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Generalized theory of Raman scattering by bulk and surface polaritons

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Abstract. We develop a generalized theory of Raman scattering by bulk and surface polaritons in semi-infinite geometry. The generalized expressions for the differential scattering cross sections for bulk and surface polaritons are derived, and found to be dependent on the incident and scattered frequencies, optical and crystal excitation wavevectors, electric field fluctuations and with Lorentzian lineshapes. We give explicit forms of the damping functions for both bulk and surface polaritons. For the case of the phonon type polaritons, our general formalism reduces to expressions reported previously, and the results are applied to GaP bounded by vacuum. Applications of the generalized formalism to other cases is discussed.

1. Introduction

Raman scattering by polaritons and other crystal excitations has been extensively studied for several years now [1–5], and a vast quantity of both experimental and theoretical knowledge has been accumulated [6–8]. Theoretically, the calculation of the Raman scattering cross section by bulk polaritons has been approached by two methods mainly, based on the linear response theory [9] and on the Green function formalism [10]. The method of linear response theory has been applied to calculate scattering cross sections by surface polaritons in semi-infinite geometry [11], thin films [12] and bilayers [13], while the Green function formalism has also been applied to study surface polaritons in the semi-infinite geometry [14] and in the thin film geometry [15].

Although expressions for the differential scattering cross sections for bulk polaritons [9, 10] and surface polaritons in the semi-infinite geometry [11, 14] have been reported, what is new in this paper is that we derive more general forms, and we show that the previous results can be derived from our general formulation. Recently, for example, the author of [2] has commented that the theoretical knowledge of Raman and Brillouin scattering in the presence of a surface needs further study. Our aim in this paper is to generalize the approach of deriving the Raman scattering cross section in the presence of a surface, and thereby further our understanding of this geometry. As we shall see in this paper, the derived expressions for the differential scattering cross sections for bulk and surface polaritons are found to be dependent on the incident and scattered frequencies, optical and crystal excitation wavevectors and electric field fluctuations and have Lorentzian lineshapes, with most of the dependence being expressed in terms of the dielectric functions of the media comprising the semi-infinite geometry. When

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we apply our results to phonon type polaritons, our general formalism recovers expressions that have been reported previously [9, 11].

This paper is organized as follows. In section 2, we derive the generalized expressions for the differential scattering cross sections for bulk and surface polaritons. Section 3 is devoted to the discussion and applications of the derived differential scattering cross sections to three cases of interest, and numerical results are presented for scattering by phonon type polaritons. Concluding remarks are made in section 4.

2. Scattering cross section

The geometry studied in this paper consists of a medium with a frequency dependent dielectric function $\epsilon(\omega)$ occupying the half space $z < 0$ (to be referred to as medium 2) and a surface inactive medium with a positive dielectric constant ϵ_1 in the other half space $z > 0$ (to be referred to as medium 1). Throughout the paper, we shall use the notation that subscripts 1 and 2 refer to quantities in media 1 and 2 respectively, unless otherwise stated. In this section, we calculate the generalized differential scattering cross sections for both bulk and surface polaritons propagating in the semi-infinite geometry.

2.1. Scattering by bulk polaritons

Using linear response theory as described in [9] and [11], the differential scattering cross section for bulk polaritons can be written in the form

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega_s} = \frac{\hbar\epsilon_1\omega_l\omega_s^3 AV\cos^2\theta_s[n(\omega)+1]|a_B\beta+b_B|^2}{4\pi^3\epsilon_0^3c^4\bar{V}[(k_{2z}^{l'}-q_{2z}'+k_{2z}^{s'})^2+(k_{2z}^{l''}-q_{2z}''+k_{2z}^{s''})^2]} \times \mathrm{Im}\left\{-\frac{1}{\epsilon(\omega)}+\frac{2}{(cq/\omega)^2-\epsilon(\omega)}\right\} \tag{1}$$

where ω_l is the frequency of the incident light, ω_s is the frequency of the scattered light, V is the scattering volume in a sample of volume $\bar{V}$, A is the area of the crystal surface through which the scattered beam emerges, θ_s is the scattering angle in medium 1, $k_{2z}^{l'}$ and $k_{2z}^{l''}$ are the real and imaginary parts of the normal component of the wavevector of the incident light in medium 2, q_{2z}' and q_{2z}'' are the real and imaginary parts of the normal component of the polariton wavevector in medium 2, $k_{2z}^{s'}$ and $k_{2z}^{s''}$ are the real and imaginary parts of the normal component of the wavevector of the scattered light in medium 2, $n(\omega)$ is the Bose–Einstein factor

$$n(\omega) = \frac{1}{[\exp(\hbar\omega/k_BT)-1]} \tag{2}$$

and

$$|a_B| = g_{fh}f_i\epsilon_i^l a_{hij}^v \tag{3}$$

$$|b_B| = g_{fh}f_i\epsilon_i^l b_{hij} \tag{4}$$

$$\beta = \frac{Z}{\omega_T^2-\omega^2-\mathrm{i}\omega\Gamma} \tag{5}$$

where g_{fh} are matrix elements of a matrix **g** given in [11], f_i are Fresnel coefficients, ϵ_i^l is a unit vector in the direction of incident light, a_{hij}^v and b_{hij} are nonlinear coefficients discussed in [9] and Z is an effective charge associated with the lattice vibrations.

In equation (1), the first term in the curly brackets is the longitudinal response function, and the second term is the transverse response function. It can be noted that the poles of the bulk response functions generate the bulk polariton dispersion relation for transverse modes, given by

$$\frac{c^2 q^2}{\omega^2} = \epsilon(\omega) \tag{6}$$

and the condition for longitudinal modes, with no dispersion

$$\epsilon(\omega) = 0. \tag{7}$$

To evaluate the imaginary part of the bulk response functions, we introduce damping by introducing a complex frequency [17, 18]

$$\omega \rightarrow \omega - \mathrm{i}\tfrac{1}{2}\Gamma(\omega) \tag{8}$$

where $\Gamma(\omega)$ is the damping function (or linewidth). We then expand the dielectric function in the complex frequency, but neglect $\Gamma^2(\omega)$ and higher order terms. Considering small damping, the scattering cross section will have a peak at a frequency ω_0, close to the undamped frequency ω defined in equation (6) for bulk polaritons, and we obtain, after some algebra, the following approximation (see appendix A)

$$\mathrm{Im}\left\{\frac{1}{c^2q^2/\omega^2 - \epsilon(\omega)}\right\} = \frac{\omega_0}{2\left\{\epsilon'(\omega_0) + \frac{\omega_0}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}\Big|_{\omega=\omega_0}\right\}} \frac{\frac{1}{2}\Gamma_b(\omega_0)}{(\omega-\omega_0)^2 + \left[\frac{1}{2}\Gamma_b(\omega_0)\right]^2} \tag{9}$$

where $\Gamma_b(\omega_0)$ is the bulk polariton damping function given by [17, 18]

$$\Gamma_b(\omega_0) = \frac{\frac{\omega_0}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}\Big|_{\omega=\omega_0}\Gamma}{\left\{\epsilon'(\omega_0) + \frac{\omega_0}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}\Big|_{\omega=\omega_0}\right\}}. \tag{10}$$

