Surface-enhanced Raman scattering at cryogenic substrate temperatures

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The recent speculation on the possibility of achieving gigantic enhancement for surface-enhanced Raman scattering at cryogenic substrate temperatures is examined using a simple theoretical model. The surface-plasmon enhancement mechanism is modeled using the Fermi-electron gas approach instead of the Drude model as used previously in the literature. Due to the diminution of substrate polarizability from quantum effects, it is concluded that dramatic enhancement is unlikely to be achieved by just cooling the surface to such low temperatures.

INTRODUCTION

Although surface-enhanced Raman scattering (SERS) has been intensively studied and has become a relatively well-established area since its first discovery in 1974, certain aspects of the phenomenon remain intriguing to this date.[1,2] Among these, the effect due to the change in substrate temperature has recently drawn some interest from researchers, after the first observation of the possibility of sustaining SERS at elevated temperatures (up to those needed for realistic catalytic photochemical conditions to take place).[3] Both theoretical[4,5] and experimental[6,7] studies have been carried out. In particular, the recent systematic study carried out by Pang, Hwang, and Kim[6] has provided evidence for the qualitative validity of a model based on the temperature variation of the substrate optical properties.[4,5] The main observation of this later experiment on the SERS of 1-Propanehiol on a silver island film involves a reversible change of the SERS signal with the change of substrate temperatures over the range 15–300 K. While the original theoretical models[4,5] were aimed at SERS at elevated temperatures ($T > 300\,\mathrm{K}$), it was nevertheless applied in an interesting way by the researchers in Refs. 6 and 7 via an extrapolation of the original models into the low-temperature regimes. From this study the authors concluded with an intriguing speculation that, with all the conditions optimized, one might be able to achieve gigantic enhancement for SERS by cooling the substrate down to cryogenic temperatures.[6]

Since in the previous models[4–7] the surface-plasmon enhancement mechanism was described using the Drude model for the dielectric response of the substrate, they cannot be extrapolated into the low-temperature regime without limitation. For one thing at least, at cryogenic temperatures, the free-electron gas should be described as a Fermi gas and not a classical ideal gas as in the Drude model. In fact, it is known that the Drude model will break down at such a low temperature of the metal, where the mean free path of the electrons is comparable to or much greater than the optical wavelengths, and nonlocal effects will play an important role.[8] Hence it is the purpose of this work to reexamine our previous models[4,5] using a more appropriate dielectric response function for the surface electrons at cryogenic temperatures. We begin by providing further details of the previous experimental analysis and our present model in the following.

In their experiment,[6] Pang *et al.* observed a reversible change in the SERS enhancement ratio (R) which amounted to few times increase from the room temperature (300 K) value for admolecules in the vicinity of ellipsoidal silver islands, when the silver temperature was cooled down to 15 K. To analyze their results, the previous model[4,5] with a temperature-dependent electromagnetic enhancement mechanism was then applied. The temperature dependence enters mainly through the collision frequency (ω_c) of the Drude model where both electron-phonon and electron-electron interactions were included. It was then observed[6] that a more-or-less monotonic increase in R could be achieved by lowering the substrate temperature from room temperatures towards cryogenic temperatures. Hence it was speculated that, at least in principle, gigantic SERS enhancement could be obtained by optimizing all the parameters in the experiment (e.g., scattering frequency, island morphology, etc) and lowering the substrate temperature to that of liquid helium.

While this remains an exciting and intriguing possibility,[9] we would like to point out that the previous models[4,5] were strictly limited to ''high'' temperatures [$T \gtrsim 100\,\mathrm{K}$ (Ref. 10)], since the Drude model will fail at cryogenic temperatures as discussed above. At such low temperatures, one must account for the quantum-mechanical properties of the free electrons in the metal surface plasmon. For a strongly degenerate Fermi-gas system, several well-known dielectric functions have been worked out in the literature,[11–15] and each one of these has its own distinct features suited for certain specific applications. Though it is well known that the hydrodynamic model[11] is simple and suited for the description of collective motions of the electrons like the plasmon excitation, it is, however, limited to a small wave-vector response in which only the lowest-order nonlocal effect is accounted for. Hence for our present application to electrons at very low temperature where large nonlocal effects are expected, we resort to the choice of the Linhard function[12] (L) and its extension and generalizations. These include the Linhard-Mermin model[13] (LM) in which damping (collision loss) is incorporated in a consistent and phenomenological manner; and the Hu-O'Connell (HO) approach[14] in which fluctuation effects at large wave-vector values are included.

