The effect of the natural variation in the polarization of a near-surface layer on electromagnetic surface waves

M. I. Ryazanov

Moscow State Engineering Physics Institute, 115409 Moscow, Russia

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This paper describes how the natural variations in the polarization and dielectric constant near the surface of a material affect electromagnetic surface waves. It is shown that when this variation is taken into account, it becomes possible for bound *TE*-waves to exist at the surface between nonmagnetic media, waves that do not appear unless this effect is included. Dispersion relations for these waves are derived. © *1996 American Institute of Physics.* [S1063-7761(96)01509-0]

1. INTRODUCTION

As is well known, the polarization of a medium is proportional to the average local field $\mathbf{E}^{\mathrm{loc}}$ acting on a molecule, and not the average macroscopic field. The connection between the local field and the average macroscopic field is established from additional considerations, which take into account the properties of the medium under study.[1–7]

On the other hand, the average local field acting on a surface molecule of a material is always anisotropic, because the neighboring molecules that generate this field are located on only one side. From this it follows that the polarization of a near-surface layer differs from its value in the bulk of the material. In particular, a "natural" anisotropy will arise in the near-surface layer; this was observed experimentally in Ref. 8 as an anisotropy in the reflection of light from the (110) surface of single-crystal germanium, and was explained theoretically in Ref. 9.

The thickness of a natural surface layer with properties different from those of the rest of the material is the same order as the dimensions L of the region in which the local field is generated, i.e., it is small compared to the wavelength of the field but large compared to intermolecular distances.

Previous investigations of electromagnetic surface waves have not included this natural variation in the polarization at a surface.

It is interesting to estimate how the existence of a natural variation in the polarization of a near-surface layer influences the properties of electromagnetic surface waves.

2. LOCAL FIELD AND POLARIZATION AT THE SURFACE OF A MATERIAL

In order to compute the local field in a medium, let us investigate the microscopic field $\mathbf{E}^{mic}$ acting on a molecule of the medium located at a point $\mathbf{R}$.

This field consists of a primary field $\mathbf{E}^0$ (which has not yet interacted with any of the molecules) and a sum of all the secondary fields created by the dipole moments $\mathbf{d}(\mathbf{R}',t)$ of the remaining molecules. Therefore, we can write for the time Fourier transform of the field[10]

$$E_i^{mic}(\mathbf{R},\omega)=E_i^0(\mathbf{R},\omega)+(1/2\pi)^2\sum_{\mathbf{R}'}\int d^3pQ_{ij}(\mathbf{p})d_j(\mathbf{R}',\omega)\times\exp(i\mathbf{p}(\mathbf{R}-\mathbf{R}')),\qquad(1)$$

where the summation runs over the coordinates R' of all the remaining molecules of the material except the one under study, and we have introduced the notation

$$Q_{is}(\mathbf{p})=(p^2\delta_{is}-p_ip_s)/[p^2-(\omega/c)^2].\qquad(2)$$

Equation (1) is transformed into an integral equation for the field if we assume that $\mathbf{d}(\mathbf{R}',\omega)=\alpha(\omega)\mathbf{E}^{mic}(\mathbf{R}',\omega)$, where $\alpha(\omega)$ is the polarizability of the molecules of the material. The effective field acting on a molecule is generated by adding the fields of many molecules lying in a certain region with linear dimensions L that are large compared to the intermolecular distance $n^{-1/3}$, but small compared to the wavelength

$$n^{-1/3}\ll L\ll c/\omega.\qquad(3)$$

When this inequality is satisfied, the values of the microscopic field acting on a molecule are close to its value averaged over the positions of the other molecules. We will refer to this field as the local field $\mathbf{E}^{\mathrm{loc}}$. In order to find the local field, let us average (1) over the coordinates of all the molecules of the material except the one under study. Then the microscopic field acting on a molecule is replaced by the local field; to average the sum, it is sufficient to multiply each term by the probability of a molecule being located at a distance $\mathbf{R}''=\mathbf{R}-\mathbf{R}'$ in a volume element dV', $dW(\mathbf{R}'')=g(R'')(dV'/V)$ (where $g(R'')$ is the so-called radial distribution function), and then integrate over all $\mathbf{R}''$.