Using equation (9) in equation (1), we obtain the differential scattering cross section for bulk transverse modes as

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega_s} = \frac{\hbar\epsilon_1\omega_l\omega_s^3 A V \cos^2\theta_s[n(\omega_0)+1]}{8\pi^3\epsilon_0^3 c^4 \bar{V}[(k_{2z}^{l'} - q_{2z}' + k_{2z}^{s'})^2 + (k_{2z}^{l''} - q_{2z}'' + k_{2z}^{s''})^2]} \frac{\omega_0|a_B\beta + b_B|^2}{\left\{\epsilon'(\omega_0) + \frac{\omega_0}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}\Big|_{\omega=\omega_0}\right\}}$$
$$\times \frac{\frac{1}{2}\Gamma_b(\omega_0)}{(\omega-\omega_0)^2 + \left[\frac{1}{2}\Gamma_b(\omega_0)\right]^2}. \tag{11}$$

Equation (11) is one of the important results of this paper; let us consider it in two limits of physical interest. *First*, consider the case when the crystal is opaque to the incident radiation, in which case the imaginary parts of the optical wavevectors are much larger than the real parts. For the crystal excitation wavevectors, we take q_{2z} as real since we are considering the small damping limit. With these approximations, and replacing a summation by an integral in the steps towards the derivation of equation (1), we obtain

$$\sum_{q_{2z}} \frac{1}{|k_{2z}^l - q_{2z} + k_{2z}^s|^2} \rightarrow \frac{\bar{L}}{2\pi}\int_{-\infty}^{\infty} \frac{\mathrm{d}q_{2z}}{[(k_{2z}^{l'} - q_{2z} + k_{2z}^{s'})^2 + (k_{2z}^{l''} + k_{2z}^{s'})^2]} \tag{12}$$

$$= \frac{\bar{L}}{2(k_{2z}^{l''} + k_{2z}^{s''})}. \tag{13}$$

Using equation (13) in equation (11), and noting that

$$\bar{V} = A\bar{L} \tag{14}$$

the differential scattering cross section in equation (11) becomes

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega_s} = \frac{\hbar\epsilon_1\omega_l\omega_s^3 V\cos^2\theta_s[n(\omega_0)+1]}{16\pi^3\epsilon_0^3 c^4(k_{2z}^{l''}+k_{2z}^{s''})}\frac{\omega_0|a_B\beta+b_B|^2}{\left\{\epsilon'(\omega_0)+\frac{\omega_0}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}\Big|_{\omega=\omega_0}\right\}} \times\frac{\frac{1}{2}\Gamma_b(\omega_0)}{(\omega-\omega_0)^2+\left[\frac{1}{2}\Gamma_b(\omega_0)\right]^2} \quad (15)$$

and thus the differential scattering cross section in equation (15) is proportional to the scattering volume V, and not the sample volume $\bar{V}$ which cancels out. The dependence where the differential cross section is inversely proportional to the sum of the optical wavevectors has been observed by several authors [19–23].

Secondly, consider the case when the crystal is transparent to the incident radiation, in which case $q_{2z}, k_{2z}^l, k_{2z}^s$ are real, and again, replacing a summation by an integral in the steps towards the derivation of equation (1), and taking appropriate limits, we obtain

$$\sum_{q_{2z}}\frac{1}{|k_{2z}^l-q_{2z}+k_{2z}^s|^2}\to\lim_{k_{2z}^{l''},k_{2z}^{s''}\to 0}\frac{\bar{L}}{2\pi}\int_{-\infty}^{\infty}\frac{\mathrm{d}q_{2z}}{[(k_{2z}^{l'}-q_{2z}+k_{2z}^{s'})^2+(k_{2z}^{l''}+k_{2z}^{s''})^2]} \quad (16)$$

$$= 2\pi\bar{L}\delta(k_{2z}^{l'}-q_{2z}+k_{2z}^{s'}) \quad (17)$$

and the diferential scattering cross section in equation (11) becomes

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega_s} = \frac{\hbar\epsilon_1\omega_l\omega_s^3 V\cos^2\theta_s[n(\omega_0)+1]}{4\pi^2\epsilon_0^3 c^4}\frac{\omega_0|a_B\beta+b_B|^2}{\left\{\epsilon'(\omega_0)+\frac{\omega_0}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}\Big|_{\omega=\omega_0}\right\}} \times\frac{\frac{1}{2}\Gamma_b(\omega_0)}{(\omega-\omega_0)^2+\left[\frac{1}{2}\Gamma_b(\omega_0)\right]^2}. \quad (18)$$

One of our objectives in this paper has been met by having obtained equation (11) and its limiting expressions given in equations (15) and (18), since these equations give the differential scattering cross section for bulk polaritons propagating in a semi-infinite medium of a frequency dependent dielectric function $\epsilon(\omega)$, bounded by another medium with a positive dielectric constant ϵ_1.

2.2. *Scattering by surface polaritons*

The method of linear response theory was used to study Raman scattering by surface phonon–polaritons by Nkoma and Loudon [11], and, following their approach, the differential scattering cross section for surface polaritons can be written in the form

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega_s} = \frac{\hbar\epsilon_1\omega_l\omega_s^3 A\bar{A}\cos^2\theta_s[n(\omega)+1]|a_S\beta+b_S|^2}{4\pi^3\epsilon_0^2 c^4[(k_{2z}^{l'}-q'_{2z}+k_{2z}^{s'})^2+(k_{2z}^{l''}-q''_{2z}+k_{2z}^{s''})^2]}\,\mathrm{Im}\,\{\langle\langle S\rangle\rangle_{xx}+\langle\langle S\rangle\rangle_{zz}\} \quad (19)$$

where A is the area of the crystal surface through which the scattered beam emerges (or scattering area), $\bar{A}$ is the surface area of the sample, a_S, b_S and β have similar definitions as those given in equations (3) to (5). The terms in the curly brackets of equation (19) are elements of the matrix $\langle\langle S\rangle\rangle$, given in equation (20) below, for the surface response functions.