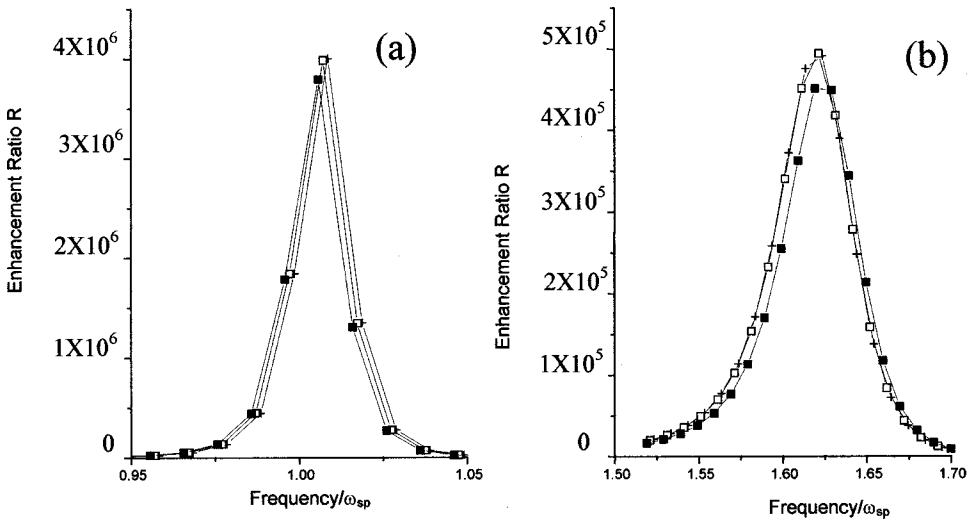

FIG. 1. Calculated spectrum of the enhancement ratio based on (a) the Drude model and (b) the LM model for temperatures at 1 K (+), 51 K (□), and 101 K (■). Scattering frequency is normalized to ω_{sp} at $T=300$ K.

There also exist other improved versions of the Linhard function by including higher-order correlation effects (e.g., hole correlation),[15] but we shall not go beyond the level of the random-phase approximation (RPA), and we limit our present choice of dielectric function for the low-temperature Fermi electron gas to include the lowest-order correlation effects. Hence in the following, we shall calculate R using the various L, LM, and HO models and compare the results with those from before where the classical Drude model has been applied.[4–7] Thus, in a sense, the present work complements the previous work[4,5] by extending the model to the regime of low substrate temperatures using a quantum-mechanical description for the dielectric response of the surface electrons.

FORMULATION OF THE MODEL

In order to study the electromagnetic (EM) enhancement for SERS, we follow our previous adoption of a simple model published by Gerstein and Nitzan (GN).[16] In the GN model, surface roughness is modeled in the form of a spheroidal particle and the enhanced surface EM field is calculated in the long-wavelength approximation. In order to extend the GN model to cryogenic surface temperature where nonlocal dielectric response is of prime importance, we shall consider here only the highly simplified geometry when the surface structure is a spherical particle of radius a. Though it is understood that in reality, ellipsoidal particles are more efficient ''enhancers'' and are most often present in experiments using either thin island films or metallic colloids, it seems nevertheless possible in principle to fabricate almost-perfect spherical particles in certain ''single-island'' experiments.[17] Hence the following model is not only simple (in handling nonlocal effects), but may also be testable in these specially designed ''single-island'' experiments. In any case, we believe that the nonlocal effects obtained in the spherical case should be qualitatively similar to those expected for the ellipsoidal case. Thus, for a molecular dipole interacting with a spherical metal island, the SERS enhancement ratio can be obtained as[16]

