THEORY OF RAMAN SCATTERING BY SURFACE POLARITONS OF A COMPOSITE MEDIUM

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Abstract

The theory of Raman scattering by surface polaritons propagating along an interface of a composite medium bounded by vacuum is developed. The effective dielectric function of the composite medium is modelled using the Maxwell-Garnett formulation. We apply linear response theory to obtain response functions which are used to calculate electric field fluctuations by utilising the fluctuation dissipation theorem. The differential scattering cross section is derived. It is shown that the dispersion relation, electric field fluctuations, damping function and the differential scattering cross section are strongly dependent on the filling factor, $f$, which is a measure of the constituents of the composite medium. Our results are applied to a composite medium of KCl and Ag bounded by vacuum.

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June 1998

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I. INTRODUCTION

In recent years, there has been increasing attention towards the study of surface polaritons, and a vast quantity of both experimental and theoretical knowledge has been accumulated.\textsuperscript{1–3} Theoretical studies have considered several configurations,\textsuperscript{4–9} such as semi-infinite systems, thin films, bilayers, superlattices and curved surfaces such as spheres and cylinders. The main experimental techniques for studying surface polaritons have been attenuated total reflection\textsuperscript{10} and Raman spectroscopy.\textsuperscript{11–13} In most of these studies, attention was focused on homogeneous media, rather than inhomogeneous media such as composite systems. A theory of attenuated total reflection by surface polaritons in a composite media has been presented.\textsuperscript{14} To our knowledge, no theoretical treatment of Raman scattering by surface polaritons of a composite system has been reported, and it is the purpose of this paper to present such a formal calculation. Properties of composites differ strikingly from those of the constituent media.\textsuperscript{15}

This paper is organised as follows. In the later part of this introductory section, the scattering geometry and the model dielectric function of the system we are studying will be described. In section II, we derive the response functions, and apply the fluctuation-dissipation theorem to obtain the electric field fluctuations. The differential scattering cross section is derived in section III. Section IV is devoted to the presentation of numerical results and discussion of the main issues. Concluding remarks are made in section V.

The system we are studying is schematically represented in figure 1, where the composite medium with an effective dielectric function $\varepsilon_{\text{eff}}(\omega)$ occupies the half space $z < 0$ (to be referred to as medium 2), and a surface inactive medium with a positive dielectric constant $\varepsilon_1$ occupies the other half space $z > 0$ (to be referred to as medium 1). The composite medium is modelled as consisting of spherical grains of a dielectric function $\varepsilon_s(\omega)$ embedded in a medium with a background dielectric function $\varepsilon_b(\omega)$. According to the Maxwell-Garnett theory,\textsuperscript{16} such a system has an effective dielectric function $\varepsilon_{\text{eff}}(\omega)$ satisfying

\begin{equation}
\frac{f [\varepsilon_b(\omega) - \varepsilon_b(\omega)]}{[\varepsilon_b(\omega) + 2\varepsilon_b(\omega)]} - \frac{[\varepsilon_{\text{eff}}(\omega) - \varepsilon_b(\omega)]}{[\varepsilon_{\text{eff}}(\omega) + 2\varepsilon_b(\omega)]} = 0
\end{equation}

where $f$ is a filling factor, usually small, and such that

\begin{equation}
0 \leq f \leq 1
\end{equation}

and $f = 0$ corresponds to the case when there is only the host material and no spherical grains, while $f = 1$ corresponds to the case when the host constituent has been replaced by the grains constituent, $\varepsilon_b(\omega)$, the dielectric function of the background material, is of the form

\begin{equation}
\varepsilon_b(\omega) = \varepsilon(\omega) + \frac{S\omega_p^2}{\omega_p^2 - \omega^2 - i\omega\Gamma}
\end{equation}

where $\varepsilon(\omega)$ is the high frequency dielectric constant, $S$ gives the strength of the resonance, $\omega_p$ is the TO phonon frequency. $\varepsilon_s(\omega)$, the dielectric function of the spherical grains, is of the form

\begin{equation}
\varepsilon_s(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma}
\end{equation}

where $\omega_p$ is the plasma frequency.

From equation (1), an explicit form of the effective dielectric function $\varepsilon_{\text{eff}}(\omega)$ is obtained as

\begin{equation}
\varepsilon_{\text{eff}}(\omega) = \varepsilon_b(\omega) + \frac{3f \varepsilon_b(\omega)[\varepsilon_b(\omega) - \varepsilon_b(\omega)]}{[\varepsilon_b(\omega) + 2\varepsilon_b(\omega)] - f[\varepsilon_s(\omega) - \varepsilon_b(\omega)]}
\end{equation}

and is generally complex

\begin{equation}
\varepsilon_{\text{eff}}(\omega) = \varepsilon'_{\text{eff}}(\omega) + i\varepsilon''_{\text{eff}}(\omega)
\end{equation}
II. RESPONSE FUNCTIONS AND FLUCTUATIONS