$$\langle\langle S\rangle\rangle = \begin{bmatrix} \dfrac{\mathrm{i}q_{2z}^* q_{1z}}{\bar{A}[\epsilon(\omega)q_{1z}-\epsilon_1 q_{2z}]} & \dfrac{\mathrm{i}q_{2z}^* q_{2x} q_{1z}}{\bar{A}[\epsilon(\omega)q_{1z}-\epsilon_1 q_{2z}]q_{2z}} \\ \dfrac{-\mathrm{i}q_{2z}^* q_{2x} q_{1z}}{\bar{A}[\epsilon(\omega)q_{1z}-\epsilon_1 q_{2z}]q_{2z}} & \dfrac{-\mathrm{i}q_{2z}^* q_{2x}^2 q_{1z}}{\bar{A}[\epsilon(\omega)q_{1z}-\epsilon_1 q_{2z}]q_{2z}^2} \end{bmatrix} \quad (20)$$

where q_{1z}, q_{2z} are normal components of the surface polariton wavevectors $\boldsymbol{q}_1$, $\boldsymbol{q}_2$ respectively. The poles of the surface response functions generate the surface polariton dispersion relation, given by

$$\frac{c^2 q_{2x}^2}{\omega^2} = \frac{\epsilon_1 \epsilon(\omega)}{\epsilon_1 + \epsilon(\omega)} \tag{21}$$

where q_{2x} is the tangential component of the surface polariton wavevector and is conserved across the boundary at $z = 0$.

Inserting the response functions from equation (20) in equation (19), the differential scattering cross section for surface polaritons becomes

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega_s} = \frac{\hbar\epsilon_1\omega_l\omega_s^3 A\cos^2\theta_s[n(\omega)+1]|a_S\beta + b_S|^2}{4\pi^3\epsilon_0^3 c^4[(k_{2z}^{l'} - q_{2z}' + k_{2z}^{s'})^2 + (k_{2z}^{l''} - q_{2z}'' + k_{2z}^{s''})^2]}\,\mathrm{Im}\left\{\frac{\mathrm{i}q_{2z}^* q_{1z} - \mathrm{i}q_{2z}^* q_{2x}^2 q_{1z}/q_{2z}^2}{\epsilon(\omega)q_{1z} - \epsilon_1 q_{2z}}\right\}. \tag{22}$$

We introduce a complex frequency [17, 18], as in equation (8), and calculate to first order in $\Gamma(\omega_0)$ the imaginary part of surface response functions in the expression appearing in equation (22). We obtain, after some algebra, the following approximation (see appendix B)

$$\mathrm{Im}\left\{\frac{\mathrm{i}q_{2z}^* q_{1z} - \mathrm{i}q_{2z}^* q_{2x}^2 q_{1z}/q_{2z}^2}{\epsilon(\omega)q_{1z} - \epsilon_1 q_{2z}}\right\} = \frac{\omega_0\epsilon_1|q_{2z}''|}{\left\{\epsilon'(\omega_0)[\epsilon_1 + \epsilon'(\omega_0)] + \epsilon_1\frac{\omega_0}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}\Big|_{\omega=\omega_0}\right\}} \times \frac{\frac{1}{2}\Gamma_s(\omega_0)}{(\omega-\omega_0)^2 + \left[\frac{1}{2}\Gamma_s(\omega_0)\right]^2} \tag{23}$$

where $\Gamma_s(\omega_0)$ is the surface polariton damping function given by [17, 18]

$$\Gamma_s(\omega_0) = \frac{\epsilon_1\frac{\omega_0}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}\Big|_{\omega=\omega_0}\Gamma}{\left\{\epsilon'(\omega_0)[\epsilon_1 + \epsilon'(\omega_0)] + \epsilon_1\frac{\omega_0}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}\Big|_{\omega=\omega_0}\right\}}. \tag{24}$$

By using equation (23) in (22), the differential scattering cross section for surface polaritons, in the limit of small damping, is obtained as

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega_s} = \frac{\hbar\epsilon_1^2\omega_l\omega_s^3 A\cos^2\theta_s[n(\omega_0)+1]|q_{2z}''|}{4\pi^3\epsilon_0^3 c^4[(k_{2z}^{l'} - q_{2z}' + k_{2z}^{s'})^2 + (k_{2z}^{l''} - q_{2z}'' + k_{2z}^{s''})^2]} \times \frac{\omega_0|a_S\beta + b_S|^2}{\left\{\epsilon'(\omega_0)[\epsilon_1 + \epsilon'(\omega_0)] + \epsilon_1\frac{\omega_0}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}\Big|_{\omega=\omega_0}\right\}}\,\frac{\frac{1}{2}\Gamma_s(\omega_0)}{(\omega-\omega_0)^2 + \left[\frac{1}{2}\Gamma_s(\omega_0)\right]^2}. \tag{25}$$

Equation (25) is another important result of this paper since it meets our objective of deriving a generalized differential scattering cross section for surface polaritons propagating along an interface between a semi-infinite medium of a frequency dependent dielectric function $\epsilon(\omega)$, bounded by another medium with a positive dielectric constant ϵ_1.

3. Numerical results and discussion

In the previous sections, we have developed a generalized theory of Raman scattering by bulk and surface polaritons in the semi-infinite geometry. Let us apply this theory to some cases of practical interest.

3.1. Case I: scattering by phonon type polaritons

For scattering by phonon type polaritons, we consider a dielectric function of the form

$$\epsilon(\omega) = \epsilon(\infty) + \frac{S\omega_T^2}{\omega_T^2 - \omega^2 - \mathrm{i}\omega\gamma} \tag{26}$$

where $\epsilon(\infty)$ is the high frequency dielectric constant, S gives the strength of the resonance and ω_T is the TO phonon frequency. Numerical results will be illustrated using the following parameters for GaP [24]: $\epsilon(\infty) = 9.09$, $\omega_T = 366.0$ cm^{-1}, $S = 2.01$, $\Gamma = 0.005\omega_T$.

