

Decay of molecules at spherical surfaces: Nonlocal effects

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The decay rates for molecules in the vicinity of a metallic sphere are investigated in a phenomenological approach for very close molecule-surface distances d . The Fuchs-Claro model [Phys. Rev. B **35**, 3722 (1987)] is adopted to describe the polarizability of the sphere with the nonlocal dielectric response being accounted for within the hydrodynamic description. The results show significant differences when compared with those obtained previously within a local description for $d \lesssim 50$ Å, with extra resonances observed in the high-frequency regime, a phenomenon similar to that noted previously by Ruppin in his calculation of the extinction cross section for such spheres.

The problem of fluorescence lifetimes for molecules in the vicinity of spherical particles has been studied considerably in the past decade.¹⁻⁶ Motivations for such studies include the intriguing effects on such lifetimes observed in metallic cavities,⁷ in the vicinity of rough surfaces (which can be represented as a collection of such particles in the "island surface" model),^{2,3} and in the vicinity of other particulate systems, such as colloidal solutions.⁸ Following the success of the phenomenological electrodynamic formulation for such a problem in the case of flat surfaces,⁹ such an approach has been adopted by many previous researchers for the case of spherical substrates because of its simplicity.¹⁻⁵ In particular, the case with an isolated sphere with the admolecule located both outside and inside the sphere,^{4,5} as well as the case of a collection of spheres,^{2,3} have all been studied thoroughly, either in the electrostatic limit (the image theory)^{2,3} or in the more exact electrodynamic treatment.^{1,4,5} However, it is well known that all such phenomenological treatments will break down when the molecule is very close to the surface, due mainly to the neglect of the nonlocal responses of the substrate, among other microscopic (quantum) effects. The simplest way to comprehend such failure is to note that the local dielectric function used in all these theories^{1-5,7} will be justified only in regions when the electric field varies smoothly, which is, of course, not the case in the vicinity of the surface at which such field becomes discontinuous according to the local description.¹⁰ Such failure has already been noted in the case of flat surfaces, and modifications for such phenomenological molecular decay rates have already been obtained previously in the literature.¹¹ The results show that for molecule-surface distances $d \lesssim 50$ Å, the nonlocal effects become important and lead to deviations from the d^{-3} dependence, consistent with the more recent microscopic calculation using the density-functional approach.¹²

The nonlocal electromagnetic effects in the vicinity of a substrate surface have been studied intensively in the past 15 years, notably by Feibelman, and earlier work can be found in his momentous 1982 article.¹³ More recently, other microscopic approaches, such as the density func-

tional theory, and other phenomenological approaches have been extended to substrate of different geometries including both spherical and cylindrical particles.^{6,14-17} In particular, Fuchs and Claro have published a very interesting and simple nonlocal treatment of the multipolar response of small metallic spheres.¹⁵ It is the purpose of this Brief Report to apply their model to investigate such nonlocal effects on the lifetimes (inverse decay rates) of admolecules near such spheres, leading to results which will be modifications to the previous works by us and others.¹⁻⁵ Since we expect such effects to be noticeable only for small molecule-surface distances, and since we have clarified in our previous investigations⁵ that for such distances ($d \lesssim 50$ Å) the static or long-wavelength limit formulation will be accurate enough, we shall adopt the simple image theory in our following study of the nonlocal effects on the molecular decay rates.

Within the image theory, the normalized decay rates for a molecular dipole located outside a sphere (radius a) can be expressed as follows (according to the two linearly independent orientations of the dipole moment):^{2,5}

$$\frac{\gamma_{\perp}}{\gamma_0} = 1 + \frac{3}{2k^3} \sum_{n=1}^{\infty} \left[\text{Im} \alpha_n(\omega) \frac{(n+1)^2}{d^{2(n+2)}} \right], \quad (1)$$

$$\frac{\gamma_{\parallel}}{\gamma_0} = 1 + \frac{3}{2k^3} \sum_{n=1}^{\infty} \left[\text{Im} \alpha_n(\omega) \frac{n(n+1)}{2d^{2(n+2)}} \right], \quad (2)$$

where \perp and \parallel denote, respectively, the radial and tangential orientations of the molecular dipole, ω and k the frequency and wave number of the oscillating dipole, and α_n denotes the n th polarizability of the substrate sphere, which is given by

$$\alpha_n(\omega) = \frac{n(\epsilon - 1)}{n(\epsilon + 1) + 1} a^{2n+1}, \quad (3)$$

with ϵ being the complex dielectric function of the sphere. γ_0 in Eqs. (1) and (2) denotes the decay rate of an isolated molecule. In the local description, one simply uses a frequency-dependent ϵ , which may be taken as the Drude form for metal spheres. The main ideas of the Fuchs-Claro model for the nonlocal description of α_n are

