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SURFACE MODES OF TWO SPHERES EMBEDDED INTO A THIRD MEDIUM *

John S. Nkoma **
International Centre for Theoretical Physics, Trieste, Italy.

ABSTRACT

Surface modes of two spheres embedded into a third medium are studied. We obtain a result which relates the dependence of frequency on the distance between the two spheres. The derived expression reproduces previous results in the limit where the separation between the spheres is very large. Two surface mode branches are shown to exist for each order n. We apply the theory to three cases of practical interest: *first*, two similar metallic spheres in vacuum; *secondly*, two similar metallic spheres embedded into a different metal; *thirdly*, two spherical voids embedded into a metal.

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** Permanent address: Physics Department, University of Botswana, Private Bag 0022, Gaborone, Botswana.

1 Introduction

There have been considerable interest in the properties of *surface* modes of solids and liquids over the past two decades [1,2,3]. The main interest has been in understanding the properties of surface excitations propagating along planar interfaces of semi-infinite media, thin films, bilayers, superlattices. Apart from planar surfaces and interfaces, it is also important to understand the properties of surface modes in curved surfaces such as spherical crystals [4, 5], a spherical particle coupled to a semi-infinite medium [6,7,8,9]. In this paper, we study the properties of surface modes of two spheres embedded into a third medium (hereafter to be referred to as TSEITM). Some of the earlier work on such a system include the work of Cohen *et.al* [10] on granular Ag and Au films, A.A.Lucas and coworkers [11,12], Aravind *et.al* [13] and Ruppin [14]. This study is pursued for several reasons. *First*, we obtain an expression that relates the frequency of the surface modes to distance between the two spheres, and it is shown that there are two surface modes for each order n. *Secondly*, the geometry of the TSEITM mimics several systems of practical interest, and therefore the theory has a direct bearing on practical systems. Examples of such systems are powders, composite materials in which foreign metals are embedded into a host medium, porous materials and others.
The results derived in this paper give intrinsic properties of surface modes in a TSEITM system, and experimental tools that can be used to study this geometry include Raman scattering [7, 9] and infrared absorption [15, 16].
This paper is organised as follows. In section 2, the bispherical coordinate system is applied to the TSEITM system and potentials in various regions of the geometry are obtained by solving Laplace's equation. Boundary conditions are applied at the surfaces of the two spheres and this enables us to obtain a result that relates the frequency of surface modes of a TSEITM system to the distance between the two spheres. In section 3, numerical results are presented by considering three cases. *First*, two similar metallic spheres embedded in vacuum; *secondly*, two similar metallic spheres embedded into a different metal; *thirdly*, two spherical voids embedded into a metal. Concluding remarks are made in section 4.

2 The frequency-distance relation for a TSEITM system

The TSEITM geometry is illustrated in Figure 1. A sphere of radius R with a dielectric function ϵ_1 occupies region I while the other sphere with a dielectric function ϵ_3 occupies region III, and both spheres are embedded in region II which has a dielectric function ϵ_2. In order to study the TSEITM system, bispherical coordinates (η, α, ψ) are used, and these are related to the rectangular coordinate system (x, y, z) by [17]

$$x = \frac{a \sin\alpha \cos\psi}{\cosh\eta - \cos\alpha} \tag{1}$$

$$y = \frac{a \sin\alpha \sin\psi}{\cosh\eta - \cos\alpha} \tag{2}$$

$$z = \frac{a \sinh\eta}{\cosh\eta - \cos\alpha} \tag{3}$$

where

$$a = (D^2 - R^2)^{1/2} \tag{4}$$

$$D = a \coth\eta_o \tag{5}$$

The surface modes we are considering satisfy Laplace's equation.