If we examine the second term of equation (11) (or the limiting expressions in equations (15) and (18)) for the differential scattering cross section for bulk polaritons, and use equation (26) in the limit of small damping, then the following identity holds

$$\frac{1}{\left\{\epsilon_b'(\omega_0) + \frac{\omega_0}{2}\frac{\partial\epsilon_b'(\omega)}{\partial\omega}\Big|_{\omega=\omega_0}\right\}} = \frac{(\omega_T^2 - \omega_0^2)^2}{\{\epsilon(\infty)(\omega_T^2 - \omega_0^2)^2 + S\omega_T^4\}}. \tag{27}$$

The differential scattering cross sections can therefore be rewritten using the identity given in equation (27), and, in particular, equation (18) becomes

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega_s} = \frac{\hbar\epsilon_1\omega_l\omega_s^3 V\cos^2\theta_s[n(\omega_0)+1]}{4\pi^2\epsilon_0^3c^4}\frac{\omega_0|a_B Z + b_B(\omega_T^2 - \omega_0^2)|^2}{\{\epsilon(\infty)(\omega_T^2 - \omega_0^2)^2 + S\omega_T^4\}} \times \frac{\frac{1}{2}\Gamma_{bp}(\omega_0)}{(\omega-\omega_0)^2 + \left[\frac{1}{2}\Gamma_{bp}(\omega_0)\right]^2} \tag{28}$$

where

$$\Gamma_{bp}(\omega_0) = \frac{\omega_0^2\omega_T^2 S\Gamma}{\epsilon(\infty)(\omega_T^2 - \omega_0^2)^2 + S\omega_T^4}. \tag{29}$$

Equation (28) captures the essence of equation (3.69) of [9], with second and third terms being exactly the same, and a slight difference in some factors in the first term because in this paper we are considering bulk polaritons in a semi-infinite medium, whereas in [9] they were considering bulk polaritons in an infinite medium. Hence, our general formalism for bulk polaritons practically reduces to a previous result. The damping function in equation (29) is obtained by using equation (26) in equation (10) in the limit of small damping.

The magnitude of electric field fluctuations for bulk polaritons, calculated by the fluctuation-dissipation theorem [9], is given by

$$\langle|E_0(t)|^2_{trans}\rangle_{Av} = \frac{\hbar\omega_0[n(\omega_0)+\frac{1}{2}](\omega_T^2 - \omega_0^2)^2}{\bar{V}\epsilon_0\{\epsilon(\infty)(\omega_T^2 - \omega_0^2)^2 + S\omega_T^4\}}. \tag{30}$$

One can see, by inspection, from equation (28) that the differential scattering cross sections for transverse bulk polaritons are proportional to transverse electric field fluctuations given in equation (30).

Similarly, if we examine the second term of equation (25) for the differential scattering cross section for surface polaritons, and use equation (26) in the limit of small damping, then the following identity holds

$$\frac{1}{\left\{\epsilon'(\omega_0)[\epsilon_1 + \epsilon'(\omega_0)] + \epsilon_1\frac{\omega_0}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}\Big|_{\omega=\omega_0}\right\}} = \frac{(\omega_T^2 - \omega_0^2)^2}{\{\epsilon(\infty)[\epsilon_1 + \epsilon(\infty)](\omega_s^2 - \omega_0^2)^2 + \epsilon_1 S\omega_T^2\omega_s^2\}} \tag{31}$$

where ω_s is the upper limiting frequency for surface polaritons given by

$$\omega_s = \left[\frac{\epsilon_1 + \epsilon(\infty) + S}{\epsilon_1 + \epsilon(\infty)}\right]^{1/2} \omega_T. \tag{32}$$

By using equation (31) in (25), we obtain the following differential scattering cross section for surface polaritons

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega_s} = \frac{\hbar\epsilon_1^2\omega_l\omega_s^3 A\cos^2\theta_s[n(\omega_0)+1]|q''_{2z}|}{4\pi^3\epsilon_0^3c^4[(k^{l'}_{2z} - q'_{2z} + k^{s'}_{2z})^2 + (k^{l''}_{2z} - q''_{2z} + k^{s''}_{2z})^2]} \times \frac{\omega_0|a_S Z + b_S(\omega_T^2 - \omega_0^2)|^2}{\{\epsilon(\infty)[\epsilon_1 + \epsilon(\infty)](\omega_s^2 - \omega_0^2)^2 + \epsilon_1 S\omega_T^2\omega_s^2\}} \frac{\frac{1}{2}\Gamma_{sp}(\omega_0)}{(\omega - \omega_0)^2 + \left[\frac{1}{2}\Gamma_{sp}(\omega_0)\right]^2} \tag{33}$$

where

$$\Gamma_{sp}(\omega_0) = \frac{\epsilon_1 S\omega_T^2\omega_0^2\Gamma}{\epsilon(\infty)[\epsilon_1 + \epsilon(\infty)](\omega_s^2 - \omega_0^2)^2 + \epsilon_1 S\omega_T^2\omega_s^2}. \tag{34}$$

Our general formalism for differential scattering by surface polaritons given in equation (25) reduces to equation (33), which recovers equation (109) of [11], exactly. The damping function in equation (34) is obtained by using equation (26) in equation (34) in the limit of small damping.

The magnitude of electric field fluctuations for surface polaritons, calculated by the fluctuation-dissipation theorem [11], is given by

$$\langle|E_0(t)|^2_{Surface}\rangle_{Av} = \frac{2\epsilon_1\hbar\omega_0|q_{2z}|[n(\omega_0) + \frac{1}{2}](\omega_T^2 - \omega_0^2)^2}{\bar{A}\epsilon_0\{\epsilon(\infty)[\epsilon_1 + \epsilon(\infty)](\omega_s^2 - \omega_0^2)^2 + \epsilon_1 S\omega_T^2\omega_s^2\}}. \tag{35}$$

One can see, by inspection, from equation (33) that the differential scattering cross section for surface polaritons are proportional to surface electric field fluctuations given in equation (35).

In figure 1(a), the frequency dependence of the bulk electric field fluctuations, given in equation (30), is illustrated, and it can be observed that the fluctuations decrease as $\omega_0/\omega_T \to 1$, and increase with frequency for $\omega_0/\omega_T > \omega_L/\omega_T$.