A. Response Functions

To obtain the response functions, we calculate the response of the electric fields in the two media to an externally applied polarization \( \mathbf{P}^{\text{ext}} \) which exists only in medium 2, using linear response theory.\(^4\)

\[
\mathbf{P}^{\text{ext}} = \mathbf{P}_0^{\text{ext}} \exp \left[ i (\mathbf{Q} \cdot \mathbf{r} - \omega t) \right]
\]

\[
\nabla \nabla \nabla \mathbf{E}_1 - c_1 \frac{\omega^2}{c^2} \mathbf{E}_1 = 0
\]

\[
\nabla \nabla \nabla \mathbf{E}_2 - c_{eff}(\omega) \frac{\omega^2}{c^2} \mathbf{E}_2 = \frac{\omega^2}{c^2 \epsilon_0} \mathbf{P}_0^{\text{ext}} \exp i (\mathbf{Q} \cdot \mathbf{r})
\]

Noting that equation (8) is homogeneous while equation (9) is inhomogeneous, and applying the usual electromagnetic boundary conditions at \( z = 0 \), the solution of the electric field in medium 2 can be written in the form

\[
\mathbf{E}_2 = \sum_j R_{ij}(z) \mathbf{P}_0^{\text{ext}} \exp (i q_{z,j} z)
\]

where the coefficients \( R_{ij}(z) \) are given by

\[
R_{xx}(z) = - \frac{[Q_x^2 - \epsilon_{eff}(\omega)\omega^2/c^2]}{\epsilon_0 \epsilon_{eff}(\omega) [Q^2 - \epsilon_{eff}(\omega)\omega^2/c^2]} \left[ \exp (i Q_x z) - \exp (i q_{z,j} z) \right]
\]

\[
R_{xz}(z) = - \frac{Q_x Q_z [\exp (i Q_z z) - \exp (i q_{z,j} z)]}{\epsilon_0 \epsilon_{eff}(\omega) [Q^2 - \epsilon_{eff}(\omega)\omega^2/c^2]} \left[ 1 - \frac{Q_z}{Q_z + q_{z,j}} \right]
\]

\[
R_{zx}(z) = - \frac{Q_z Q_x \exp (i q_{z,j} z) + q_{z,j} Q_x \exp (i q_{z,j} z)}{\epsilon_0 \epsilon_{eff}(\omega) [Q^2 - \epsilon_{eff}(\omega)\omega^2/c^2]} \left[ 1 - \frac{Q_z}{Q_z + q_{z,j}} \right]
\]

\[
R_{zz}(z) = - \frac{[Q_x^2 - \epsilon_{eff}(\omega)\omega^2/c^2] \exp (i Q_z z) - (q_{z,j}^2 Q_x / Q_z) \exp (i q_{z,j} z)}{\epsilon_0 \epsilon_{eff}(\omega) [Q^2 - \epsilon_{eff}(\omega)\omega^2/c^2]} \left[ 1 - \frac{Q_z}{Q_z + q_{z,j}} \right]
\]

where \( q_{1z}, q_{2z}, Q_z \) are tangential components and \( q_{1z}, q_{2z}, Q_z \) are normal components of the wavevectors \( \mathbf{q}_1, \mathbf{q}_2, \mathbf{Q} \) respectively. We are using the notation that subscripts 1 and 2 refer to quantities in media 1 and 2 respectively, unless otherwise stated. The components of the wavevectors satisfy

\[
q_{1x}^2 + q_{1z}^2 = c_1 \frac{\omega^2}{c^2} = q_{1}^2
\]
\[ q_{2x}^2 + q_{2z}^2 = \epsilon_{eff}(\omega) \frac{\omega^2}{c^2} = q_2^2 \]  

\[ Q_{x}^2 + Q_{z}^2 = \xi^2 \]  

where the tangential components of the wavevectors are conserved

\[ q_{lx} = q_{lx} = Q_x \]  

and generally, the normal components are unequal

\[ q_{lx} \neq q_{lz} \neq Q_z \]  

It can be noted that the responses given in equations (11) to (14) consist of two contributions, with the first term corresponding to the bulk response with a term identical to that discussed by Barker and Loudon \(^\text{17}\) and Abrikosov et al.\(^\text{18}\) in the form

\[ \frac{- [Q_j Q_j - \epsilon_{eff}(\omega) \omega^2/c^2 \delta_{ij}]} {c_0 \epsilon_{eff}(\omega) [Q^2 - \epsilon_{eff}(\omega) \omega^2/c^2]} \]  

and the second term corresponds to the surface response, including the \( Q_z \) dependence.