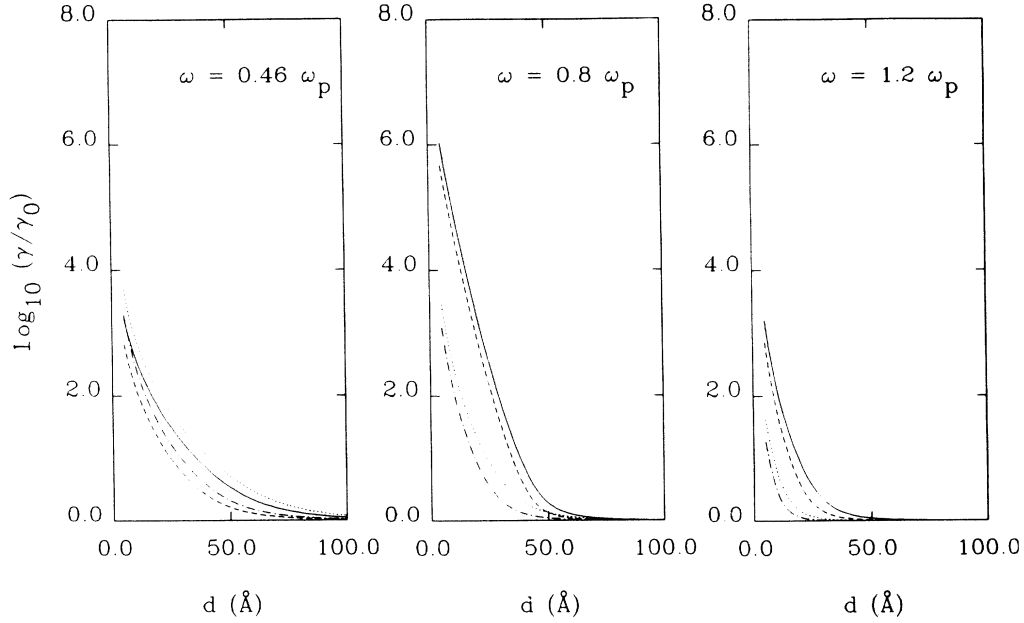


FIG. 1. Normalized decay rates for admolecules near a tin sphere (radius $a = 30 \text{ \AA}$) for distance $d \leq 100 \text{ \AA}$ at three fixed emission frequencies given in terms of the bulk plasmon frequency. The relevant numerical data (from Ref. 15) are $\omega_p = 1.17 \times 10^{16} \text{ s}^{-1}$, $\beta = \sqrt{3/5}v_F$, with the Fermi velocity v_F equal to $1.24 \times 10^8 \text{ cm s}^{-1}$, and the damping of the sphere $\Gamma = 0.003\omega_p$. The solid line (nonlocal) and the dotted line (local) are results for radial molecular dipoles, while the dashed line (nonlocal) and the dash-dotted line (local) are for tangential dipoles. Note the logarithmic scale used.

the following. The condition which leads to the abrupt change of the electric field across the boundary (namely, the continuity of the normal component of the displacement field) is now replaced by an artificial discontinuity condition characterized by a parameter δ ,¹⁴ which amounts to a fictitious external surface charge on the sphere. The potential functions (defined for both the \mathbf{D}

and the \mathbf{E} fields) inside the sphere can then be expressed in terms of δ . These functions and those for the outside fields are then required to match the ordinary boundary conditions. By eliminating δ from these matching equations, one can then arrive at an expression for α_n in terms of a nonlocal dielectric function $\epsilon(\mathbf{k}, \omega)$ in the form¹⁵