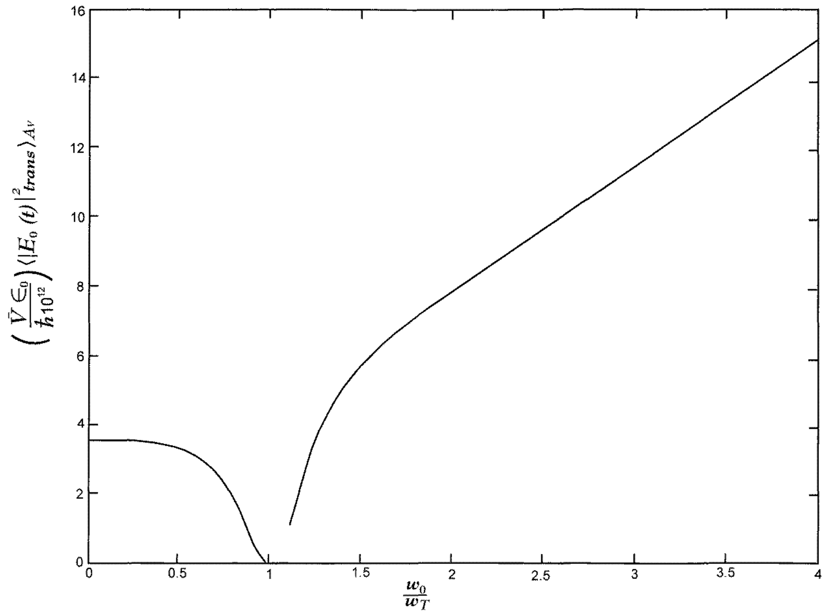
In figure 1(b), the frequency dependence of the surface electric field fluctuations, given in equation (35), is illustrated, and it can be observed that the fluctuations increase with increasing frequency, peaking at the upper limiting frequency for surface polaritons.

In figure 2(a), the frequency dependence of the bulk damping function, given in equation (29), is plotted, and it is noted that the function increases with increasing frequency for $\omega_0/\omega_T < 1$, with $\{\Gamma_{bp}(\omega_0)/\Gamma\} \to 1$ at the TO phonon frequency, and decreases with increasing frequency for $\omega_0/\omega_T > \omega_L/\omega_T$.

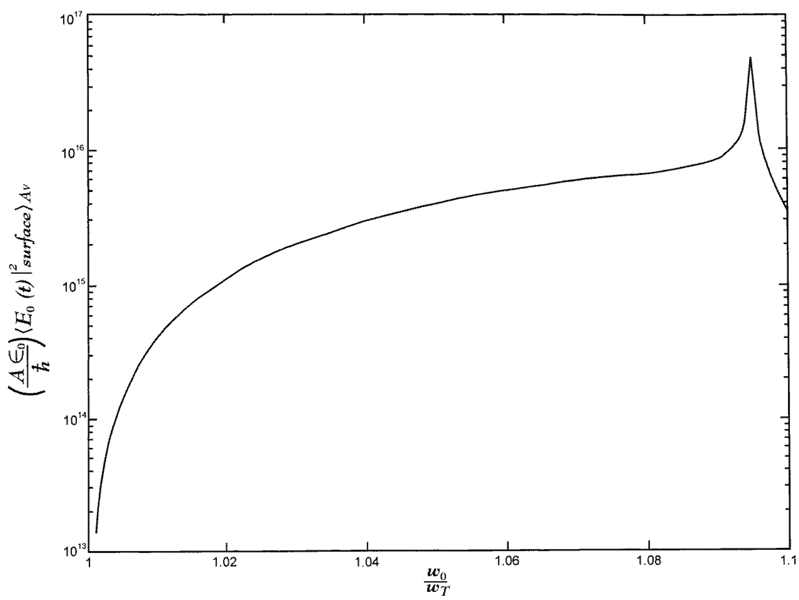
In figure 2(b), the frequency dependence of the surface damping function, given in equation (34), is plotted, and it is noted that the function increases with increasing frequency, with $\{\Gamma_{sp}(\omega_0)/\Gamma\} \to 1$ at the upper limiting frequency.

In figure 3(a), the frequency dependence of the Lorentzian lineshape which appears in the last part of the differential scattering cross section for bulk polaritons in GaP, given by equation (28), is plotted for the lower mode, and labelled $L_B(\omega_0)$ for $\omega_0/\omega_T = 0.2, 0.6$. Similarly, in figure 3(b), the frequency dependence of the Lorentzian lineshape in the differential scattering cross section for bulk polaritons in GaP is plotted for the upper mode for $\omega_0/\omega_T = 1.5, 3.0$.

In figure 4, the frequency dependence of the Lorentzian lineshape which appears in the last part of the differential scattering cross section for surface polaritons in GaP–vacuum geometry, given by equation (33), is plotted and labelled $L_S(\omega_0)$ for $\omega_0/\omega_T = 1.02, 1.04, 1.06, 1.08$.



(a)

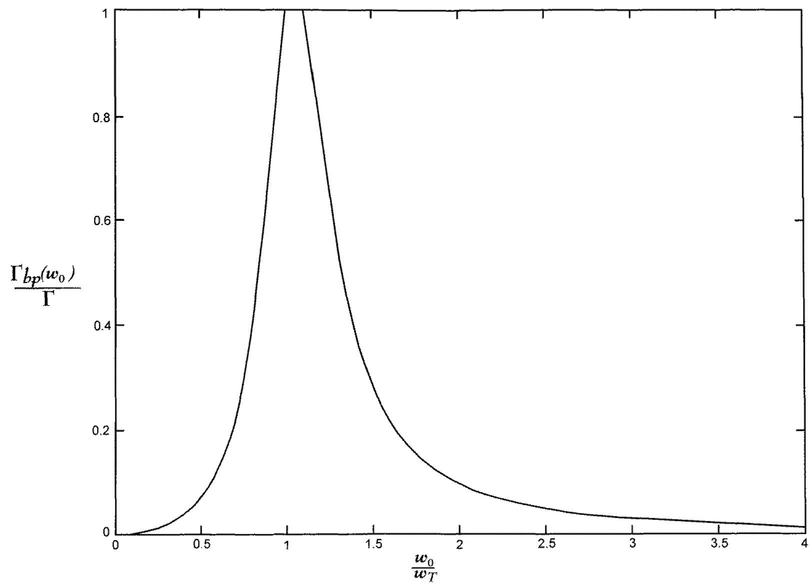


(b)

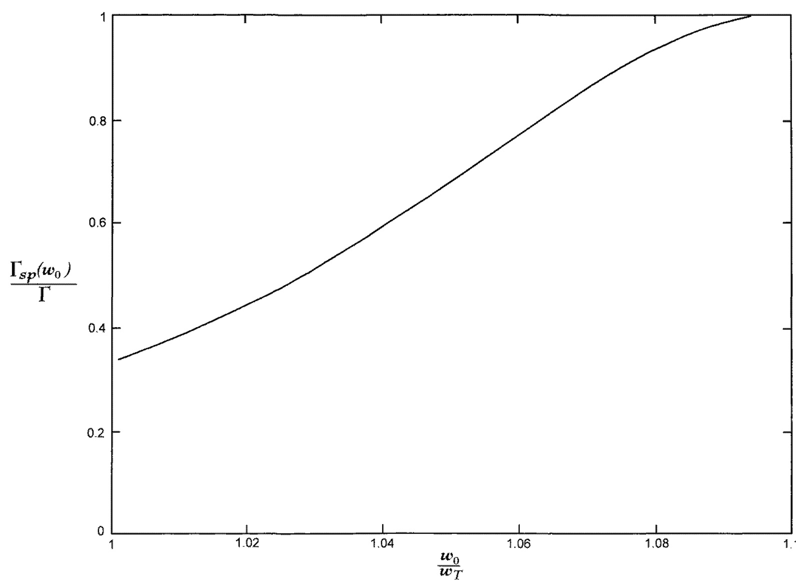
Figure 1. (a) The frequency dependence of electric field fluctuations for bulk polaritons in GaP. (b) The frequency dependence of electric field fluctuations for surface polaritons propagating along an interface in the semi-infinite geometry consisting of GaP bounded by vacuum.