The surface polariton wavevectors \( q_{lx} \) and \( q_{lz} \) are independent of \( Q_z \), as can be seen from equations (15) and (16). To obtain the response functions, we can, without any loss of generality, put \( Q_z = 0 \) in equations (11) to (14), and they then reduce to the following equations

\[ R_{xx}(z) = - \frac{1}{\epsilon_0 \epsilon_{eff}(\omega)} [1 - \exp(i q_{2z} z)] - \frac{q_{1z}^2 \exp(i q_{2z} z)}{D_z} \]  

\[ R_{zz}(z) = - \frac{q_{1z} q_{2z}}{D_z q_{2z}} \exp(i q_{2z} z) \]  

\[ R_{xz}(z) = - \frac{q_{2z}}{\epsilon_0 \epsilon_{eff}(\omega) q_{zz}} \exp(i q_{2z} z) + \frac{q_{1z} q_{2z}}{D_z q_{2z}} \exp(i q_{2z} z) \]  

\[ R_{zx}(z) = - \frac{q_{2z}^2}{\epsilon_0 \epsilon_{eff}(\omega) q_{zz}^2} + \frac{q_{2z}^2 q_{1z}}{D_z q_{2z}^2} \exp(i q_{2z} z) \]  

where

\[ D_z = [\epsilon_{eff}(\omega) q_{1z} - \epsilon_{1} q_{2z}] \]  

Equations (21) to (24) were discussed in Ref. 4 in the \( f = 0 \) limit, where \( \epsilon_{eff}(\omega) \to \epsilon_{B}(\omega) \). In this paper, we have obtained equations (21) to (24) as a special case of equations (11) to (14) when \( Q_z = 0 \). The main feature, however, which was mentioned earlier, is that the responses consist of two contributions, with the first term corresponding to the bulk response, and the second term with the denominator \( D_z \) corresponding to the surface response.

\[ R_{ij}(z) = R_{ij}^{Bulk}(z) + R_{ij}^{Surface}(z) \]  

and the poles of the second term, in the form of

\[ D_s = 0 \]  

generates the well-known surface polariton dispersion relation, given below

\[ \frac{c^2 q_{2z}^2}{\omega_i^2} = \frac{\epsilon_i \epsilon_{eff}(\omega)}{\epsilon_1 + \epsilon_{eff}(\omega)} \]
noting that in this case there will be several dispersion curves depending on the filling factor $f$ of the composite medium. A graph of the dispersion curves is illustrated in figure 2, and discussed in section IV.

It is also possible to express the electric fields in terms of response functions $\ll S \gg_{ij}$ and the generalized force $P_j$ as follows \(^4\)

$$E_2(0) = \sum_i \ll S \gg_{ij} P_j$$  \hspace{1cm} (29)

where

$$P_j = \frac{AP_{22j}}{-iq_{z2}}$$  \hspace{1cm} (30)

By comparison of (29) and (10) when $Q_x = 0$, the response functions are obtained as

$$\ll S \gg_{ij} = -\frac{iq_{z2}}{A} R_{ij}^{S/ar(fac)}(0)$$  \hspace{1cm} (31)

and we can put the response functions in a matrix form as

$$\ll S \gg = \begin{bmatrix} \frac{iq_{z2}^2}{AD_i} & \frac{iq_{z2}^2}{AD_i} \\ -\frac{iq_{z2}^2}{AD_i} & -\frac{iq_{z2}^2}{AD_i} \end{bmatrix}$$  \hspace{1cm} (32)

### B. Fluctuations

The electric field fluctuations in components $i$ and $j$ are obtained by using the fluctuation-dissipation theorem and are given by

$$< F_{x'} F_{y'>} >_\omega = \left( \frac{i \hbar}{2\pi} \right) [n(\omega) + 1] (\ll S \gg_{ij} + \ll S \gg_{ji})$$  \hspace{1cm} (33)

where the response functions on the right-hand side of equation (33) are the components of the matrix $\ll S \gg$ given in equation (32), and $n(\omega)$ is the Bose-Einstein factor

$$n(\omega) = \frac{1}{[\exp(\hbar\omega/k_B T) - 1]}$$  \hspace{1cm} (34)

The electric field fluctuations are obtained \(^4,10\) as

$$< |E_0(t)|^2 >_\omega = \int_{-\infty}^{\infty} d\omega < |E_0(t)|^2 >_\omega$$  \hspace{1cm} (35)

$$= \frac{\hbar}{\pi} \int_{-\infty}^{\infty} d\omega [n(\omega) + 1] \text{Im} \{\ll S \gg_{xx} + \ll S \gg_{zz}\}$$  \hspace{1cm} (36)

$$= \frac{2\epsilon_1 \hbar |q_{22}| \left[n(\omega) + \frac{1}{2}\right]}{A\epsilon_0 \left[\epsilon(\omega) \left[\epsilon_1 + \epsilon_{eff}(\omega)\right] + \epsilon_{eff}(\omega) \right] + \epsilon_{eff}(\omega)}$$  \hspace{1cm} (37)

where equation (37) has been evaluated in the limit when damping tends to zero.