$$R=\left|\frac{1}{1-\alpha G_{\perp}}\left[1+\frac{2\alpha_1^S}{(a+d)^3}\right]\right|^4, \tag{1}$$

where α is the molecular polarizability (taken as 10 Å^3), a the sphere radius, and d the molecule-sphere distance, respectively, and $G_{\perp}$ is the ''image-field factor'' which is a function of the nth pole nonlocal polarizability (α_n^S) of the sphere given by[16]

$$\alpha_n^S=\frac{n(\varepsilon_n-1)}{n(\varepsilon_n+1)+1}a^{2n+1}, \tag{2}$$

with the frequency-dependent dielectric function given in terms of the nonlocal function in the following way:[18]

$$\varepsilon_n(\omega)=\left(\frac{2}{\pi}(2n+1)a\int_0^{\infty}\frac{j_n^2(ka)}{\varepsilon(\vec{k},\omega)}dk\right)^{-1}, \tag{3}$$

where j_n is the spherical Bessel function and $\varepsilon(\vec{k},\omega)$ is one of the quantum-mechanical dielectric functions we discussed above.

For our present modeling, we will use $\varepsilon(\vec{k},\omega)$ in the following form:

$$\varepsilon(\vec{k},\omega)=1-\frac{4\pi e^2}{k^2}\sum_q\frac{f(E_{k+q})-f(E_q)}{E_{k+q}-E_q+\hbar\omega-i\hbar\gamma}, \tag{4}$$

where $E_q=\hbar^2q^2/2m$ the kinetic energy and $f(E_q)$ is the Fermi-Dirac distribution function of the electrons. Since the GN model is established in the ''long-wavelength limit,'' we need only to consider here the longitudinal dielectric response. Equation (4) can further be divided into the following three cases as discussed above: *Case (i)*, the Linhard (L) function with $\gamma\rightarrow 0$; *case (ii)*, the Linhard-Mermin (LM) function with γ taken as ω_c—the empirical collision frequency, and the Mermin equation[13] applied to calculate the overall effective consistent dielectric function with damping; and *case (iii)*, the Hu-O'Connell (HO) function with $\gamma\rightarrow Dq^2$, D a constant. Standard integration over q will then