3.2. Case II: scattering by polaritons in a composite medium

The advantage of having expressed the differential scattering cross sections in the forms given in equations (11), (15), (18) for bulk polaritons or in equation (25) for surface polaritons is



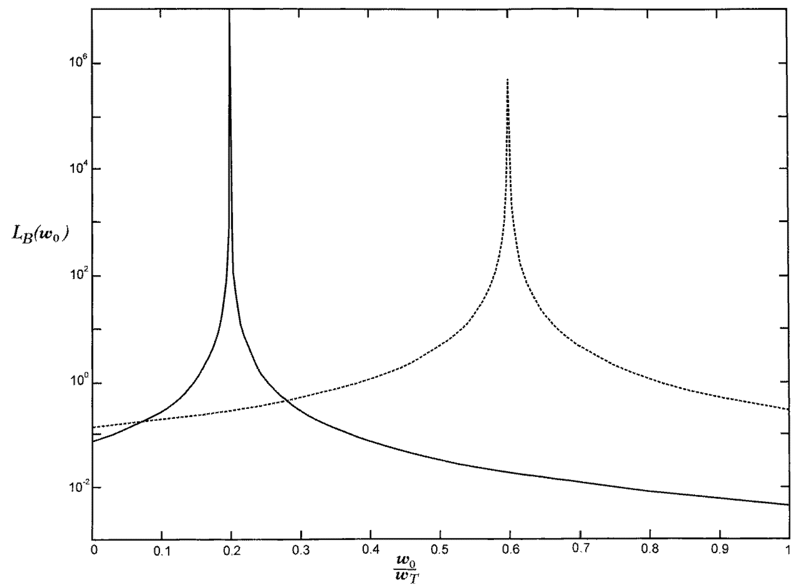
(a)



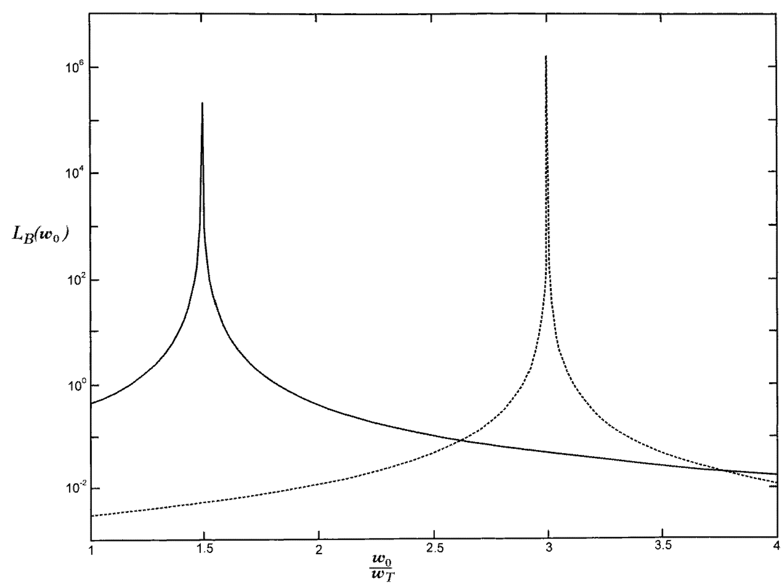
(b)

Figure 2. (a) The frequency dependence of $\Gamma_{bp}(\omega_0)/\Gamma$, the damping function for bulk polaritons in GaP. (b) The frequency dependence of $\Gamma_{sp}(\omega_0)/\Gamma$, the damping function for surface polaritons propagating along an interface in the semi-infinite geometry consisting of GaP bounded by vacuum.

that one can use these cross sections for several types of dielectric function other than that considered in case I above, and this is very convenient. For example, to study the differential scattering cross sections for bulk or surface polaritons in composite media one would make



(a)



(b)

Figure 3. (a) The frequency dependence of the Lorentzian lineshape, $L_B(\omega_0)$, of the differential scattering cross section for bulk polaritons in GaP for the lower mode, for $\omega_0/\omega_T = 0.2$ (full curve), $\omega_0/\omega_T = 0.6$ (dashed curve). (b) The frequency dependence of the Lorentzian lineshape, $L_B(\omega_0)$, of the differential scattering cross section for bulk polaritons in GaP for the upper mode, for $\omega_0/\omega_T = 1.5$ (full curve), $\omega_0/\omega_T = 3.0$ (dashed curve).

the replacement $\epsilon(\omega) \to \epsilon_{eff}(\omega)$, where $\epsilon_{eff}(\omega)$ is an appropriate effective dielectric function [25], in equations (11), (15), (18) or (25). The results of studying the application of this case

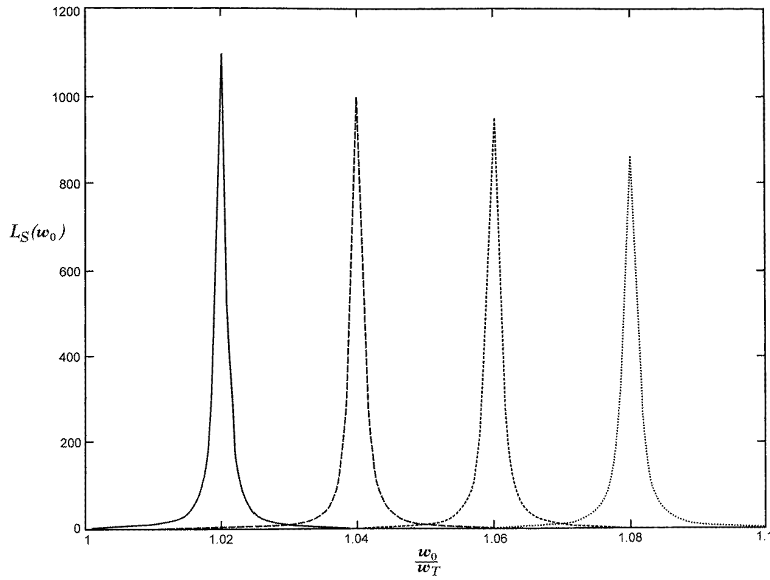


Figure 4. The frequency dependence of the Lorentzian lineshape, $L_S(\omega_0)$, of the differential scattering cross section for surface polaritons propagating along an interface in the semi-infinite geometry consisting of GaP bounded by vacuum for $\omega_0/\omega_T = 1.02$ (full curve), $\omega_0/\omega_T = 1.04$ (curve with longer dashes), $\omega_0/\omega_T = 1.06$ (curve with shorter dashes), $\omega_0/\omega_T = 1.08$ (curve with dots).