After this, the dependence on $\mathbf{R}'$ disappears from the terms of the sum, so that the summation reduces to multiplication by the number of remaining molecules of the material $N-1=N$. The radial distribution function $g(R'')$ reduces to zero for $\mathbf{R}''\gg n^{-1/3}$, because the probability of unbounded approach of two molecules in a uniform material equals zero. On the other hand, the positions of distant molecules are uncorrelated, because $g(R'')=1$ for $R''\gg n^{-1/3}$. Therefore, it is convenient to introduce the notation $f(R'')=1-g(R'')$

and $f(0)=1$, $f(R'')=0$ for $R''\gg n^{-1/3}$. Taking this into account, it is not difficult to obtain the average of (1) in the form

$$E_i^{\rm loc}(\mathbf{R},\omega)=E_i^0(\mathbf{R},\omega)+(n\alpha(\omega)/2\pi^2)\int d^3pQ_{is}(\mathbf{p})\int d^3R''[1-f(\mathbf{R}'')]E_s^{\rm loc}(\mathbf{R}-\mathbf{R}'',\omega)\exp(i\mathbf{pR}''). \qquad (4)$$

The polarization of the material is related to the local field by the expression

$$\mathbf{P}(\mathbf{R},\omega)=n\alpha(\omega)\mathbf{E}^{\rm loc}(\mathbf{R},\omega), \qquad (5)$$

which allows us to transform (4) to the form

$$P_i(\mathbf{R},\omega)=n\alpha(\omega)E^0(\mathbf{R},\omega)+(n\alpha(\omega)/2\pi^2)\int d^3pQ_{is}(\mathbf{p})\int d^3R''[1-f(\mathbf{R}'')]P_s(\mathbf{R}-\mathbf{R}'',\omega)\exp(i\mathbf{pR}''). \qquad (6)$$

It is important that the primary field $\mathbf{E}^0$ satisfy the Maxwell equations in vacuum, with the very same field sources as those entering into the Maxwell equations for the average macroscopic field in the material. This allows us to obtain a relation between the primary field $\mathbf{E}^0$, the macroscopic field $\mathbf{E}$, and the polarization of the medium $\mathbf{P}$:

$$E_i^0(\mathbf{R},\omega)=E_i(\mathbf{R},\omega)+4\pi P_i(\mathbf{R},\omega)-4\pi\int d^3R''P_j(\mathbf{R}-\mathbf{R}'',\omega)\int d^3p(2\pi)^{-3}Q_{ij}(\mathbf{p})\exp(i\mathbf{pR}''). \qquad (7)$$

Equations (6) and (7) for the field in the bulk of the material differ from those equations for the field at the surface only by the fact that in the first case the integration over $\mathbf{R}''$ is carried out over infinite volume, while in the second place we must take into account that the molecule can be located only in a region of positive Z', i.e., $Z''<Z$. Eliminating the primary field from (6) with the help of (7), we are led to the equation

$$n\alpha(\omega)E_i(\mathbf{R},\omega)=P_i(\mathbf{R},\omega)-4\pi n\alpha(\omega)P_i(\mathbf{R},\omega)+4\pi n\alpha(\omega)\int d^3R''f(R'')P_j(\mathbf{R}-\mathbf{R}'',\omega)\times(2\pi)^{-3}\int d^3pQ_{ij}(\mathbf{p})\exp(i\mathbf{pR}''). \qquad (8)$$