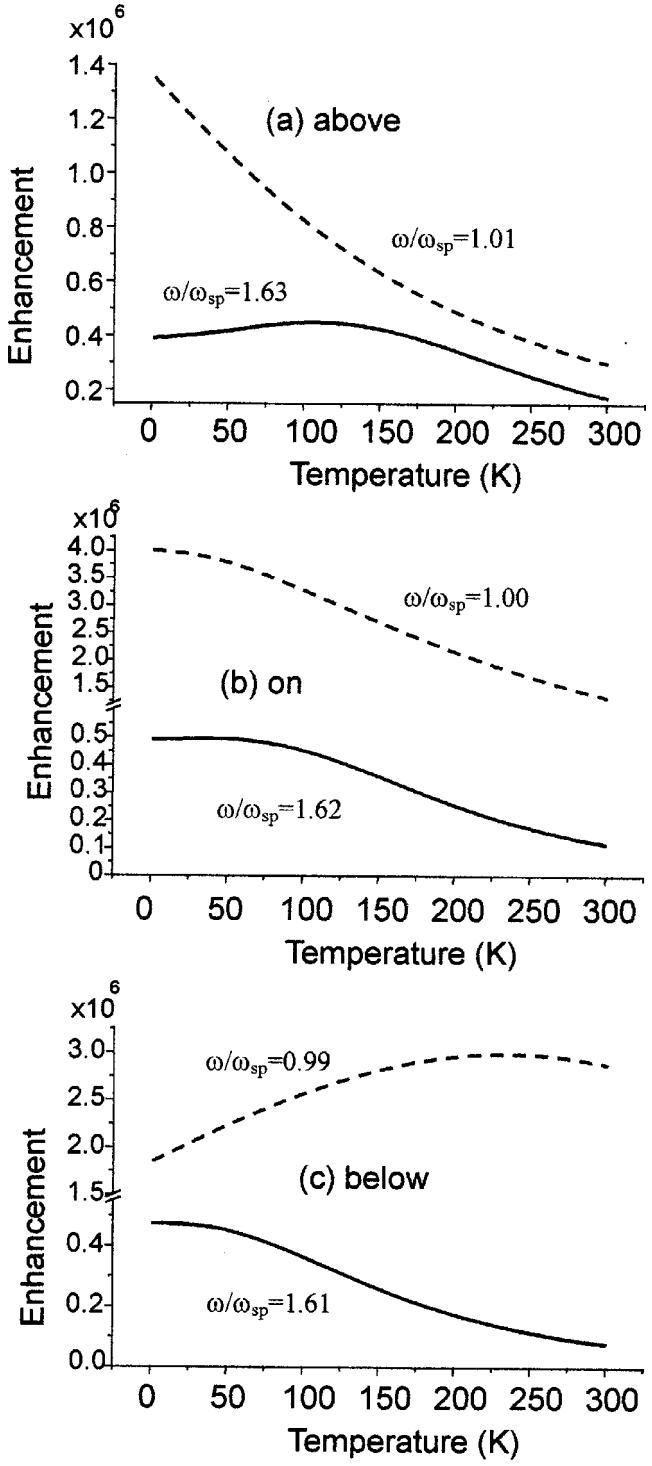

FIG. 2. Temperature-dependent behavior of the enhancement ratio calculated from the Drude model (dashed lines) and the LM model (solid lines) for normalized frequencies (a) above, (b) on, and (c) below the resonance peaks in each of the two models.

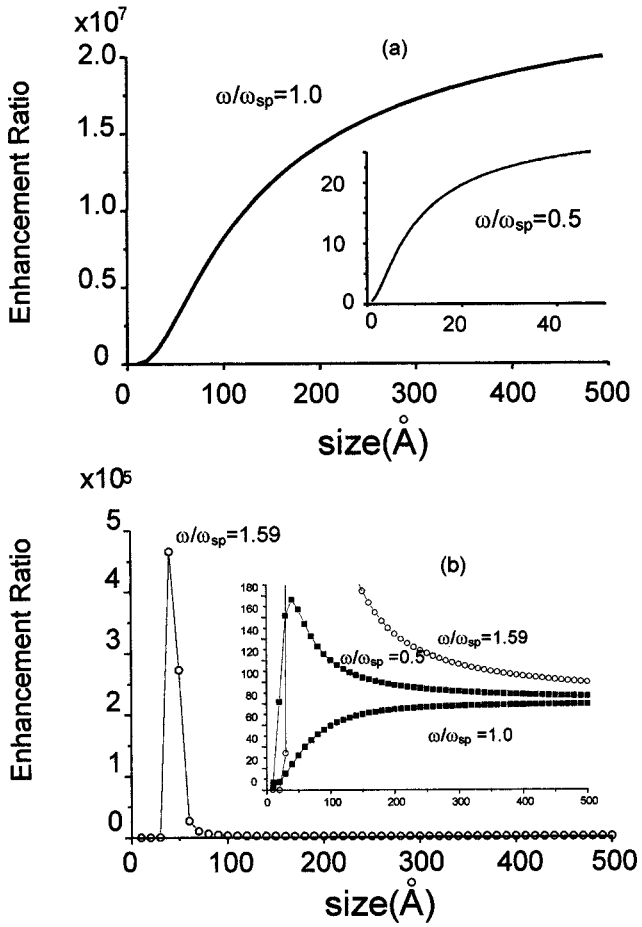

FIG. 3. Particle-size-dependent behavior of the enhancement ratio at 300 K calculated from the (a) Drude and (b) LM models for different normalized frequencies.

lead to the various analytical expressions for $\varepsilon(\vec{k},\omega)$ which can be found from the literature.[14,15]