In the $f = 0$ limit, equation (37) reduces to electric field fluctuations due to the background medium with a dielectric function $\epsilon_b(\omega)$, and we obtain

$$< |E_0(t)|^2 >_\omega = \frac{2\epsilon_1 \hbar |q_{22}| \left[n(\omega) + \frac{1}{2}\right] (\omega_{b1}^2 - \omega_1^2)^2}{A\epsilon_0 \left[\epsilon(\omega) \left[\epsilon_1 + \epsilon(\omega)\right] (\omega_{b1}^2 - \omega_1^2)^2 + \epsilon_1 \omega_{b1}^2\omega_2^2\right]}$$  \hspace{1cm} (38)
where $\omega_{ab}$ is given by
\[
\omega_{ab} = \left[ \frac{\epsilon_1 + \epsilon(\infty) + S}{\epsilon_1 + \epsilon(\infty)} \right]^{1/2} \omega_F
\]  
(39)

In the $f = 1$ limit, equation (37) reduces to electric field fluctuations due to the spherical grains with a dielectric function $\epsilon_s(\omega)$, and we obtain
\[
<|\varepsilon(0)|^2>_{\omega_0} = \frac{2\epsilon_1 \hbar \omega |q_2|}{A_0(1 + \epsilon_1) \left\{ (\omega^2 - \omega_s^2)^2 + \epsilon_1 \omega_s^4 \right\}^{1/2}}
\]  
(40)

where $\omega_{ss}$ is given by
\[
\omega_{ss} = \frac{\omega_0}{\sqrt{1 + \epsilon_1}}
\]  
(41)

A graph of the electric field fluctuations against frequency is plotted in figure 3, and discussed in section IV.

III. SCATTERING CROSS SECTION

In the scattering process, light of an electric field $E'_1$, frequency $\omega_1$, wavevector $k'_1$ in medium 1 is incident at the surface $z = 0$ at an angle of incidence $\theta_i$ and is transmitted into medium 2 where it becomes $E'_2$ with wavevector $k'_2$, and the components of the electric fields are related by
\[
E'_2 = f_i E'_1
\]  
(42)

describe Fresnel coefficients given by
\[
f_x = \frac{2 \epsilon_1 k'_{2x}}{\epsilon_{sff}(\omega_1)k'_{1x} + \epsilon_1 k'_{2x}}
\]  
(43)
\[
f_y = \frac{2k'_{1y}}{k'_{1x} + k'_{2x}}
\]  
(44)
\[
f_z = \frac{2\epsilon_1 k'_{1z}}{\epsilon_{sff}(\omega_1)k'_{1x} + \epsilon_1 k'_{2x}}
\]  
(45)

and the wavevectors satisfy
\[
k'_{1x} = k'_{2x} = (\epsilon_1^{1/2} \omega_1/e) \sin \theta_i
\]  
(46)
\[
k'_{1z} = -(\epsilon_1^{1/2} \omega_1/e) \cos \theta_i
\]  
(47)
\[
k'_{2x} = k'_{2x} + ik'_{2z} = -(\omega_1/e) \left[ \epsilon_{sff}(\omega_1) - \epsilon_1 \sin^2 \theta_i \right]^{1/2}
\]  
(48)

The electric field $E'_2$ in medium 2 interacts with a crystal excitation of wavevector $q'_2$ and frequency $\omega$ to produce a polarization
\[
P^s \exp \left[ i(K \cdot r - \omega_s t) \right]
\]  
(49)

where
\[
\omega_s = \omega_1 - \omega
\]  
(50)
\[
K = k'_{2x} - q'_2
\]  
(51)

The polarization in equation (49) produces scattered light of an electric field $E'_1$, frequency $\omega_s$, wavevector $k'_1$ in medium 1 at a scattering angle $\theta_s$, and electric field $E'_2$, frequency $\omega_s$, 

6
wavevector \( k_2^s \) in medium 2. The calculation of these electric fields is similar to that of solving equations (8) and (9), and a component of the scattered field in medium 1 is given as

\[
E_{1f}^s = \frac{\omega_y}{c_0 c(K_x + k_{2z}^s)} g_{jk} P_k^s \exp i(k_1^s \cdot r)
\]

where \( g_{jk} \) are matrix elements of a matrix \( g \) given by

\[
g = \begin{bmatrix}
-\frac{k_{2z}^s c/\omega_y}{c_{jff}(\omega)k_{1z}^s - c_1 k_{2z}^s} & 0 & -\frac{-K_x k_{2z}^s c/\omega_y}{c_{jff}(\omega)k_{1z}^s - c_1 k_{2z}^s} \\
0 & \frac{\nu c}{k_{1z}^s - k_{2z}^s} & 0 \\
\frac{k_{2z}^s c/\omega_y}{c_{jff}(\omega)k_{1z}^s - c_1 k_{2z}^s} & 0 & \frac{k_{2z}^s c/\omega_y}{c_{jff}(\omega)k_{1z}^s - c_1 k_{2z}^s}
\end{bmatrix}
\]

where

\[
k_{1z}^s = k_{2z}^s = K_x = (\epsilon_1^{1/2} \omega_y/c) \sin \theta_x
\]

\[
k_{2z}^s = (\epsilon_1^{1/2} \omega_y/c) \cos \theta_x
\]

\[
k_{2s}^s = k_{2z}^s + i k_{2z}^s = -i(\omega_y/c) \left[ c_{jff}(\omega) - \epsilon_1 \sin^2 \theta_x \right]^{1/2}
\]