will be reported elsewhere. For example, in a recent paper [26], the authors are reporting optical investigations of oxygen ordering and persistent photo-doping in the high temperature superconductor YBCO by using effective dielectric functions. Our formalism in this paper can also be applied to model Raman scattering by bulk and surface polaritons in YBCO using the appropriate effective dielectric functions for YBCO in equations (11), (15), (18) or (25).

3.3. Case III: scattering by polaritons in systems with other forms of dielectric functions

The representation of crystal excitations by dielectric functions is well known in condensed matter physics [27]. Here, again, our formalism allows one to study the differential scattering cross sections for bulk or surface polaritons in systems with other forms of dielectric functions by making a replacement $\epsilon(\omega) \rightarrow \epsilon_{other}(\omega)$, where $\epsilon_{other}(\omega)$ is an appropriate form of a dielectric function, of which there are many examples, in equations (11), (15), (18) or (25). This application is also being studied and the results will be reported elsewhere.

4. Conclusions

In conclusion, we state that we have developed a formalism that generalizes the derivation of the Raman scattering cross section in the presence of a surface, for scattering by both bulk and surface polaritons. The main results of this paper are equations (11) (and its limiting expressions given in equations (15) and (18)) for the differential scattering cross section for bulk polaritons, and equation (25) for the differential scattering cross section for surface polaritons. The derived cross sections contain all the important factors, 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 expressions.

What is important in our general formalism is that it allows the use of several forms for appropriate dielectric functions in equations (11), (15), (18) for bulk polaritons, or equation (25) for surface polaritons. We have demonstrated this for case I, where equation (18) reduces to a previous result, given in equation (28), for bulk polaritons, and equation (25) reduces to another previous result, given in equation (33), for surface polaritons. Application of case I has been studied in detail by applying our results to GaP bounded by vacuum. The frequency dependence of the different parts of the differential scattering cross section have been illustrated in figures 1(a), 2(a), 3(a) and 3(b) for bulk polaritons, and in figures 1(b), 2 (b) and 4 for surface polaritons, as discussed in section 3. Further, case II can be used to study scattering by bulk and surface polaritons in composite media if an appropriate effective dielectric function [25] is used, and case III is an extension to study scattering by bulk and surface polaritons in systems with other forms of dielectric functions.

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Appendix A: Evaluation of the imaginary part of the bulk response function

We seek to evaluate the magnitude of the imaginary part of the bulk response function

$$\left\{\frac{1}{c^2q^2/\omega^2 - \epsilon(\omega)}\right\} = \text{RHS}. \tag{A1}$$

Consider a complex frequency defined as

$$\omega \to \omega - \mathrm{i}\tfrac{1}{2}\Gamma(\omega). \tag{A2}$$

Expanding the dielectric function in the complex frequency, we obtain

$$\epsilon(\omega - \mathrm{i}\tfrac{1}{2}\Gamma(\omega)) = \epsilon'(\omega - \mathrm{i}\tfrac{1}{2}\Gamma(\omega)) + \mathrm{i}\epsilon''(\omega - \mathrm{i}\tfrac{1}{2}\Gamma(\omega)) \tag{A3}$$

$$= \epsilon'(\omega) + \mathrm{i}\left\{-\frac{\Gamma(\omega)}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega} + \epsilon''(\omega)\right\} \tag{A4}$$

where $\Gamma^2(\omega)$ and higher order terms and products of $\Gamma(\omega)$ and $\epsilon''(\omega)$ are considered to be negligible.

$$\text{RHS} = \frac{\omega^2 - \mathrm{i}\omega\Gamma(\omega)}{c^2q^2 - [\omega^2 - \mathrm{i}\omega\Gamma(\omega)]\left[\epsilon'(\omega) + \mathrm{i}\left\{-\frac{\Gamma(\omega)}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega} + \epsilon''(\omega)\right\}\right]} \tag{A5}$$

$$= \frac{\omega^2 - \mathrm{i}\omega\Gamma(\omega)}{c^2q^2 - \omega^2\epsilon'(\omega) - \mathrm{i}\omega\left\{-\Gamma(\omega)\left[\epsilon'(\omega) + \frac{\omega}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}\right] + \omega\epsilon''(\omega)\right\}} \tag{A6}$$

where in the evaluation of RHS we have used equations (A2) and (A4). We make the following approximations in the limit of small damping. In the numerator, the imaginary part is small and negligible, that is, $\omega^2 - i\omega\Gamma(\omega) \to \omega^2$. In the denominator, $\epsilon''(\omega)$ is small and considered negligible. With these approximations, we obtain

$$\mathrm{RHS} = \frac{1}{\left\{\epsilon'(\omega) + \frac{\omega}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}\right\}} \left\{ \frac{\omega^2}{\left[\frac{c^2q^2-\omega^2\epsilon'(\omega)}{\epsilon'(\omega)+\frac{\omega}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}}\right] + i\omega\Gamma(\omega)} \right\}. \tag{A7}$$

In small damping, the scattering cross section will have a peak at a frequency ω_0, close to the undamped frequency ω defined in equation (6) for bulk polaritons. It is therefore possible to define for every q a frequency ω_0, and we make the following approximation in the first term in the denominator of the large curly brackets in equation (A7)

$$\left[\frac{c^2q^2 - \omega^2\epsilon'(\omega)}{\epsilon'(\omega) + \frac{\omega}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}}\right] \approx \frac{\omega_0^2\epsilon'(\omega_0) - \omega^2\epsilon'(\omega)}{\epsilon'(\omega) + \frac{\omega}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}} \tag{A8}$$

$$\approx \frac{\omega_0^2 - \omega^2}{1 + \frac{\omega}{2\epsilon'(\omega)}\frac{\partial\epsilon'(\omega)}{\partial\omega}} \tag{A9}$$

$$\approx \omega_0^2 - \omega^2 \tag{A10}$$

where we have used the approximations $\epsilon'(\omega) \approx \epsilon'(\omega_0)$ and

$$\frac{\omega}{2\epsilon'(\omega)}\frac{\partial\epsilon'(\omega)}{\partial\omega} \to 0. \tag{A11}$$