$$\nabla^2 \phi_i = 0 \tag{6}$$

where $i = 1, 2, 3$ for the solutions in the three regions I, II and III. The solutions are

$$\phi_1 = (\cosh\eta - \cos\alpha)^{1/2} \sum_{n=0}^{\infty} C_n^o e^{-(n+\frac{1}{2})\eta} P_n(\cos\alpha) \tag{7}$$

$$\phi_2 = (\cosh\eta - \cos\alpha)^{1/2} \sum_{n=0}^{\infty} \{A_n^o e^{-(n+\frac{1}{2})(\eta-\eta_o)} + B_n^o e^{(n+\frac{1}{2})(\eta-\eta_o)}\} P_n(\cos\alpha) \tag{8}$$

$$\phi_3 = (\cosh\eta - \cos\alpha)^{1/2} \sum_{n=0}^{\infty} D_n^o e^{(n+\frac{1}{2})\eta} P_n(\cos\alpha) \tag{9}$$

where $P_n(\cos\alpha)$ are Legendre polynomials. Applying boundary conditions in bispherical coordinates at $\eta = \eta_o$ and $\eta = -\eta_o$, we have

$$\phi_1(\eta_o) = \phi_2(\eta_o) \tag{10}$$

$$\epsilon_1 (\frac{\partial \phi_1}{\partial \eta})_{\eta_o} = \epsilon_2 (\frac{\partial \phi_2}{\partial \eta})_{\eta_o} \tag{11}$$

$$\phi_2(-\eta_o) = \phi_3(-\eta_o) \tag{12}$$

$$\epsilon_2 (\frac{\partial \phi_2}{\partial \eta})_{-\eta_o} = \epsilon_3 (\frac{\partial \phi_3}{\partial \eta})_{-\eta_o} \tag{13}$$

From equations (10) to (13) and equating coefficients of the Legendre polynomials of order n, and after some algebra, a relation giving the frequency dependence on distance D is obtained as

$$[\epsilon_2 - \epsilon_1][\epsilon_2 - \epsilon_3] e^{-2(2n+1)\eta_o} - [\epsilon_2 f(n, \eta_o) - \epsilon_1][\epsilon_2 f(n, \eta_o) - \epsilon_3] = 0 \tag{14}$$

where

$$f(n, \eta_o) = \frac{1 + (2n+1)\coth\eta_o}{1 - (2n+1)\coth\eta_o} \tag{15}$$

The main result of this paper is Equation (14), and it relates the frequencies of surface modes of a TSEITM system and the distance D and the parameter η_o given by

$$\eta_o = \coth^{-1}(\frac{1}{1 - 1/s^2})^{1/2} \tag{16}$$

and

$$s = \frac{D}{R} \tag{17}$$

When the distance between the two spheres gets very large, it can be noted that

$$\text{As } D/R \to \infty, \coth\eta_o \to 1, \eta_o \to \infty \tag{18}$$

and hence the first term in equation (14) becomes negligible, and we obtain that the second term implies, either

$$\frac{\epsilon_1}{\epsilon_2} = -(\frac{n+1}{n}) \tag{19}$$

or

$$\frac{\epsilon_3}{\epsilon_2} = -(\frac{n+1}{n}) \tag{20}$$

where we have used

$$\lim_{\eta_o \to \infty} f(n, \eta_o) = -(\frac{n+1}{n}) \tag{21}$$

Equations (19) and (20) can be recognised as the conditions for the existence of surface modes for the spheres when they are isolated (See, for example, Ruppin and Englman [4]). Thus the expression that has been obtained in equation (14) correctly reproduces expected results in the limit of large D/R, in addition to explaining the behaviour in the low separation limit as $D/R \to 1$.

The characteristics of the surface modes is very sensitive as to which of ϵ_1, ϵ_2 or ϵ_3 is frequency dependent (active medium) and which is frequency independent (inactive medium). Several possible applications of the TSEITM geometry exist, and we shall consider three cases illustrated in Figure 2 (a) to (c). In Figure 2(a), two similar metallic

spheres embedded in vacuum are illustrated, while in figure 2(b) two similar metallic spheres are embedded into a different metal, and finally in Figure 2(c) the case of a metal into which two spherical voids are embedded is considered.
The dielectric functions for active and inactive media satisfy the following:

$$\epsilon_i = \begin{cases} \epsilon_i(\omega) & \text{for active medium} \\ \epsilon_i & \text{for inactive medium} \end{cases} \tag{22}$$

where $i = 1, 2, 3$ and for metals, the dielectric function of the form

$$\epsilon_i(\omega) = 1 - \frac{\omega_{pi}^2}{\omega^2} \tag{23}$$

is used, and ω_{pi} is the plasma frequency.