The surface polariton wavevectors are such that the tangential components given in equation (18) are real, while the normal components are such that \( q_{1z} \) is pure imaginary and \( q_{2z} \) is complex

\[
q_{1z} = iq_{1z}''
\]

\[
q_{2z} = q_{2z}' + i q_{2z}''
\]

From equations (6), (16) and (58), equating real and imaginary parts, and solving the equations simultaneously, we obtain

\[
q_{2z}' = \frac{1}{4} \left( \frac{\left| c_{jff}(\omega) \right| \omega^2}{c^2} - q_{2z}^2 \right) + \sqrt{\left[ \frac{\left| c_{jff}(\omega) \right| \omega^2}{c^2} - q_{2z}^2 \right]^2 + \left| c_{jff}(\omega) \right|^2 \frac{\omega^4}{c^4}} \right)^{1/2}
\]

\[
q_{2z}'' = \frac{c_{jff}(\omega) \omega^2}{2 q_{2z}'' c^2}
\]

and that \( q_{2z}'' < 0, q_{2z}' < 0 \). The frequency dependence of \( q_{2z}' \) and \( q_{2z}'' \) is illustrated in figure 4 and discussed in section IV.

We now proceed to calculate the differential scattering cross section. There have been several approaches to the calculation of the light scattering cross section, \(^1-6,13\) and we follow the approach of Nkoma and Loudon \(^4\) where the differential scattering cross section is given by

\[
\frac{d^2 \sigma}{d \Omega d \omega_y} = \frac{\epsilon_1 \omega_0 A A}{4 \pi^2 c^6 \omega_y^4 |E_1|^2} \sum_{q_{2z}} \frac{\omega_y^3 \cos^2 \theta_y}{|k_{2z}^s - q_{2z} + k_{2s}^s|^2} \sum_f |g_{jk} P_k^s|^2 > \omega_y
\]

The polarisation \( P^s_k \) is a result of the coupling of the field \( E_{0i}^l \) of the incident light to the vibrational coordinates \( W_{ij}^{\nu} \) and electric field \( E_{ij}^s \) associated with the surface polaritons, and can be written in the form

\[
P^s_k = a_{kij} E_{0i}^l W_{ij}^{\nu} + b_{kij} E_{0i}^l E_{ij}
\]

where the nonlinear coefficients \( a_{kij}^l \) and \( b_{kij} \) are discussed in Ref. 17. Inserting equation (62) in (61), the differential scattering cross section becomes

\[
\frac{d^2 \sigma}{d \Omega d \omega_y} = \frac{\epsilon_1 \omega_0 A A \cos^2 \theta_y \sum_f |g_{jk} k_{2z}^s (a_{kij} W_{ij}^{\nu} + b_{kij} E_{ij})|^2 > \omega_y}{4 \pi^2 c^6 |E_1|^2 \left[ (k_{2z}^s - q_{2z} + k_{2s}^s)^2 + (k_{2z}^s - q_{2z} + k_{2s}^s)^2 \right]}
\]
Using the fluctuation-dissipation theorem in equation (63), we obtain

\[
\frac{d^2 \sigma}{d \Omega d \omega} = \frac{h e_1 \omega \omega_0^4 A A \cos^2 \theta_s [n(\omega) + 1]}{4 \pi^2 e_0^4 [\omega_0^2 (k_{2x}^n - q_{2z}^n + k_{2z}^m)^2 + (k_{2x}^m - q_{2z}^n + k_{2z}^m)^2]} \times \text{Im} \left\{ \langle \langle S \rangle \rangle_{xx} + \langle \langle S \rangle \rangle_{zz} \right\} 
\]

(64)

where

\[
|a_s| = f_{jh_1} f_i \epsilon_j^\alpha h_{h_1j} 
\]

(65)

\[
|b_s| = f_{jh_1} f_i \epsilon_j^\beta h_{h_1j} 
\]

(66)

\[
\beta = \frac{2}{\omega_0^2 - \omega^2 - i \omega \Gamma} 
\]

(67)

and \( g_{jh} \) are matrix elements of a matrix \( g \) given in equation (53), \( f_i \) are Fresnel coefficients given in equations (43) to (45), \( \epsilon_j^\alpha \) is a unit vector in the direction of incident light, \( a_{h_1j}^\alpha \) and \( b_{h_1j}^\beta \) are nonlinear coefficients defined just after equation (62), \( Z \) is an effective charge associated with the lattice vibrations.