Using equation (A10) in (A7), we obtain

$$\mathrm{RHS} = \frac{1}{\left\{\epsilon'(\omega) + \frac{\omega}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}\right\}} \left\{ \frac{\omega^2}{(\omega_0^2 - \omega^2) + i\omega\Gamma(\omega)} \right\}. \tag{A12}$$

Provided that the scattering cross section has a narrow spread about its maximum at ω_0, the frequency ω can be replaced by ω_0 everywhere except in the term of the ‘difference’ in ‘the difference of two squares’ in equation (A12). We obtain

$$\mathrm{RHS} = \frac{1}{\left\{\epsilon'(\omega_0) + \frac{\omega_0}{2}\frac{\partial\epsilon'(\omega_0)}{\partial\omega}\Big|_{\omega=\omega_0}\right\}} \left\{ \frac{\omega_0^2}{2\omega_0(\omega_0 - \omega) + i\omega_0\Gamma(\omega_0)} \right\} \tag{A13}$$

and taking the imaginary part of equation (A13), its magnitude is

$$\mathrm{Im}\left\{\frac{1}{c^2q^2/\omega^2 - \epsilon(\omega)}\right\} = \frac{\omega_0}{2\left\{\epsilon'(\omega_0) + \frac{\omega_0}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}\Big|_{\omega=\omega_0}\right\}} \frac{\frac{1}{2}\Gamma(\omega_0)}{(\omega - \omega_0)^2 + \left[\frac{1}{2}\Gamma(\omega_0)\right]^2} \tag{A14}$$

which is equation (9) in the main text.

Appendix B: Evaluation of the imaginary part of the surface response function

We seek to evaluate the magnitude of the imaginary part of the surface response function

$$\left\{\frac{iq_{2z}^*q_{1z} - iq_{2z}^*q_{2x}^2q_{1z}/q_{2z}^2}{\epsilon(\omega)q_{1z} - \epsilon_1 q_{2z}}\right\} = \mathrm{RHS}. \tag{B1}$$

Note that part of the term in the curly brackets of equation (B1) can be written in the form

$$\frac{1}{[\epsilon(\omega)q_{1z} - \epsilon_1 q_{2z}]} = \frac{[\epsilon(\omega)q_{1z} + \epsilon_1 q_{2z}]}{[\epsilon(\omega) - \epsilon_1]\{\epsilon_1\epsilon(\omega)\omega^2/c^2 - q_{2x}^2[\epsilon(\omega) + \epsilon_1]\}}. \tag{B2}$$

Combining equation (B2) and relations for the polariton wavevectors, we obtain

$$\text{RHS} = \frac{2|q_{1z}^2||q_{2z}''|}{\{\epsilon_1\epsilon(\omega)\omega^2/c^2 - q_{2x}^2[\epsilon(\omega) + \epsilon_1]\}}. \tag{B3}$$

Inserting the expression for the complex frequency and the expansion of the dielectric function as in appendix A, we obtain

$$\text{RHS} = [2|q_{1z}^2||q_{2z}''|]\Bigg[\frac{\epsilon_1\epsilon'(\omega)\omega^2}{c^2} - [\epsilon_1 + \epsilon'(\omega)]q_x^2 + \mathrm{i}\frac{\epsilon_1}{c^2[\epsilon_1 + \epsilon'(\omega)]}\Bigg\{ - \omega\Gamma(\omega)\Bigg[\epsilon'(\omega)[\epsilon_1 + \epsilon'(\omega)] + \frac{\omega}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}\Bigg] + B\Bigg\}\Bigg]^{-1} \tag{B4}$$

where

$$B = \epsilon''(\omega)\epsilon_1\omega^2. \tag{B5}$$

In the limit of small damping, $\epsilon''(\omega)$ is small and considered negligible, and hence the term in B is negligible in equation (B4). In small damping, the scattering cross section will have a peak at a frequency ω_0, close to the undamped frequency ω defined in equation (21) for surface polaritons. It is therefore possible to define for every q_x a frequency ω_0, and using the approximations $\epsilon'(\omega) \approx \epsilon'(\omega_0)$ and

$$\frac{\epsilon_1}{\epsilon'(\omega)[\epsilon_1 + \epsilon'(\omega)]}\frac{\omega}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega} \to 0 \tag{B6}$$

we obtain

$$\text{RHS} = \frac{2\omega^2\epsilon_1|q_{2z}''|}{\left\{\epsilon'(\omega)[\epsilon_1 + \epsilon'(\omega)] + \epsilon_1\frac{\omega}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}\right\}}\left\{\frac{1}{(\omega_0^2 - \omega^2) - \mathrm{i}\omega\Gamma(\omega)}\right\}. \tag{B7}$$

Replacing the frequency ω by ω_0 everywhere except in the term of the ‘difference’ in ‘the difference of two squares’ in equation (B7), we obtain

$$\text{RHS} = \frac{2\omega_0^2\epsilon_1|q_{2z}''|}{\left\{\epsilon'(\omega_0)[\epsilon_1 + \epsilon'(\omega_0)] + \epsilon_1\frac{\omega_0}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega_0}\Big|_{\omega=\omega_0}\right\}}\left\{\frac{1}{2\omega_0(\omega_0 - \omega) - \mathrm{i}\omega_0\Gamma(\omega_0)}\right\} \tag{B8}$$

and taking the imaginary part of equation (B8), its magnitude is

$$\text{Im}\left\{\frac{\mathrm{i}q_{2z}^*q_{1z} - \mathrm{i}q_{2z}^*q_{2x}^2q_{1z}/q_{2z}^2}{\epsilon(\omega)q_{1z} - \epsilon_1q_{2z}}\right\} = \frac{\omega_0\epsilon_1|q_{2z}''|}{\left\{\epsilon'(\omega_0)[\epsilon_1 + \epsilon'(\omega_0)] + \epsilon_1\frac{\omega_0}{2}\frac{\partial\epsilon'(\omega)}{\partial\omega}\Big|_{\omega=\omega_0}\right\}} \times\frac{\frac{1}{2}\Gamma(\omega_0)}{(\omega - \omega_0)^2 + \left[\frac{1}{2}\Gamma(\omega_0)\right]^2} \tag{B9}$$

which is equation (23) in the main text.

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