As is well known, the L function in case (i) accounts for the Pauli exclusion principle that the metallic electrons must obey, especially at cryogenic temperatures; the LM function in (ii) further improves this by incorporating damping (due to electron-phonon and electron-electron collision, etc.) in a phenomenological and consistent formalism; and the HO function accounts for damping from the fluctuation in the center-of-mass motion for the Fermi-gas system. As far as the temperature dependence is concerned, there are two main sources which lead to the variation of $\varepsilon(\vec{k},\omega)$ with temperature. The first comes from the variation in the number density of the free electrons which will lead to the variation of the plasmon frequency of the metal with temperature,[9] and the second comes from the temperature dependence of the damping. In the LM case we shall simply use the Holstein-Debye model for electron-phonon collision and the Lawrence model for electron-electron collision, respectively, as we used before for the SERS calculation with the classical Drude model.[4,5] In the HO case, D is governed by the rate of random collision with impurities, and hence we shall not attempt to implement a general model for its variation with temperature. Instead, we shall treat D as a parameter in our modeling.[14] Finally, the dependence of the distribution function $f(E_q)$ on temperature (T) is completely insignificant since $T \ll T_F$, the Fermi temperature in all our application. This can be more explicitly seen by going to the limit of the hydrodynamic model, where corrections of the order of $(T/T_F)^2 \sim 10^{-8}$ for the sound velocity (β) of the Fermi gas can be worked out. For the Linhard case, one can also show directly from Eq. (4) that the temperature dependence of $f(E_q)$ has a completely insignificant effect on $\varepsilon(\vec{k},\omega)$ (see

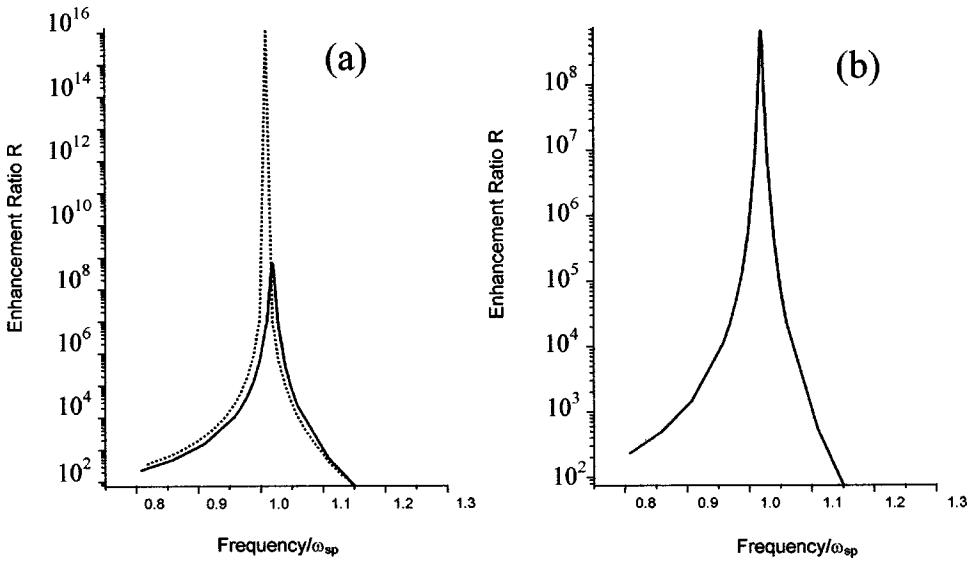

FIG. 4. Calculated enhancement ratio with almost zero damping (see text) based on the (a) Drude (dashed line) and LM models (solid line) and (b) the HO model.

the Appendix). Thus we shall only consider the temperature dependence of the electron density and damping in our present modeling.[19]