Inserting the expressions for the response functions in equation (61), we obtain

\[
\frac{d^2 \sigma}{d \Omega d \omega} = \frac{h e_1 \omega \omega_0^4 A \cos^2 \theta_s [n(\omega) + 1]}{4 \pi^2 e_0^4 [\omega_0^2 (k_{2x}^n - q_{2z}^n + k_{2z}^m)^2 + (k_{2x}^m - q_{2z}^n + k_{2z}^m)^2]} \times \text{Im} \left\{ \frac{i q_{2z} - i q_{2z}^n q_{2z}^m q_{2z}^n / q_{2z}^m}{e_{\text{eff}}(\omega) q_{1z} - q_{1q_{2z}}} \right\}
\]

(68)

Note that part of the term in the curly brackets of equation (68) can be written in the form

\[
\frac{1}{[e_{\text{eff}}(\omega) q_{1z} - q_{1q_{2z}}]} = \frac{[e_{\text{eff}}(\omega) q_{1z} + q_{1q_{2z}}]}{[e_{\text{eff}}(\omega) - 1] \left\{ e_{\text{eff}}(\omega) \omega^2 / c^2 - q_{2z}^2 (e_{\text{eff}}(\omega) + 1) \right\}}
\]

(69)

Using equation (69), and considering small damping, the expression for the differential scattering cross section (68) becomes, after some algebra,

\[
\frac{d^2 \sigma}{d \Omega d \omega} = \frac{h e_1 \omega \omega_0^4 A \cos^2 \theta_s [n(\omega) + 1]}{4 \pi^2 e_0^4 \omega_0^2 [\omega_0^2 (k_{2x}^n - q_{2z}^n + k_{2z}^m)^2 + (k_{2x}^m - q_{2z}^n + k_{2z}^m)^2]} \times \left\{ e_{\text{eff}}(\omega) \left[ 1 + e_{\text{eff}}(\omega) \right] + e_{\text{eff}}(\omega) \omega^2 / c^2 - q_{2z}^2 (e_{\text{eff}}(\omega) + 1) \right\} \times \frac{\Gamma'(\omega_0)}{(\omega - \omega_0)^2 + [\frac{1}{2} \Gamma'(\omega_0)]^2}
\]

(70)

where \( \Gamma'(\omega_0) \) is the damping function given by

\[
\Gamma'(\omega_0) = \frac{e_1 \frac{d^2}{d \omega^2} \omega_{\text{eff}}(\omega)|_{\omega=\omega_0} \Gamma}{e_{\text{eff}}(\omega) \left[ 1 + e_{\text{eff}}(\omega) \right] + e_{\text{eff}}(\omega) \omega^2 / c^2 - q_{2z}^2 (e_{\text{eff}}(\omega) + 1)}
\]

(71)

Equation (70) is the main result of this paper, and it gives the differential scattering cross section for surface polaritons propagating along an interface of a composite medium of effective dielectric function \( e_{\text{eff}}(\omega) \) bounded by a medium of a dielectric constant \( e_1 \). This equation generalises equation (109) of Ref. 4, which was derived for phonon type surface polaritons for a medium of
a dielectric function $\epsilon_k(\omega)$. This can be seen by noting that in the $f = 0$ limit, $\epsilon_{eff}(\omega) \to \epsilon_k(\omega)$ and the following identity holds

$$\frac{1}{\left\{ \epsilon_1'(\omega_0) \left[ \epsilon_1 + \epsilon_1''(\omega) \right] + \epsilon_1 \frac{\partial \epsilon_1''(\omega)}{\partial \omega} \bigg|_{\omega = \omega_0} \right\}} = \frac{(\omega^2 - \omega_0^2)^2}{(\epsilon(\infty) [\epsilon_1 + \epsilon(\infty)] (\omega_{sh}^2 - \omega_0^2)^2 + \epsilon_1 S \omega_{sh}^2 \omega_0^2)}$$

(72)

where $\epsilon_1'(\omega)$ is of the form given in equation (3) with $\Gamma \to 0$. By using equation (72) in (70) in the limit $f = 0$, we recover equation (109) of Ref. 4.

Similarly, in the $f = 1$ limit, $\epsilon_{eff}(\omega) \to \epsilon_s(\omega)$, the following identity holds

$$\frac{1}{\left\{ \epsilon_1'(\omega_0) \left[ \epsilon_1 + \epsilon_1''(\omega_0) \right] + \epsilon_1 \frac{\partial \epsilon_1''(\omega)}{\partial \omega} \bigg|_{\omega = \omega_0} \right\}} = \frac{\omega_0^4}{(1 + \epsilon_1) \left\{ (\omega_{ss}^2 - \omega_0^2)^2 + \epsilon_1 \omega_{ss}^4 \right\}}$$

(73)

where $\epsilon_1'(\omega)$ is of the form given in equation (4) with $\Gamma' \to 0$.