3 Numerical results and discussion

In this section we present numerical results by applying the theory developed in section 2 to three cases of practical interest.

3.1 Case (a): $\epsilon_1(\omega) = \epsilon_3(\omega)$ and $\epsilon_2 = 1.0$

Consider the case illustrated in Figure 2(a) in which region I and region III are occupied by active medium with the *same* dielectric function, and region II is occupied by vacuum. Typical values for the plasma frequency of metals are used as $\omega_{p1} = \omega_{p3} = 10$ eV. Equation (14) is solved numerically and the ratio of the dielectric functions, $\epsilon_1(\omega)/\epsilon_2$, is plotted versus D/R in Figure 3. The results show that this ratio is negative, which is true within the surface modes frequency range, and there are two surface modes, with the lower mode having increasing values with increasing D/R, and being -2.25, -1.52 and -1.32 at $D/R = 3.0$, while the upper mode has decreasing frequency values reaching -1.64, -1.41 and -1.30 at $D/R = 3.0$. These results agree with the results of Ruppin [8] who stated that the ratio $\epsilon_1(\omega)/\epsilon_2$ should vary as a function of D/R, and in this paper we have explicitly given the governing relation as equation (14). The results can be accounted for since at large separations, the isolated characteristics for the spheres set in and by equations (19) and (20) $\epsilon_1(\omega)/\epsilon_2$ will have values of -2, -3/2 and -4/3 for $n = 1, 2$ and 3 respectively.
In Figure 4, the reduced frequency ω/ω_p is plotted versus D/R. Two surface modes are found for each order n, with the lower branch having values of 0.55, 0.63 and 0.66

for $n = 1, 2, 3$ respectively when $D/R = 3.0$, while the upper mode branch has the values of 0.62, 0.64 and 0.66 for the same respective values of n. These values can be explained by noting that for every order n there are two branches of surface modes, and as the separation between the spheres gets very large, the two modes tend to merge to frequencies of the isolated spheres given by $\sqrt{1/3}, \sqrt{2/5}$ and $\sqrt{3/7}$ for $n = 1, 2, 3$ respectively using the following equation, which is obtained by using (20) and (23).

$$\frac{\omega_n}{\omega_{p3}} = \sqrt{\frac{n}{n(1+\epsilon_2)+1}} \tag{24}$$

3.2 Case (b): $\epsilon_1(\omega) = \epsilon_3(\omega) \neq \epsilon_2(\omega)$

In this case, as illustrated in Figure 2(b), the two spheres have the same dielectric function and are embedded into a third medium which is also active but has a *different* dielectric function. This is a suitable model for impurity metallic spheres in a host metallic medium, and usually Maxwell-Garnett theory is applied in studying such composite systems. The results are illustrated by taking plasma frequencies as $\omega_{p1} = \omega_{p3} = 5$ eV and $\omega_{p2} = 10$ eV. In Figure 5, a graph of ω/ω_p versus D/R shows that there are two branches of surface modes for each order n. The reduced frequency values for the upper branch are 0.88, 0.84 and 0.82 for $n = 1, 2, 3$ respectively when $D/R = 3.0$, while the lower branch has values of 0.85, 0.83 and 0.82. At large D/R the two branches tend to merge to frequencies given by

$$\frac{\omega_n}{\omega_{p2}} = \sqrt{\frac{(n+1) + n(\frac{\omega_{p1}^2}{\omega_{p2}^2})}{2n+1}} \tag{25}$$

which gives 0.86, 0.83 and 0.82 for $n = 1, 2, 3$.