NUMERICAL RESULTS

With the above clarifications, we have carried out some numerical calculation of the SERS enhancement ratio R by applying the several different quantum-mechanical dielectric functions for the modeling of the EM enhancement mechanism. Figure 1 shows R as a function of scattering frequency (normalized to the surface-plasmon frequency $\omega_{sp}=\omega_p/\sqrt{3}$ at $T=300\,\mathrm{K}$) for three different temperatures: $T=1$, 51, and 101 K, respectively, according to both the Drude and the LM models for the dielectric function. The surface island is modeled as a silver sphere of radius 50 Å and the molecule-surface distance is fixed as 10 Å. We allow both the electron density and the sphere radius to vary with temperature.[9] The damping and other parameters for Ag are used as in the previous modeling.[4,5] We observe from Fig. 1 that for the Drude model, maximum R occurs at normalized frequencies slightly above one due to the slight increase of the plasma frequency with the decrease of temperature.[9] For the LM model we see that the resonance peak is blueshifted to about $1.62\omega_{sp}$. This is due to the nonlocal nature and the frequency-dependent damping in the electronic collision frequency[5] of the model. Most importantly, we observe that the LM model yields the maximum possible value for R at 1 K almost an order of magnitude smaller than that predicted from the classical Drude model. This is actually no surprise since it is well known that due to quantum-mechanical effects, the higher-order multipole polarizabilities of the metal island are strongly suppressed in the LM model.[18] In addition, the magnitude of the dipole polarizability of the island (which corresponds to the surface-plasmon enhancement effect) is also less in the LM model since the average charge separation (polarization) is expected to be less in the nonlocal model together with effects from Pauli's exclusion principle. We have also computed R (not shown) with the HO function and found that the resonance characteristics is not much different from that of the Drude model, except that the magnitudes in R are not directly comparable since the damping constants (collision frequency vs diffusion constant) are not rigorously correlated. Figure 2 shows the enhancement R versus temperature for different scattering frequencies for all the three cases: above, on, and below resonance for each of the Drude and LM model calculations. Note that the frequency is set differently for each comparison made on account of the blueshifted resonance frequency in the LM model mentioned above. We remark here again that the monotonic increase of R towards low T's in the Drude model only occurs for frequencies above resonance.[9] From all three cases, we again see the suppression of R in the LM model up to an order of magnitude with respect to the values in the Drude model. Furthermore, we also note that the particle size we have been using (50 Å) for the above computations might be too small compared to realistic ones in most experiments. To ensure that the difference between the Drude and LM models prevails for a larger range of particle sizes, we have plotted in Fig. 3 R versus a up to a size of 500 Å for both models. We notice the dramatic difference between the results from each of the models for both the resonant and off-resonant cases. In particular, at the Drude resonance frequency, the LM model gives results for R five orders of magnitudes smaller for particle sizes up to 500 Å. In addition, there is a ''resonance behavior'' in R versus a only for the LM model for frequencies close to that for resonance. This is due to the well-known fact that the resonance frequency is size dependent in most nonlocal dielectric models, but equals to a constant value $(\omega_p/\sqrt{3})$ in the Drude model.[18] Finally, we consider the ideal limit of enhancement in the absence of all damping of the surface plasmon. In Fig. 4 we show the R values for all the three models at $T=1\,\mathrm{K}$ with the damping constant set to $10^{-8}\,\mathrm{s}^{-1}$ in both the Drude and the LM models, and the diffusion constant D set to 10^{-5} SI unit in the HO model. We found that the effect of damping via diffusion in the HO model is very mild and that the calculation almost identifies with that from the L (LM

with $\gamma \to 0$) model for values of D up to 10^{-2} SI units. The most interesting feature from Fig. 4 is the illustration of the ''quantum suppression'' effect in this ideal limit: while the classical Drude model leads to ''gigantic enhancement'' with $R \sim 10^{16}$, the L or LM model yields a diminution of almost eight orders of magnitude from the classical calculation.

DISCUSSION AND CONCLUSION

We have thus provided evidence from our modeling that the recent speculation implied from low-temperature experiments on SERS,[6] concerning the possible gigantic enhancement at cryogenic substrate temperatures, is unlikely to be realized. In fact, a previous experiment on the study of the very-low-frequency surface acoustic mode via SERS did not report dramatic enhancement at liquid-helium temperature down to $T = 1.6\,\mathrm{K}$.[20] Although the decrease in surface-plasmon damping leads to greater enhancement at such low temperatures, diminution in substrate polarizability due to quantum effects sets a limit to the situation. Of course, this does not exclude other SERS mechanisms to lead to dramatic enhancement at cryogenic temperatures, future systematic experiments will be of interest to clarify this issue. Since it is a frequent practice in spectroscopic experiments to work at cryogenic temperatures to achieve high signal-noise ratio, our modeling results should be relevant to these experiments whenever the proximity of a metal surface is involved.