In the $f = 0$ limit, equation (71) reduces to the damping function due to the background medium with a dielectric function $\epsilon_1'(\omega)$, given by

$$\Gamma_b(\omega_0) = \frac{\epsilon_1 S \omega^2 \omega_0^2 \Gamma}{\epsilon(\infty) \left[ \epsilon_1 + \epsilon(\infty) \right] (\omega_{sh}^2 - \omega_0^2)^2 + \epsilon_1 S \omega_{sh}^2 \omega_0^2}$$

(74)

where $\omega_{sh}$ is given by equation (39).

In the $f = 1$ limit, equation (71) reduces to the damping function due to the spherical grains with a dielectric function $\epsilon_s(\omega)$, given by

$$\Gamma_s(\omega_0) = \frac{\epsilon_1 \omega_0^2 \omega_{ss}^2 \Gamma}{(\omega_{ss}^2 - \omega_0^2)^2 + \epsilon_1 \omega_{ss}^4}$$

(75)

where $\omega_{ss}$ is given by equation (11).

A graph of the damping function against frequency is plotted in figure 5, and discussed in section IV. The Lorentzian lineshape in the last part of equation (70) is plotted in figure 6, and labelled as $L(\omega_0)$, and is discussed in section IV.

IV. NUMERICAL RESULTS AND DISCUSSION

In this section we present numerical results and discussion for Raman scattering by surface polaritons propagating along the boundary of a composite medium bounded by vacuum. Our model composite medium consists of silver and potassium chloride. The following parameters from the work reported in Ref. 20 are used: For KCl, $\epsilon(\infty) = 2.1, \omega_T = 141 \text{ cm}^{-1}, S = 2.13$ and for Ag, $\omega_p = 73100 \text{ cm}^{-1}$. Cummings et al. 20 were studying the bulk reflectance measurements of a Ag/KCl composite and their results are outside the frequency range for the surface polaritons considered in this paper. Where damping constants are needed, we take these as 0.005$\omega_T$ and 0.005$\omega_p$ for KCl and Ag respectively.

In figure 2, a graph of the dispersion curves for $f = 0, 0.1, 0.3, 0.5$ is illustrated, based on the dispersion equation given in equation (28), and it shows that for a composite medium, as $f$ increases, the upper limiting frequency for surface polaritons increases for a fixed tangential wavevector, while as $\epsilon_{eff}/\omega_T \to 1$ all the curves converge. For $f = 0$, the upper limiting frequency $\omega_{sh}$ for surface polaritons is given by equation (39).

In figure 3, the frequency dependence of the electric field fluctuations, given in equation (37), is illustrated for $f = 0, 0.1, 0.3, 0.5$, and it can be observed that the fluctuations converge as $\omega/\omega_T \to 1$ for all values of $f$. Also, they all show a peak at the upper limiting frequency for each value of $f$.

It is also of interest to study the frequency dependence of the real and imaginary parts of the
normal component of the surface polariton wavevector in medium 2, given in equations (59) and (60). These are plotted in figure 4 as $q_{12}^0/\omega_T$ and $q_{22}^0/\omega_T$ against $\omega/\omega_T$ for $f = 0.5$. It can be noted that $|q_{22}^0|$ is much larger than $|q_{12}^0|$ except when $\omega/\omega_T \to 1$, and that for $q_{22}^0/\omega_T$ there is a dip at the upper limiting frequency. Similar variation is observed for other values of $f$.

In figure 5, the frequency dependence of the damping function, given in equation (71), is plotted for $f = 0.01, 0.3, 0.5$, and it is noted that for all values of $f$, the function increases with increasing frequency, with $\{\Gamma(\omega_0)/\Gamma\} \to 1$ at the upper limiting frequency.

In figure 6, the frequency dependence of the Lorentzian lineshape in equation (70) is illustrated for values of $\omega_0/\omega_T = 1.1, 1.15, 1.2, 1.25$, and it has been labelled as $L(\omega_0)$.

The main result of this paper is equation (70), which is a very general form of a differential scattering cross section that can be applied to a wide range of surface crystal excitations depending on the form of the dielectric function, apart from our focus on surface polaritons of a composite medium. It contains the important factors for a light scattering cross section, such as dependence on the incident and scattered frequencies and the optical and crystal excitation wavevectors contained in the first part of the expression, dependence on electric field fluctuations contained in the middle part of the expression, and the Lorentzian lineshape contained in the last part of the expression. The frequency dependence of these different parts of the differential scattering cross section have been illustrated in figures 3, 4, 5 and 6, discussed above.