Effective values of the variable of integration $\mathbf{R}''$ in (8) are determined by the function $f(R'')$, which is nonzero only at distances of the same order as intermolecular distances. At these distances, when inequality (3) is fulfilled the polarization of the medium changes only slightly and we may remove it from the integral sign in (8), after which this equation becomes algebraic. In an isotropic medium, we can assume that $f(R)$ does not depend on the direction of $\mathbf{R}$, so that in an infinite medium the integration reduces to taking the integral

$$\int d^3pf(p)Q_{ij}(\mathbf{p})=\delta_{ij}\int d^3pf(p)=(2/3)\delta_{ij}.$$

After this, Eq. (8) takes the form

$$n\alpha(\omega)\mathbf{E}(\mathbf{R},\omega)=\{1-(4\pi/3)n\alpha(\omega)\}\mathbf{P}(\mathbf{R},\omega), \qquad (9)$$

which reduces to the Clausius–Mosotti equation:

$$(4\pi/3)n\alpha(\omega)=[\varepsilon(\omega)-1]/[\varepsilon(\omega)+2]. \qquad (10)$$

In a semi-infinite medium it is convenient to introduce the notation

$$M_{ij}(Z)=(2\pi)^{-3}\int d^3pQ_{ij}(\mathbf{p})\int_{Z''<Z}d^3R''f(R'')\exp(i\mathbf{pR}''), \qquad (11)$$

where the dependence on Z arises from the fact that integration over Z'' is carried out in the region $Z''<Z$. From what we said above it follows that in an infinite medium $M_{ij}(\infty)=(2/3)\delta_{ij}$. Using this value, we can transform (11) to the form $M_{ij}(Z)=(2/3)\delta_{ij}-V_{ij}(Z)$, where

$$V_{ij}(Z)=(2\pi)^{-3}\int_{Z''>Z}d^3R''f(R'')\int d^3pQ_{ij}(\mathbf{p})\exp(i\mathbf{pR}'').$$

Taking into account the latter fact, with the help of (11), (12) we can transform (8) to the form

$$n\alpha(\omega)E_i(\mathbf{R},\omega)=P_j(\mathbf{R},\omega)\{\delta_{ij}[1-(4\pi/3)n\alpha(\omega)]+4\pi n\alpha(\omega)V_{ij}(Z)\},$$

or, using (10)

$$[\varepsilon(\omega)-1]E_i(\mathbf{R},\omega)=4\pi P_j(\mathbf{R},\omega)\{\delta_{ij}+[\varepsilon(\omega)-1]V_{ij}(Z)\}. \qquad (13)$$

3. DIELECTRIC PROPERTIES OF THE NEAR-SURFACE LAYER

Because the tensor $V_{ij}(Z)$ has only one preferred direction, i.e., the normal to the surface (which coincides with the Z axis), this tensor possesses axial symmetry with respect to the Z axis, $V_{xx}(Z)=V_{yy}(Z)$, but the principal value $V_{zz}(Z)$ does not coincide with the two other values.

Since the coordinate axes coincide with the principal axes of the tensor $V_{ij}(Z)$, it is easy to express the components of the polarization from (13) in terms of the components of the average macroscopic field:

$$4\pi P_x(\mathbf{R},\omega)=E_x(\mathbf{R},\omega)[\varepsilon(\omega)-1]/\{1+[\varepsilon(\omega)-1]V_{xx}(Z)\},$$

$$4\pi P_y(\mathbf{R},\omega)=E_y(\mathbf{R},\omega)[\varepsilon(\omega)-1]/\{1+[\varepsilon(\omega)-1]V_{yy}(Z)\},$$

$$4\pi P_z(\mathbf{R},\omega)=E_z(\mathbf{R},\omega)[\varepsilon(\omega)-1]/\{1+[\varepsilon(\omega)-1]V_{zz}(Z)\}. \qquad (14)$$

When inequality (3) holds, the width of the near-surface layer is large compared to intermolecular distances, and we can describe the properties of this layer macroscopically by using a dielectric constant. It follows from (13) that the dielectric constant is a tensor that depends on the coordinate Z with principal values

$$\varepsilon_{xx}(z,\omega)=\varepsilon_{yy}(z,\omega)=\{\varepsilon(\omega)+[\varepsilon(\omega)-1]V_{xx}(z)\}/\{1+[\varepsilon(\omega)-1]V_{xx}(z)\},$$

$$\varepsilon_{zz}(z,\omega)=\{\varepsilon(\omega)+[\varepsilon(\omega)-1]V_{zz}(z)\}/\{1+[\varepsilon(\omega)-1]V_{zz}(z)\}. \tag{15}$$