To conclude, although our model is somewhat oversimplified, we believe this ''quantum suppression'' of SERS due to the diminution in dipolar and higher multipolar polarizabilities of the substrate should have general validity. There are certain features one can introduce to improve the model, such as the inclusion of surface scattering[21] as well as interband transitions in our treatment of the temperature-dependent dielectric functions,[4,5] the quantum confinement effect for the electrons in nanoparticles at $T = 1$ K, or modeling the surface structure as a spheroidal rather than a spherical particle; moreover, we believe this will not change our overall conclusion on the SERS effect. Further experimental studies will be of interest to confirm this conclusion.

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APPENDIX

Here we provide an explicit formulation of the temperature dependence of the Linhard dielectric function, showing quantitatively that this dependence through the Fermi-Dirac (FD) distribution is completely negligible for all practical purposes. This issue is seldom pointed out in the literature[22] and the L function has often been taken implicitly to be applicable at all temperatures.[18]

We begin with the following standard expansion in handling integrals related to the FD function:[23]

$$I = \int_0^\infty f(E)h(E)dE \approx H(\mu) + \frac{\pi^2}{6}(k_B T)^2 H''(\mu) + \cdots, \tag{A1}$$

where $f(E)$ is the finite-temperature FD distribution function, $h(E)$ is any well-behaved function of energy, k_B the Boltzman constant, and $H'(\mu) = h(\mu)$. $\mu(T) \sim E_F[1 - \pi^2/12 \times (T/T_F)^2 + \ldots]$ is the chemical potential at finite temperature with E_F and T_F being the Fermi energy and temperature, respectively. To apply this to our problem, we recall that in the RPA, the L function in Eq. (4) (with $\gamma = 0$) can be written in terms of the polarization function (P) in imaginary frequency as follows:[15]

$$\varepsilon(\vec{k}, i\omega) = 1 - \frac{4\pi e^2}{k^2} P^{(1)}(\vec{k}, i\omega), \tag{A2}$$

where

$$P^{(1)}(\vec{k}, i\omega) = -\frac{m^2}{2k\pi^2\hbar^4} \int_0^\infty f(E) \left\{ \ln\left(\frac{A + B\sqrt{E}}{A - B\sqrt{E}}\right) + \ln\left(\frac{C + B\sqrt{E}}{C - B\sqrt{E}}\right) \right\} dE, \tag{A3}$$

with $E = \hbar^2 k'^2/2m$, m the effective electron mass, and the coefficients A, B, C are given as follows: $A = E + i\hbar\omega$, $B = (2/m)^{1/2}\hbar k$, and $C = E - i\hbar\omega$. The final dielectric function is obtained from Eq. (A2) via analytical continuation: $i\omega \to \omega + i\delta$.

To investigate the finite-temperature correction to $\varepsilon(\vec{k}, \omega)$, we apply Eqs. (A1) to (A3) and obtain the following correction term to $P^{(1)}(\vec{k}, i\omega)$:

$$P^{(1)}(\vec{k}, i\omega) = P_0^{(1)}(\vec{k}, i\omega) + \Delta P^{(1)}, \tag{A4}$$

where we have assumed $P_0^{(1)}$ to be simply the function at $T = 0$ with $\mu \sim E_F$ and the correction term given by

$$\Delta P^{(1)} = -\frac{m^2}{12k\hbar^4\sqrt{\mu}} (k_B T)^2 B \left[\frac{A}{A^2 - \mu B^2} + \frac{C}{C^2 - \mu B^2} \right]. \tag{A5}$$

Numerical computation of Eq. (A5) shows that for a temperature range from 1 to 1000 K, $\Delta P^{(1)}$ amounts to no more than about 0.1% of $P_0^{(1)}$ with about 10^{-5}% at $T = 1$ K. This is true for a large range of values for k and ω. The result actually scales very close to $(T/T_F)^2$. Thus we conclude that such an effect is completely negligible in our modeling.

