

Both the decay length $\kappa^{-1} \approx 2.6$ and the period $\lambda \approx 1.1$ for the (Friedel) oscillations are controlled by the Fermi wavelength and independent of $q$, but the amplitude $\rho_0 \propto |q|$ is found to decrease almost linearly with $|q|$. Indeed, as seen in Fig. 1(b), the charges localized about one surface, measured by $\rho_{tot} = \int_0^\pi dz \rho(z) \approx \rho_0$ as $|q|$ decreases.

Now it is clear that, though it has frequency $\omega_p/\sqrt{2}$ at infinite wavelength, the mode corresponding to the pole is empty of charges. Hence, it is not a SPW, in contrast to the prevailing conventional point of view.
Our results prove that the widely accepted claim made by Feibelman is mistaken that SPWs could exist on any metal surface with a universal infinite-wavelength frequency. The mode usually designated as SPW in the IBM has been demonstrated of a disparate character than SPWs. The same situation was shown true of the mode in the hydrodynamic model equipped with hard-wall conditions. One may see that this is also so with the specular reflection model, since this model is the classical limit of the IBM.

One can not help but wondering, what are the necessary conditions for the existence of SPWs? The answer has been spelled out in Ref. Here we briefly discuss the most elementary aspects of the answer. Let us consider a semi-infinite metal for the sake of definiteness. One may divide the metal into two regions: a surface region, where the equations of electronic motion explicitly involve the presence of the termination, and a bulk region, where the equations of motion are the same as in an infinite system and surface effects only enter in the form of some parameters that are not determined by the equations of motion in this region. Not in all models are both regions existent and relevant. In the IBM, for example, only the bulk region exists as electrons are abruptly confined by a hard wall. In the hydrodynamic model, the surface region is unwittingly cut off from the bulk region by the hard-wall boundary conditions imposed artificially on the velocity field. In such models, the surface is either non-existent or irrelevant. Since they are density waves largely localized in the surface region, SPWs are absent from these models.

\[ \text{haiyao.deng@gmail.com} \]

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38. In the numerical evaluation of Eqs. and , we need to truncate the cosine series at some wavenumber such as so large that . The results presented in Figs. and were obtained for large with for numerical convergence.