Laser-Induced Forces in Metallic Nanosystems: The Role of Plasmon Resonances

Ping Chu* and D. L. Mills†

Department of Physics and Astronomy, University of California, Irvine, California 92697, USA

(Received 21 March 2007; published 17 September 2007)

We present calculations of the laser-induced force between metallic nanospheres, similar and dissimilar in character, and that between a metallic nanosphere and a planar surface. When the separation between these objects is in the 0.5–2 nm range, we find very strong resonances in the laser-induced force associated with excitation of plasmon resonances. Measurement of such forces will provide direct access to the plasmon enhancements of laser fields so critical to optical spectroscopy in the nanoenvironment.

DOI: 10.1103/PhysRevLett.99.127401 PACS numbers: 78.67.−n, 73.22.Lp, 78.20.Bh

When two metallic nanospheres are in close proximity, and the pair is illuminated by laser radiation, there is a laser-induced attractive force between them which scales in strength linearly with power. When arrays of such spheres are suspended in a liquid, this force can be exploited to promote aggregation. With this context in mind, Hallock, Redmond, and Brus have presented theoretical studies of this laser-induced attractive force, and they have compared its strength for a selected laser power with the competing van der Waals attraction [1]. In all calculations that they present, they find the force to vary monotonically with separation between the spheres.

It is also the case that when two conducting spheres are very close together, and they are illuminated by laser radiation, if the laser frequency is appropriate, a collective plasmon mode of the pair of spheres may be excited. This can produce strongly enhanced electric fields in the region between the spheres. A molecule adsorbed near the pole of one such sphere is then immersed in very intense laser fields, with the consequence that the Raman signal from the molecule is enhanced by orders of magnitude over the already very large signals associated with the classical electrochemical geometry in which surface-enhanced Raman scattering was first realized [2].

More recently strongly enhanced fields such as those just discussed play a critical role in another context. There is great interest in the study of single molecules under an STM tip, where the tip-molecule-substrate system is illuminated by a laser. Recently, for example, through exploitation of photon-induced tunneling into the lowest unoccupied molecular orbital + 1 state of a Mg porphine molecule, subangstrom spatial resolution has been achieved with an optical probe [3]. Clearly, plasmon-enhanced fields in this geometry play a central role in the success of such experiments. Detailed theoretical studies of plasmon-enhanced fields associated with the STM tip-metal substrate combination have appeared, with such optical probes in mind [4]. Very strong field enhancements indeed can be realized, and these are spread over a much broader spectral range than found on the roughened surfaces used in early surface-enhanced Raman scattering (SERS) experiments.

In this Letter, we present a series of calculations which show that, when two metallic nanospheres are very close together or when such a nanosphere is very close to a metallic substrate, laser excitation of the collective plasmon modes of the system produces extremely large enhancements of the laser-induced force between the two elements of the system. For realizable laser powers, these resonantly enhanced attractive forces can be much larger than the van der Waals attraction. For the case of a nanosphere placed near a metal surface, the forces are large enough that they should be readily measurable. Our calculations allow that, as two metallic spheres are brought together or as such a sphere is brought close to a suitable metallic substrate, at particular separations a collective plasmon excitation of the system passes through the laser frequency, thus producing a dramatic enhancement of the laser-induced force. Our results, the first to show this remarkable effect, stand in contrast to the monotonic behavior reported in Ref. [1]. It is the case, in fact, that the laser frequency employed in their studies is too low for the collective plasmon enhancement to be realized, in all calculations presented in Ref. [1].

We envision an experimental study wherein a metallic nanosphere is attached to the tip of an atomic force microscope (AFM) and brought within a nanometer or so of a conducting surface, and then a laser is focused down onto the nanosphere. The direct measurement of the magnitude of this force and comparison between data and calculations such as we present would be a most important means of confirming that indeed the enhanced fields between the sphere and substrate are truly present, with a magnitude comparable to that described by theory. We note that it is difficult to extract clear information on enhanced optical fields from nonlinear optical probes of molecules, since the basic molecular cross section can be much larger in the adsorbed state than in the liquid environment [5]. An exception is an early experiment by Tsang, Kirtley, and Theis [6], wherein SERS fields are directly and unambig-

uously measured, we might remark. Thus, an experiment such as that proposed above will offer clear insight into the nature of enhanced optical fields in the nanoenvironment.