Thus, the near-surface layer of material turns out to be one-dimensionally nonuniform in the direction normal to the surface, and is anisotropic. In describing the near-surface layer by using the dielectric constant (15), we have neglected quantities of order $(1/Ln^{1/3})$ and $(\omega/cn^{1/3})$, while keeping quantities of order $(L\omega/c)$.

4. THE INFLUENCE OF NATURAL ANISOTROPY OF A NEAR-SURFACE LAYER ON SURFACE WAVES

The variation in dielectric properties of a near-surface layer compared to the properties of the material in the bulk takes place within a rather thin layer whose thickness is small compared to a field wavelength. This allows us to include the properties of the near-surface layer approximately by introducing a corresponding surface current into the boundary conditions.[11] Then the description of the near-surface layer will be less precise than (15), because we have neglected corrections of order $(L\omega/c)$, which were included in (14) and (15). The coefficient of proportionality between the surface current and the field will depend on the properties of the near-surface layer, and becomes the fundamental phenomenological characteristic of the dielectric properties of this layer.

Let us discuss a plane surface $z=0$ between the material and vacuum. Let the dielectric constant of the material without including the surface layer be $\varepsilon(\omega)$. This implies that under the action of a field in the material, a bulk density of microcurrents is induced:

$$\mathbf{j}(x,y,z,\omega)=(\omega/4\pi i)\{\varepsilon(\omega)-1\}\theta(z)\mathbf{E}(x,y,z,\omega), \tag{16}$$

where $\theta(z)=1$ for $z>0$, $\theta(z)=0$ for $z<0$. Equation (16) assumes that the properties of the material do not change up to the boundary surface itself. However, the existence of a near-surface layer implies that in reality the density of microcurrents induced by the field differs from (16) by a certain quantity $\delta\mathbf{j}(\mathbf{r},\omega)$. It is obvious that this quantity reduces to zero far from the surface.

Let us introduce a surface current $\mathbf{J}(x,y,\omega)$ via the relation

$$\mathbf{J}(x,y,\omega)=\int_{-\infty}^{\infty} dz\delta\mathbf{j}(x,y,z,\omega). \tag{17}$$

The small thickness of the layer in which this current exists allows us to treat it as a surface current in the boundary conditions. From (15) it follows that the surface current can be written in the form

$$\mathbf{J}(x,y,\omega)=(\omega/4\pi i)\int_{-\infty}^{\infty} dz\{\varepsilon_{xx}(z,\omega)-\varepsilon(\omega)\}\mathbf{E}(x,y,z,\omega). \tag{18}$$

The electric field of the wave varies little over the layer thickness, so that we remove it from the integral with respect to z; after substituting (15) into (18), this relationship becomes

$$\mathbf{J}(x,y,\omega)=(\omega/4\pi i)\xi(\omega)\mathbf{E}(x,y,0,\omega), \tag{19}$$

where the quantity

$$\xi(\omega)=\int_{-\infty}^{\infty} dz\{\varepsilon_{xx}(z,\omega)-\varepsilon(\omega)\}=-[\varepsilon(\omega)-1]^2h, \tag{20}$$

$$h=\int_{-\infty}^{\infty} dz\, V_{xx}(z)/\{1+[\varepsilon(\omega)-1]V_{xx}(z)\} \tag{21}$$

may be referred to as the surface dielectric constant. In the special case where $[\varepsilon(\omega)-1]V_{zz}(z)\ll 1$, we can neglect this quantity in the denominator, after which (21) takes the form

$$h=\int_{-\infty}^{\infty} dz\, V_{xx}(z). \tag{22}$$

The field of a surface wave propagating along the surface $z=0$ that separates the material $(z>0)$ from the vacuum, is conveniently written in the form

$$\mathbf{E}\exp\{iqx-i\omega t-\Gamma z\}\quad (z>0),$$

$$\mathbf{E}^0\exp\{iqx-i\omega t+\Gamma^0 z\}\quad (z<0).$$

Substituting these fields into the Maxwell equations gives

$$\Gamma=[q^2-(\omega/c)^2\varepsilon(\omega)]^{1/2},\quad \Gamma^0=[q^2-(\omega/c)^2]^{1/2}. \tag{23}$$