3.3 Case (c): $\epsilon_1 = \epsilon_3 = 1.0$ and $\epsilon_2(\omega)$ for region II

In Figure 2(c), the case when the two spheres consist of voids with inactive equal dielectric constants, and are embedded into region II which is active with a dielectric function $\epsilon_2(\omega)$. In figure 6, a graph of ω/ω_p versus D/R shows, as in the previous cases two branches of surface modes which tend to merge as D/R gets large. At $D/R = 3.0$, the lower mode has reduced frequencies of 0.78, 0.77 and 0.75 while the upper branch has values of ω/ω_p as 0.83, 0.78 and 0.76 for $n = 1, 2, 3$ respectively. These values can be accounted for by noting that the frequencies for an isolated void or bubble are given by

$$\frac{\omega_n}{\omega_{p2}} = \sqrt{\frac{(n+1)}{n(1+\epsilon_1)+1}} \tag{26}$$

where we have used (19) which gives values of reduced frequencies of $\sqrt{2/3}, \sqrt{3/5}$ and $\sqrt{4/7}$ for $n = 1, 2, 3$ respectively.

4 Conclusions

The main result of this paper is equation (14), which describes the frequency variation with distance for surface modes of two spheres embedded into a third medium. It has been shown that there are two branches of surface modes for for every order n. The orders n imply that the effect of having spherical crystals embedded in another medium is to have a range of additional frequencies which would otherwise not have been present. In section 3, the TSEITM model has been applied to three cases of practical interest: *first* , two similar metallic spheres in vacuum; *secondly*, two similar metallic sphere embedded into a different metal; *thirdly*, two spherical voids embedded into a metal.
The numerical results that have been presented in this paper show the intrinsic properties of surface modes in the TSEITM system. Suitable experimental techniques for observing these surface modes include Raman scattering [9] and absorption measurements [18, 19].

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Figure Captions

Figure 1: The geometry of a two spheres occupying regions I and III and embedded into region II. Bispherical coordinates (η, α, ψ) are used to study the system, and $\psi = \tan^{-1}(y/x)$ where the y-axis is into the page plane. All other symbols are defined in the text.

Figure 2(a): Two similar metallic spheres in vacuum.

Figure 2(b): Two similar metallic sphere embedded into a metal with a different dielectric function.

Figure 2(c): Two spherical voids embedded into a metal.

Figure 3: The ratio of dielectric functions $\epsilon_1(\omega)/\epsilon_2$ versus reduced distance D/R. Line curve, dashed curve and points curve correspond to $n = 1,2,3$.

Figure 4: Reduced frequency ω/ω_p is plotted versus D/R for two similar metallic spheres in vacuum. Line curve, dashed curve and points curve correspond to $n = 1,2,3$.

Figure 5: Reduced frequency ω/ω_p is plotted versus D/R for two similar metallic sphere embedded into a metal with a different dielectric function. Line curve, dashed curve and points curve correspond to $n = 1,2,3$.

Figure 6: Reduced frequency ω/ω_p is plotted versus D/R for two spherical voids embedded into a metal. Line curve, dashed curve and points curve correspond to $n = 1,2,3$.