The systems we consider have all relevant dimensions very small compared to the wavelength of light, in the frequency regime of concern. Hence, one may use quasistatic theory to discuss the nature of the electromagnetic fields in the vicinity of these structures. On this length scale, the incident laser field may be viewed as spatially uniform. Some years ago, in a discussion of the collective plasmons of a system of two nearby identical spheres, it was pointed out that within bispherical coordinates one may solve the underlying electrostatic problem in terms of elementary functions [7]. Rendell and his co-workers explored plasmon effects associated with a conducting sphere near a planar surface within the same framework [8], and the studies cited above of plasmon-induced field enhancements in the STM environment [4] were based on an adaptation of their approach. Our present analysis is also carried out through use of bispherical coordinates. We have generalized the earlier studies to the case where we have two spheres, one of radius R_1 and one of radius R_2, possibly made of dissimilar materials and separated by the distance d. We study the response of such a system to spatially uniform applied fields, either parallel or perpendicular to the symmetry axis of the system. The force on a given sphere is calculated by integrating the Maxwell tensor over its surface. Our calculations of the force follow the approach in Ref. [1], where details of the calculation are discussed. The mathematical details of our analysis will be presented elsewhere [9]. We now turn to our results.

The collective modes of two spheres for which the z axis passes through the centers of both are described by the azimuthal quantum number m; the electrostatic potential associated with these modes has the angular variation $\exp(im\varphi)$, where φ is the azimuthal angle of the spherical coordinate system. When we consider a z-polarized laser field incident on the pair of spheres, only the collective modes with $m = 0$ are excited. In Fig. 1(a), we show, for two identical idealized spheres with dielectric constant $\varepsilon(\omega) = 1 - (\omega_P/\omega)^2$, three of the collective modes each characterized by $m = 0$. In addition to m, we may characterize each mode by its asymptotic frequency at large separation $\omega_l^\infty = \omega_P[l/(2l+1)]^{1/2}$. For each limiting frequency ω_l^∞, we have two branches, one whose electrostatic potential has even symmetry under reflection in the xy plane (the lower branch) and one with odd symmetry (the upper branch). A z-polarized laser field can excite only the lower branch. We see that, as the spheres are brought together, the frequency of the lower branches drops in frequency substantially, to approach finite values when the spheres just touch. In the limit of large separation, the modes in black reduce to the dipole Mie resonance of the isolated sphere, and the remaining two are the $l = 2, 3$ multiple modes in this limit. In Fig. 1(b), we show the frequency of the three first odd parity collective $m = 0$ plasmon modes for two Ag spheres whose radii are 30 nm, as a function of their separation. When their separation is in the range of 0.5–2 nm, we see that we have collective modes in the visible range of the spectrum. If we illuminate the spheres with a laser of fixed frequency, as we will see next, we will see dramatic resonant enhancement of the laser-induced force between the spheres as they are brought together, when the intersphere separation is such that a collective mode matches the laser frequency.

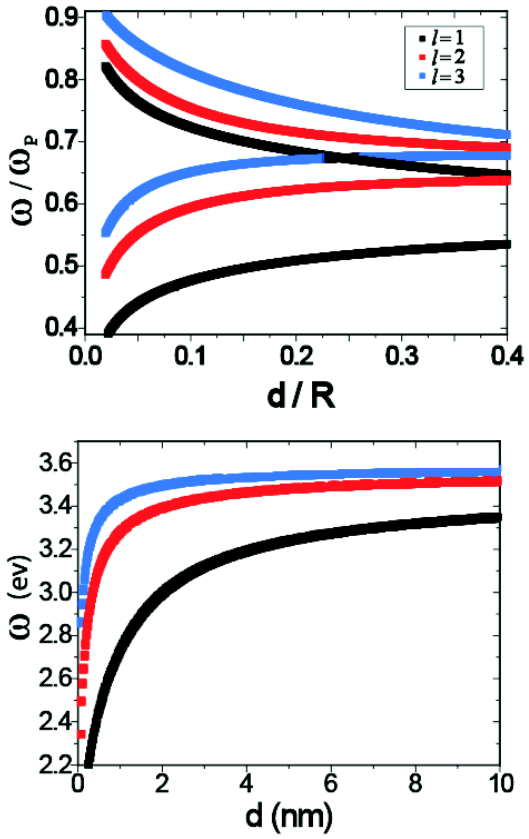

FIG. 1 (color online). An illustration of the $m = 0$ collective mode spectrum of two conducting spheres. In (a), we have two ideal metal spheres for which $\varepsilon(\omega) = 1 - \omega_P^2/\omega^2$, and, in (b), we show the lower branches for two Ag spheres with 30 nm radii.