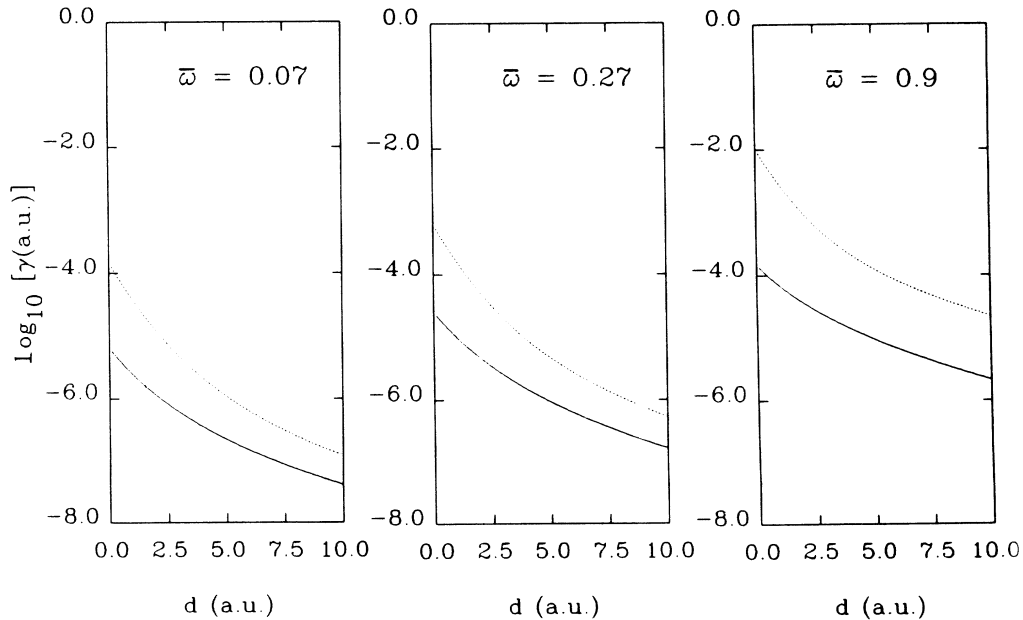


FIG. 2. Distance dependence of admolecular decay rate for a sodium sphere of radius 18.057 a.u. and only for radial dipoles. Atomic units are used in accord with Ref. 6, with $\bar{\omega}$ defined as $\sqrt{3}\omega/\omega_p$. Other data for the computation (from Ref. 6) are $\omega_p = 5.9 \text{ eV}$, $v_F = 1.07 \times 10^8 \text{ cm s}^{-1}$, and $\Gamma = 10 \text{ meV}$. The solid line is for nonlocal results and the dotted line for local results.

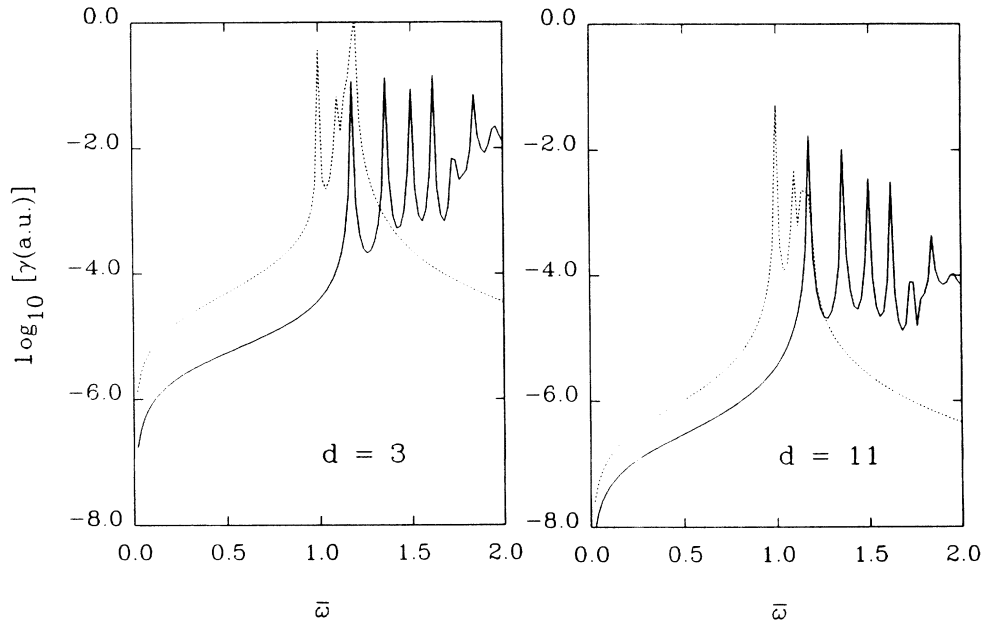


FIG. 3. Same system as in Fig. 2, except here the distance d (in a.u.) is fixed and the emission frequency is varied.