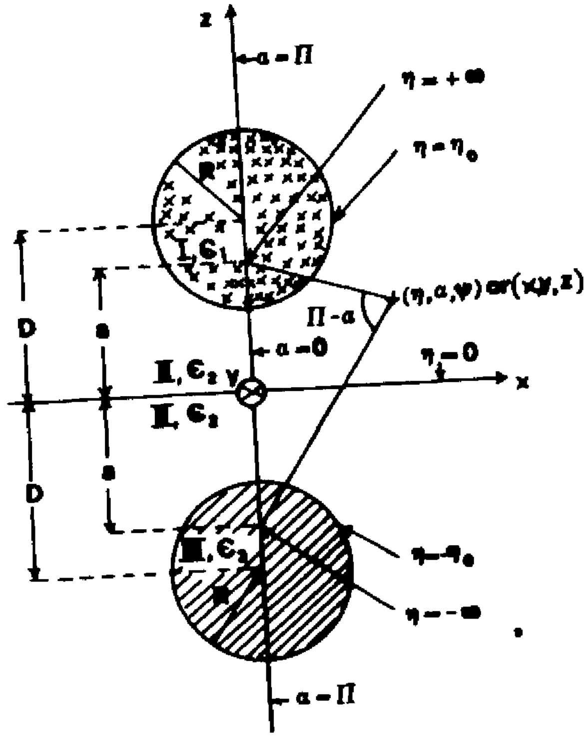


Fig.1

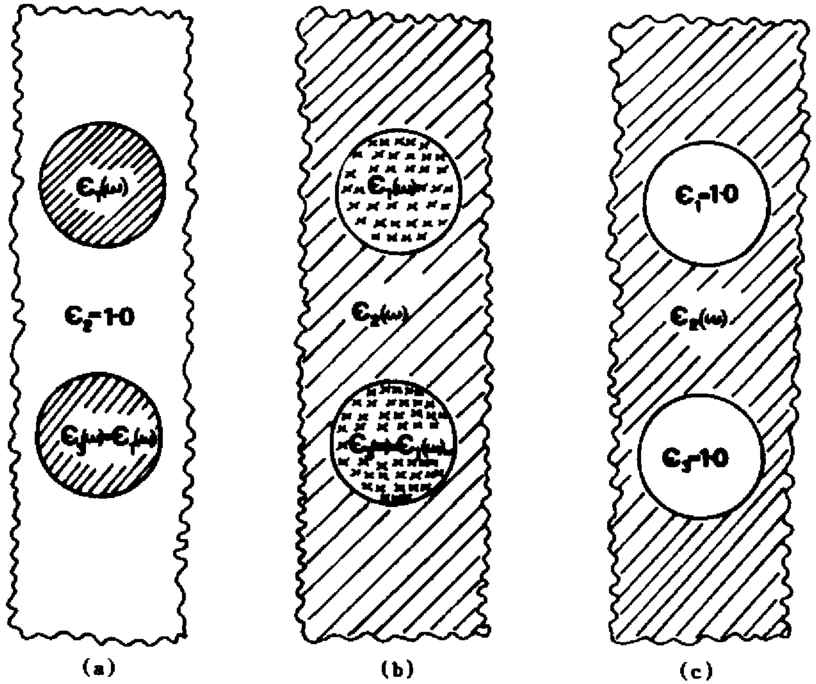

$\epsilon_1(\omega)$
$\epsilon_2=1.0$
$\epsilon_3(\omega)=\epsilon_1(\omega)$
(a)
$\epsilon_1(\omega)$
$\epsilon_2(\omega)$
$\epsilon_3(\omega)=\epsilon_1(\omega)$
(b)
$\epsilon_1=1.0$
$\epsilon_2(\omega)$
$\epsilon_3=1.0$
(c)

Fig.2

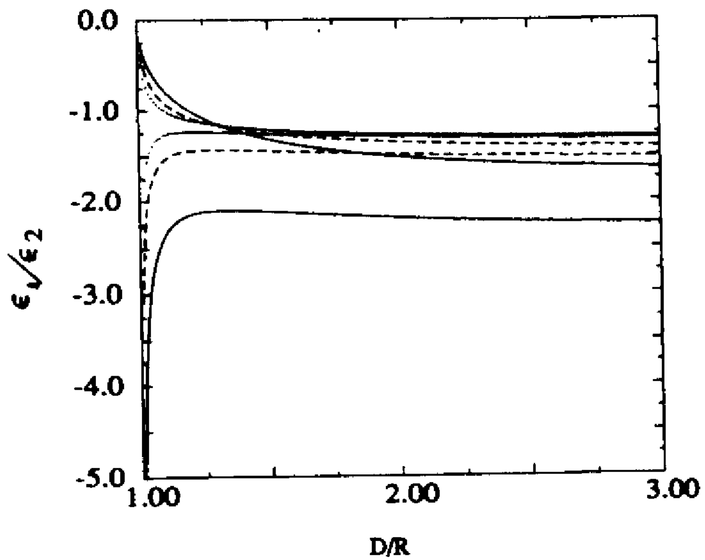
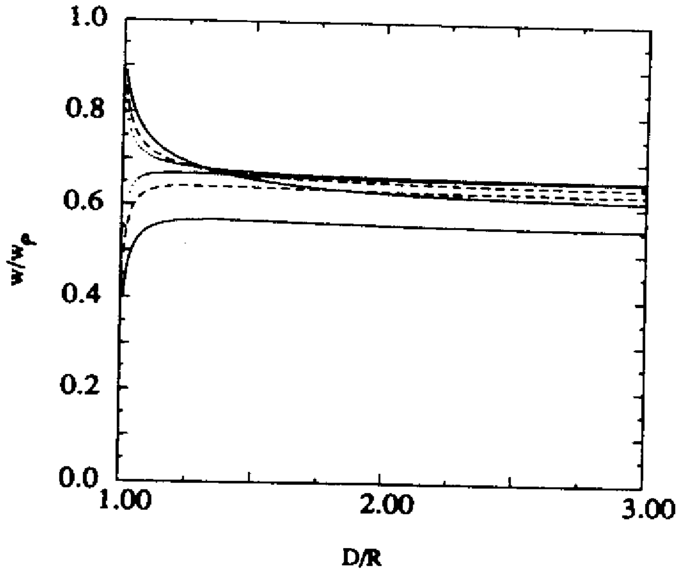