In Fig. 2, we show the time-averaged laser-induced force between two sets of spheres, for the case that they are illuminated by a laser with 3 eV photons and also for 3.3 eV photon energy. For the Ag spheres, we have used the complex dielectric constant given by Johnson and Christy [10]. The laser power is assumed to be 100 kW/cm^2. Note that, if the beam of a 1 W laser is focused down to a spot size of 5 microns, the laser power in the focal plane will be more than 1000 kW/cm^2. Thus, if desired, it should not be difficult to illuminate metallic nanostructures with laser powers in excess of those employed in Fig. 2. Recall that the laser-induced force scales linearly with laser power. The black lines in Fig. 2 are the van der Waals attraction between the two spheres, calculated through use of the formulas given in the text by

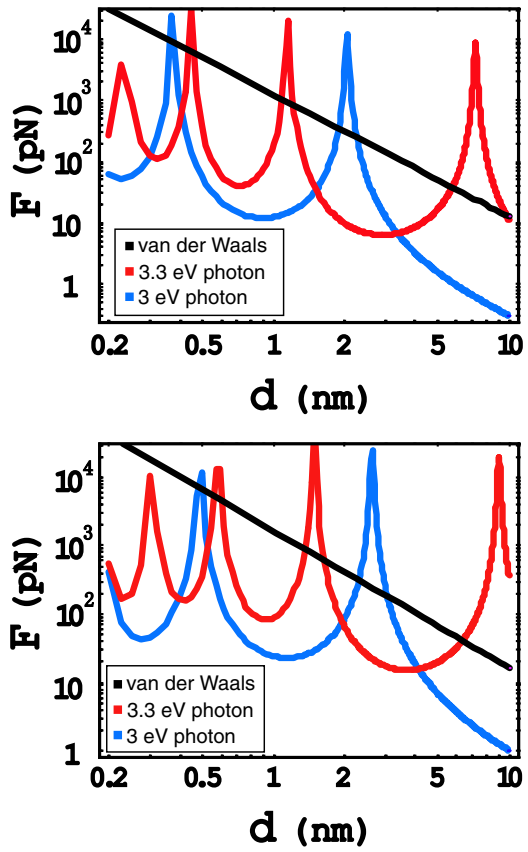

FIG. 2 (color online). We show the laser-induced resonant force for four cases, compared to the strength of the van der Waals attraction (black). In (a), we have two Ag spheres, each with radius $R = 30$ nm. In (b), we have a Ag sphere with radius 30 nm and one with radius 60 nm. Each figure has two cases of the photon energy with 3 (blue) and 3.3 eV (red). The laser power is assumed to be 100 kW/cm^2.

Israelachivili [1]. When the separation $d \ll R$, this force is given as $F = AR/12d^2$, where A is the Hamaker constant.

In Fig. 2(a), the forces between two identical Ag spheres with a radius of 30 nm are displayed. The photon energies are 3 (blue) and 3.3 eV (red), with power level 100 kW/cm^2. For 3 eV photon energy (the blue curve), we see that at resonance the force exceeds the strength of the van der Waals force considerably at two of the collective mode frequencies in Fig. 1(b). Keep in mind that the scale in Fig. 2 is logarithmic. In Fig. 2(b), again for 3 and 3.3 eV photons, we show the behavior of the forces between two dissimilar Ag spheres as a function of separation, for the case where one sphere has radius of 30 nm and the second 60 nm. The first prominent resonance for the two dissimilar spheres moves out to 3 nm at 3 eV photon energy, in contrast to 2 nm for the two identical spheres described in Fig. 2(a). For the case where the radii are not equal to each other, we have two collective modes for each asymptotic frequency, the same as in the case of two identical spheres. However, if the radii are different, the high frequency branch becomes dipole active by virtue of the absence of reflection symmetry in the xy plane, and we find resonances similar to those illustrated in Fig. 2 in the near ultraviolet as a consequence. Of course, these resonances will be more challenging to access experimentally, since an ultraviolet laser is required. When the laser frequency is increased to 3.3 eV (red curves), now we see three dramatic resonances which greatly exceed the van der Waals force, and each moves out to a larger intersphere separation. Thus, a modest increase in laser frequency has a dramatic effect on both the magnitude of the force at a fixed power level and the separations where the resonance is observed.