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[1] For recent review see, e.g., M. Moskovits, Rev. Mod. Phys. **57**, 783 (1985).

[2] See also, A. Otto, I. Mrozek, H. Grabhorn, and W. Akemann, J. Phys.: Condens. Matter **4**, 1143 (1992).

[3] B. Pettinger, X. Boa, I. C. Wilcock, M. Muhler, and G. Ertl, Phys. Rev. Lett. **72**, 1561 (1994).

[4] P. T. Leung, M. H. Hider, and E. J. Sanchez, Phys. Rev. B **53**, 12 659 (1996).

[5] H. P. Chiang, P. T. Leung, and W. S. Tse, J. Chem. Phys. **108**, 2659 (1998).

[6] Y. S. Pang, H. J. Hwang, and M. S. Kim, J. Phys. Chem. B **102**, 7203 (1998).

[7] C. H. Kwon, D. W. Boo, H. J. Hwang, and M. S. Kim, J. Phys. Chem. B **103**, 9610 (1999).

[8] F. Wooten, *Optical Properties of Solids* (Academic, New York, 1972).

[9] Note that even the previous model using the classical Drude model is subjected to be modified, with the inclusion of the temperature dependence of the plasmon frequency. This modification will have already limited the indefinite increase in the enhancement as the substrate temperature is lowered. See, H. P. Chiang, P. T. Leung, and W. S. Tse, J. Phys. Chem. B **104**, 2348 (2000).

[10] A recent experiment showed that the Drude model can be valid down to 100 K for thin Ag films. See M. Henzler, T. Luer, and A. Burdach, Phys. Rev. B **58**, 10 046 (1998).

[11] F. Bloch, Z. Phys. **81**, 363 (1933); Helv. Phys. Acta **1**, 385 (1934); A thorough discussion of the hydrodynamic model can also be found in G. Barton, Rep. Prog. Phys. **42**, 65 (1979).

[12] J. Linhard, K. Dan. Vidensk. Selsk. Mat. Fys. Medd. **28**, 8 (1954).

[13] N. D. Mermin, Phys. Rev. B **1**, 2362 (1970).

[14] G. Y. Hu and R. F. O'Connell, Phys. Rev. B **40**, 3600 (1989).

[15] A more comprehensive discussion of the different quantum-mechanical dielectric functions, including those going beyond the random-phase approximation, can be found in G. D. Mahan, *Many-Particle Physics*, 2nd ed. (Plenum, New York, 1990).

[16] J. Gersten and A. Nitzan, J. Chem. Phys. **73**, 3023 (1980).

[17] Note that single-island single-molecule SERS has been achieved, see, e.g., S. Nie and S. R. Emory, Science **275**, 1102 (1997).

[18] R. Fuchs and F. Claro, Phys. Rev. B **35**, 3722 (1987).

[19] For details of modeling these effects, refer to Refs. 4, 5, and 9.

[20] D. A. Weitz, T. J. Gramila, A. Z. Genack, and J. I. Gersten, Phys. Rev. Lett. **45**, 355 (1980); D. A. Weitz, T. J. Gramila, and A. Z. Genack, in *Surface-Enhanced Raman Scattering*, edited by R. K. Chang and T. E. Furtak (Plenum, New York, 1982).

[21] See, e.g., R. T. Beach and R. W. Christy, Phys. Rev. B **16**, 5277 (1977); S. Link and M. A. El-Sayed, J. Phys. Chem. B **103**, 8410 (1999).

[22] A rare exception can be found in the paper by Barton in Ref. 11, where the strict limit of the hydrodynamic dielectric function to zero temperature is explicitly mentioned.

[23] See, e.g., D. A. McQuarrie, *Statistical Mechanics* (Harper & Row, New York, 1975), p. 166.