0.0
-1.0
-2.0
-3.0
-4.0
-5.0
1.00
2.00
3.00
ϵ_1/ϵ_2
D/R

Fig.3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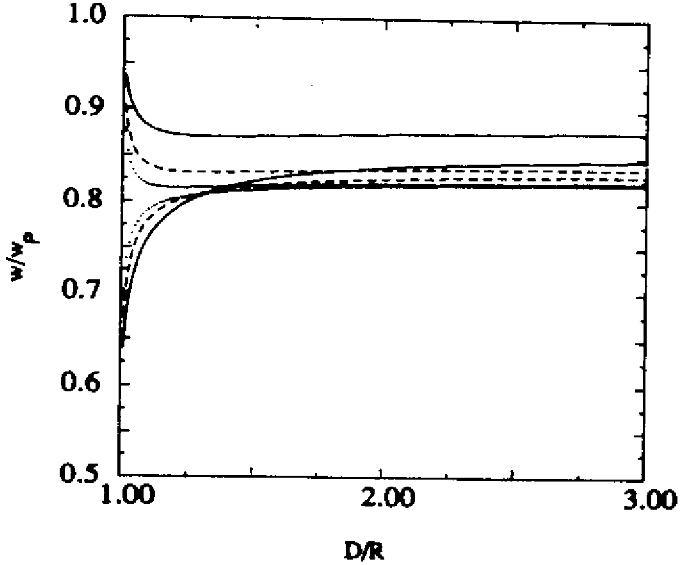
0.6
0.4
0.2
0.0
w/w_p
1.00
2.00
3.00
D/R

Fig.4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0.7
0.6
0.5
w/w_p
1.00
2.00
3.00
D/R

Fig.5

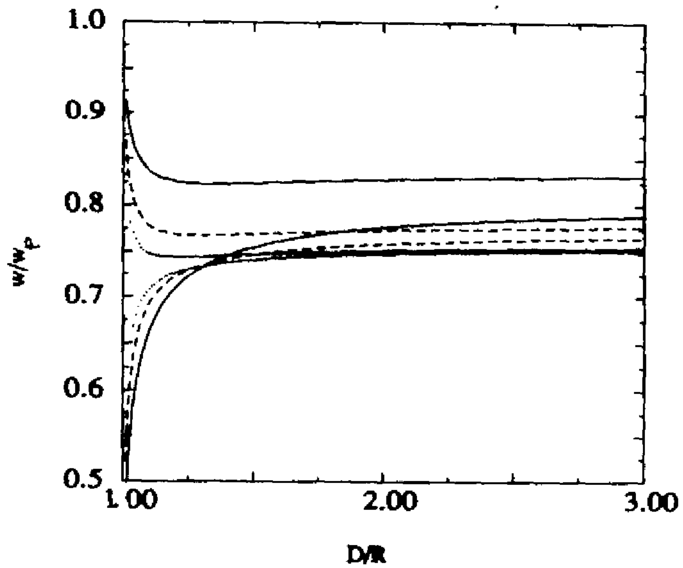

Fig.6