In Fig. 3, we show calculations for the laser-induced force between a Ag sphere and an underlying flat metal surface, as a function of distance of the "south pole" of the sphere from the surface. The calculations of the red curve explore how a Ag sphere moves in toward a Ag surface, and the blue curve shows the same between a Ag sphere and a NiAl surface [11]. We again have three prominent resonances which exceed the van der Waals force between a Ag sphere and a Ag surface. It would be most intriguing to measure the laser-induced force for a nanosphere attached to an AFM cantilever, poised over a Ag surface, as discussed above.

The calculations between a Ag sphere and a NiAl surface are motivated by the configuration used in the experiments reported in Ref. [3], where measurements of laser-induced fluorescence employ a Ag-coated STM tip near a NiAl(110) surface. The fluorescence for the case of a Ag-coated STM tip is very much more intense than that found when a W-coated tip is employed. Clearly, then, surface plasmon-enhanced fields are responsible for the difference. We remark that it is not obvious that one should expect strong enhancement effects for this tip-substrate combination, because NiAl is very lossy throughout the visible. A plot of the surface loss function $\mathrm{Im}\{-1/[1 + \varepsilon_{\mathrm{NiAl}}(\omega)]\}$ from 1 eV through the visible shows no sign of a surface plasmon resonance. One might then suppose that, when the Ag STM tip is very close to the NiAl surface, the Ag

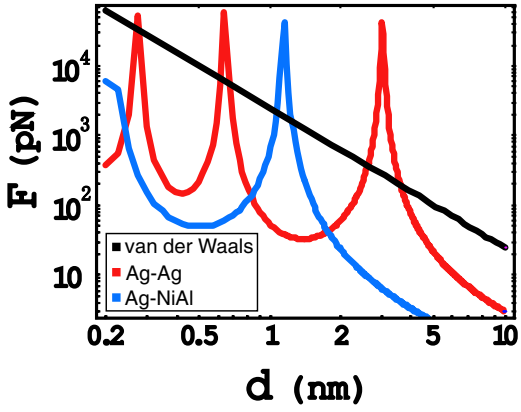

FIG. 3 (color online). The laser-induced force between a Ag sphere of radius 30 nm and a flat Ag surface (red) and a NiAl surface (blue). The photon energy is 3 eV, and the laser power is 100 kW/cm^2.

plasmons would be heavily damped by the near proximity of the tip to the lossy substrate. As we see from Fig. 3 (the blue curve), this appears not to be the case. It would be of great interest to see AFM studies of the laser-induced force between a Ag sphere and a NiAl surface and a comparison with that between a W sphere and the NiAl surface.

We have also carried out calculations when the laser field is perpendicular to the axis of symmetry of the system. Now the laser field couples to the $m = \pm 1$ collective modes of the structure. Just as in Fig. 1(a), the $m = \pm 1$ manifold consists of two sets of branches, one set with a frequency higher than the Mie resonance of the isolated sphere and one set with a lower frequency. If one has two identical spheres, in contrast to the case where the electric field is parallel to the axis of symmetry, it is now the branches above the Mie resonance of the isolated sphere which are dipole active. These increase with frequency as the two spheres approach each other, in a manner similar to the high frequency branches in Fig. 1(a). When one considers two dissimilar spheres, reflection symmetry in the xy plane is broken, with the consequence that both branches couple to the laser field as in the case of parallel excitation. When we compare the magnitude of the resonance in the laser-induced force for the case where the laser field is perpendicular to the axis of symmetry to the case where it is parallel, we find that on resonance for two Ag spheres it is weaker by roughly 2 orders of magnitude. Thus, it will be necessary to employ powers considerably larger than those used in the calculations reported here, if the resonances are to be observed in perpendicular excitation. An interesting feature of the force in this geometry is that the line shape is more complex, and just above resonance we find a spectral regime where the force is repulsive in character. The dip is shallow, unfortunately, for the cases we have explored.