$$\alpha_n(\omega) = \frac{n(E_n - 1)}{n(E_n + 1) + 1} a^{2n+1}, \quad (4)$$

with

$$E_n(\omega) = \left[\frac{2}{\pi} (2n+1) a \int_0^\infty \frac{j_n^2(ka)}{\epsilon(\mathbf{k}, \omega)} dk \right]^{-1}, \quad (5)$$

where j_n is the spherical Bessel function of order n . Adopting a hydrodynamic model for $\epsilon(\mathbf{k}, \omega)$,¹⁸ Fuchs and Claro finally obtained¹⁵

$$E_n(\omega) = \left[\frac{1}{\epsilon} + (2n+1) \left(\frac{a\omega_p}{\beta u} \right)^2 \times I_{n+1/2}(\omega) K_{n+1/2}(\omega) \right]^{-1}, \quad (6)$$

where ϵ is the local (Drude) function with the following familiar form:

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\Gamma)}. \quad (7)$$

I and K are the modified Bessel functions, and the definitions of β and u are given in Ref. 15.

We have used the α_n given in Eqs. (4)–(7) to study the nonlocal effects on the molecular decay rates Eqs. (1) and (2). Some of the results are presented in Figs. 1–3, and the details of the data for the numerical computation are given in the figure captions. Note that the values for the damping of the spheres ($\Gamma \sim 10^{-3}\omega_p$) are chosen in accordance with Refs. 15 and 6, and the discussion for such choices can be found in an earlier paper by Ekardt.¹⁹ Figure 1 shows the variation of the normalized decay rates with molecule-surface distances d for a tin sphere, from which one sees that, while the tangential orientation

leads to a lower decay rate due to the antiparallel nature of the image dipole as noted before,⁵ both the radial and tangential dipolar decay rates are reduced by the nonlocal responses of the sphere for low emission frequencies and are increased for high emission frequencies. This is consistent with the numerical results obtained by Fuchs and Claro.¹⁵ Figure 2 shows the results for radial dipoles near a sodium substrate sphere. Note that atomic units are used in order to make the comparison with the results of Ref. 6 (in which both γ and d are measured in a.u.) more apparent. In addition, we introduced the frequency variable $\bar{\omega} \equiv \omega/\omega_{sp}$, with $\omega_{sp} = \omega_p/\sqrt{3}$, in accord with Ref. 6. The γ here represents only the part induced by the sphere and with the molecular dipole moment equal to 1 a.u., γ can be expressed as⁶

$$\gamma = 4 \sum_{n=1}^{\infty} \text{Im}\alpha_n(\omega) \frac{(n+1)^2}{d^{2(n+2)}}. \quad (8)$$

From the results in Fig. 2, it can be seen that the nonlocal effects tend to lower the decay rates for emission frequencies up to $0.52\omega_p$, in contrast to those obtained by Ekardt and Penzar,⁶ who followed their previously well-developed time-dependent density-functional theory (TDDFT) and found that the microscopic (nonlocal) results lead to decay rates lying consistently above the local values. This may be due to the fact that our present description, using the hydrodynamic model for $\epsilon(\mathbf{k}, \omega)$, is known to be crude and for being incapable of accounting for single-particle excitations (e.g., electron-hole pair excitation) which are especially important in the high-frequency regime.¹⁸ Figure 3 shows the variation of the decay rates with frequencies at fixed distances for the same sodium sphere as in Fig. 2. While it is observed that extra resonances appear in the high-frequency regime, a phenomenon similar to that noted previously by

Ruppin²⁰ in his calculation of the extinction cross section for such spheres, it is of great interest to note that such results seem to have just the reverse trend when compared with those obtained by Eckardt and Penzar in their TDDFT calculations. In the later work, it seems that the peaks from the local theory are red shifted (versus the blue-shifted results, as obtained in both the present work and that of Ruppin²⁰), and the extra resonances appear in the low-frequency regime instead. Since the microscopic (TDDFT) approach is highly computational in nature,⁶ and thus far it seems that there still lacks significant experimental data for such nonlocal effects to be observed, it would be of great interest to extend the present phe-

nomenological calculation adopting other models for the dielectric function²¹ and to compare with the TDDFT results. Such comparison will lead to a more physical understanding of the nonlocal effects on such molecular decay processes. At present, work is in progress along this direction.

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