The Maxwell-Garnett effective dielectric function used in this paper is inherently asymmetric in the constituents of the composite medium. There are other formulations of modelling an effective dielectric function, for example, due to Bruggemann, where the effective dielectric function is symmetric in the materials constituting the composite medium, and satisfies

$$f \left[ \frac{\varepsilon_s(\omega) - \varepsilon_{eff}(\omega)}{\varepsilon_s(\omega) + 2\varepsilon_{eff}(\omega)} \right] + (1 - f) \left[ \frac{\varepsilon_b(\omega) - \varepsilon_{eff}(\omega)}{\varepsilon_b(\omega) + 2\varepsilon_{eff}(\omega)} \right] = 0$$

(76)

or, that due to Kirkpatrick

$$f \left[ \frac{\varepsilon_s(\omega) - \varepsilon_{eff}(\omega)}{\varepsilon_s(\omega) + (\frac{2}{3} - 1)\varepsilon_{eff}(\omega)} \right] + (1 - f) \left[ \frac{\varepsilon_b(\omega) - \varepsilon_{eff}(\omega)}{\varepsilon_b(\omega) + (\frac{2}{3} - 1)\varepsilon_{eff}(\omega)} \right] = 0$$

(77)

where $z$ is the number of nearest-neighbour bonds to a given site. Note that for a simple cubic lattice ($z = 6$), equation (77) reduces to the Bruggemann relation given in equation (76). The theory presented in this paper can easily be adapted to these other formulations of effective dielectric functions for composite media.

V. CONCLUSIONS

In this paper, we have developed the theory of Raman scattering by surface polaritons propagating along an interface of a composite medium with an effective dielectric function $\varepsilon_{eff}(\omega)$ bounded by vacuum. We have applied the method of linear response theory to obtain the response functions, which have been used to calculate electric field fluctuations by utilising the fluctuation dissipation theorem. We have derived a very general form of the differential scattering cross section for surface polaritons propagating along an interface, and this is given in equation (70). It has been shown that the dispersion relation, electric field fluctuations, damping function and the differential scattering cross section are all strongly dependent on the filling factor $f$, which is a measure of the constituents of the composite medium. Our results have been applied to a composite medium of KCl and Ag bounded by vacuum.

The Maxwell-Garnett effective dielectric function used in this paper is inherently asymmetric in the constituents of the composite medium, and it has been pointed out in section IV that this study can be extended by using other formulations of effective dielectric functions, for example, those due to Bruggemann or Kirkpatrick.
ACKNOWLEDGMENTS

I would like to acknowledge the support of SIDA and the Condensed Matter Physics Group at ICTP. This work was done within the framework of the Associateship Scheme of the Abdus Salam International Centre for Theoretical Physics, Trieste, Italy.

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Figure Captions

Figure 1: The geometry of a composite medium with an effective dielectric function $\varepsilon_{\text{eff}}(\omega)$ occupying the half space $z < 0$, and a surface inactive medium with a positive dielectric constant $\varepsilon_1$ in the other half space $z > 0$. The composite medium is modelled as consisting of spherical grains of a dielectric function $\varepsilon_s(\omega)$ embedded in a medium with a background dielectric function $\varepsilon_b(\omega)$.

Figure 2: Dispersion curves for surface polaritons propagating along an interface of a composite medium bounded by vacuum, for $f = 0$ (full curve), $f = 0.1$ (curve with longer dashes), $f = 0.3$ (curve with shorter dashes), $f = 0.5$ (curve with dots).

Figure 3: The frequency dependence of electric field fluctuations along an interface of a composite medium bounded by vacuum, for $f = 0$ (full curve), $f = 0.1$ (curve with longer dashes), $f = 0.3$ (curve with shorter dashes), $f = 0.5$ (curve with dots).

Figure 4: The frequency dependence of the real and imaginary parts of the normal component of the surface polariton wavevector in medium 2, $\text{Re} \frac{g_{zz}}{\omega_T}$ (full curve) and $\text{Im} \frac{g_{zz}}{\omega_T}$ (dashed curve) for $f = 0.5$.

Figure 5: The frequency dependence of the damping function, $\Gamma(\omega)/\Gamma$, for surface polaritons propagating along an interface of a composite medium bounded by vacuum, for $f = 0$ (full curve), $f = 0.1$ (curve with longer dashes), $f = 0.3$ (curve with shorter dashes), $f = 0.5$ (curve with dots).

Figure 6: The frequency dependence of the Lorentzian lineshape, $L(\omega_0)$, for surface polaritons propagating along an interface of a composite medium bounded by vacuum for $\omega_0/\omega_T = 1.1$ (full curve), $\omega_0/\omega_T = 1.15$ (curve with longer dashes), $\omega_0/\omega_T = 1.2$ (curve with shorter dashes), $\omega_0/\omega_T = 1.25$ (curve with dots).