We conclude by noting that Fuchs and Claro [12] have also discussed the possibility of laser-induced resonant forces between two identical metal spheres. They treat each sphere as a point dipole, a picture that breaks down qualitatively when the two spheres are close to each other. The calculations presented here show that resonant enhancement occurs only when the separation d between the objects is very small indeed compared to the radius of the two entities. Thus, the formulas in Ref. [12] are not useful for quantitative purposes. They also assume each sphere to have a single Mie resonance, whereas we have seen above that the higher order collective modes produce very strong signatures as well. We have explored the spatial variation of the plasmon-enhanced fields for the small separations where resonances are found, to find them highly localized around the south pole of the upper object and the north pole of the lower object. As noted in earlier discussions [4], the relevant length scale in the plane perpendicular to the symmetry axis is $(dR)^{1/2}$, and this is a small fraction of the radius of the sphere when $d \ll R$, which we see from our calculations is the regime where the resonance can be observed.

In conclusion, we present calculations which show that, when two metallic spheres are close to each other or when such a sphere is close to a conducting plane, there are very strong resonances in the laser-induced force between the two entities, with an origin in collective plasmon resonances excited by the laser field. These can lie in the visible frequency range under the conditions outlined and can exceed the attractive van der Waals forces when the separation between objects is in the range of 0.5–2 nm.

This research was supported by Department of Energy Grant No. DE-FG03-84ER-45083.

*pingc@uci.edu
†dlmills@uci.edu

[1] A. J. Hallock, P. L. Redmond, and L. E. Brus, Proc. Natl. Acad. Sci. U.S.A. **102**, 1280 (2005). It appears that these authors underestimate the van der Waals force, through use of an incorrect value of the Hamaker constant. For correct values, see J. Israelachivili, *Intermolecular and Surface Forces* (Academic, New York, 1992), pp. 190–191, and W. B. Russell, D. A. Saville, and W. R. Showalter, *Colloidal Dispersions* (Cambridge University Press, Cambridge, England, 1989).

[2] For examples, see M. Inoue and K. Ohtaka, J. Phys. Soc. Jpn. **52**, 3853 (1983); H. Xu, E. J. Bjerneld, M. Kall, and L. Borjesson, Phys. Rev. Lett. **83**, 4357 (1999).

[3] S. W. Wu, N. Ogawa, and W. Ho, Science **312**, 1362 (2006).

[4] D. L. Mills, Phys. Rev. B **65**, 125419 (2002); Shiwei Wu and D. L. Mills, Phys. Rev. B **65**, 205420 (2002).

[5] M. Udagawa, C. C. Chou, J. C. Hemminger, and S. Ushioda, Phys. Rev. B **23**, 6843 (1981).

[6] J. C. Tsang, J. R. Kirtley, and T. N. Theis, Solid State Commun. **35**, 667 (1980).

[7] P. K. Aravind, A. Nitzan, and H. Metiu, Surf. Sci. **110**, 189 (1981).

[8] R. W. Rendell, D. J. Scalapino, and B. Muhlschlegel, Phys. Rev. Lett. **41**, 1746 (1978); R. W. Rendell and D. J. Scalapino, Phys. Rev. B **24**, 3276 (1981).

[9] Ping Chu and D. L. Mills (to be published).

[10] P. B. Johnson and R. W. Christy, Phys. Rev. B **6**, 4370 (1972).

[11] For these calculations, we require both the real and the imaginary parts of the frequency-dependent dielectric constant of NiAl. In the literature, one finds only data on the imaginary part (or, equivalently, the real part) of the conductivity. We are grateful to Professor Joo Rull Yee for providing us his data on both the real and the imaginary parts of the optical dielectric constant of NiAl.

[12] R. Fuchs and F. Claro, Appl. Phys. Lett. **85**, 3280 (2004).