Using the boundary conditions together with the Maxwell equations leads to the relations

$$\{\Gamma+\Gamma^0\varepsilon(\omega)+h[\varepsilon(\omega)-1]^2\Gamma\Gamma^0\}E_z=0, \tag{24}$$

$$\{\Gamma+\Gamma^0-h[\varepsilon(\omega)-1]^2(\omega/c)^2\}H_z=0. \tag{25}$$

From (24), (25) it follows that two types of surface waves are possible: either $E_z=0$ and we must fulfill the condition

$$\Gamma+\Gamma^0=h(\omega/c)^2[\varepsilon(\omega)-1]^2, \tag{26}$$

or $H_z=0$ and we must fulfill the condition

$$\Gamma+\Gamma^0\varepsilon(\omega)+h\Gamma\Gamma^0[\varepsilon(\omega)-1]^2=0. \tag{27}$$

Thus, without including the natural variation of the polarization of the near-surface layer, the existence of surface waves with $E_z=0$ (TE-waves) at a surface separating two nonmagnetic media is impossible, because for $h=0$ condition (26) can never be satisfied. Once this natural variation in the properties of the surface layer is included, the existence of such waves becomes possible. The dispersion equation for surface TE-waves is easily obtained from (26):

$$2q^2=(\omega/c)^2[\varepsilon+1]+h^2(\omega/c)^4[\varepsilon-1]^4+h^{-2}[\varepsilon-1]^{-2}. \tag{28}$$

If we take into account that the wavelength of the field should be large compared to the interatomic spacing $n^{-1/3}$ in macroscopic electrodynamics, then in order to use (28) the following inequality must be satisfied:

$$q \ll n^{1/3}.$$

For very small (or very large) h, inequality (28) is not satisfied. This implies that macroscopic electrodynamics becomes unsuitable to describe such waves. Therefore, a macroscopic treatment of surface TE-waves requires that the following inequality hold:

$$h \gg n^{1/3}[\varepsilon(\omega)-1]. \tag{29}$$

5. DISCUSSION

The coordinate dependence of the medium dielectric constant in the near-surface region (15) can be treated as a phenomenological characteristic of the material, to be determined by an independent experiment. It should be emphasized that in the final analysis the form of this dependence is determined by the radial distribution function $g(R)$. The Fourier transform of the radial distribution function of the medium can be measured, e.g., using x-ray diffraction. Thus, generally speaking, the form of the coordinate dependence of the medium dielectric constant in the near-surface layer can be established experimentally. The same thing can be said for the surface dielectric constant (28).

From what we have said it follows that the natural variation in the polarization of the near-surface layer of a material leads to a qualitative effect: the potential existence of a surface TE-wave at the boundary between two nonmagnetic media. Indeed, the existence of such a wave is possible only when this effect is included. The effect on a surface TM-wave turns out to be not so important, and reduces to a small correction.

The natural change in the polarization of a near-surface layer, in accordance with (21), has a strong effect when the medium has a large dielectric constant and is much weaker for those media whose dielectric constant is close to unity.

Generally speaking, the influence of the natural variation of the polarization of a near-surface layer is important in the same situations where the influence of surface nonuniformity is. From this it follows that we must always take this variation into account when discussing the effect of various surface nonuniformities on electromagnetic phenomena. If the the natural variation of the near-surface layer polarization turns out to have a stronger effect than the surface nonuniformity, then the nonuniformities might as well be neglected. This allows us to establish the minimum size of a nonuniformity that is meaningful to discuss.

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