Size-Dependent Surface Plasmon Dynamics in Metal Nanoparticles

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We study the effect of Coulomb correlations on the ultrafast optical dynamics of small metal particles. We demonstrate that a surface-induced dynamical screening of the electron-electron interactions leads to quasiparticle scattering with collective surface excitations. In noble-metal nanoparticles, it results in an interband *resonant scattering* of *d* holes with surface plasmons. We show that this size-dependent many-body effect manifests itself in the differential absorption dynamics for frequencies close to the surface plasmon resonance. In particular, our self-consistent calculations reveal a strong frequency dependence of the relaxation, in agreement with recent femtosecond pump-probe experiments. [S0031-9007(98)07279-2]

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The absorption of light by metal nanoparticles is dominated by the surface plasmon (SP) resonance. In small particles, the strong three-dimensional confinement changes both the static and dynamic optical properties. For example, the scattering of single-particle excitations at the surface leads to SP damping and to a resonance linewidth inversely proportional to the nanoparticle size [1]. Another static effect is the size-dependent enhancement of the nonlinear optical susceptibilities [2,3]. At the same time, the effect of confinement on dynamical properties is much less understood [1]. Ultrafast optical spectroscopy allows one to address the dynamical aspects by probing the time evolution of the excited states with a resolution shorter than the dephasing or energy relaxation times.

Recently, electron relaxation in nanoparticles attracted much interest [4–9]. Ultrafast pump-probe experiments [6,8] performed on noble-metal particles reported a time-dependent spectral broadening of the SP resonance, originating from the pump-induced heating of the electron gas. The *inelastic* carrier scattering was found to be essential for understanding the differential transmission line shape [6]. Similar to metal films [10–12], the dynamics revealed an initial nonequilibrium stage during which the *e*-*e* scattering leads to thermalization of the electron distribution, followed by a relaxation to the lattice. However, certain aspects of the optical dynamics in nanoparticles were observed to differ significantly from films. In particular, experimental studies of small Cu nanoparticles [6] revealed considerably faster relaxation above and below the SP resonance. These observations suggest that, in strongly confined systems, collective surface excitations should play an important role in the electron dynamics.

In this paper we address the role of collective surface excitations in the electron relaxation in metal nanoparticles. We demonstrate that the *e*-*e* interactions *inside* small particles are strongly modified due to a surface-induced dynamical screening. This leads to a possibility of quasiparticle scattering accompanied by the emission of SP's. We show, in particular, that in noble-metal particles, this novel size-dependent many-body mechanism results in a resonant scattering of the *d* hole into the conduction band. The latter effect manifests itself in a strong frequency dependence of the optical dynamics close to the SP resonance, and can be observed experimentally with ultrafast pump-probe spectroscopy.

We consider spherical metal particles, embedded in a medium with dielectric constant ϵ_m, with radii R sufficiently small, so that only dipole surface modes can be optically excited. The optical properties of such a colloid are determined by the dielectric function, $\epsilon_m + 3p\epsilon_m(\epsilon - \epsilon_m)/(\epsilon + 2\epsilon_m)$, where $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$ is that of a single metal particle and $p \ll 1$ is the volume fraction occupied by the nanoparticles. For noble metals, $\epsilon(\omega)$ includes the (complex) interband dielectric function, $\epsilon_d(\omega)$, associated with the *d* electrons. The absorption coefficient is then given by [1]

$$\alpha(\omega) = -9p \frac{\omega}{c} \epsilon_m^{3/2} \operatorname{Im} \frac{1}{\epsilon_{\mathrm{sp}}(\omega)}, \qquad (1)$$

with

$$\epsilon_{\mathrm{sp}}(\omega) = \epsilon_d(\omega) - \omega_p^2/\omega(\omega + i\gamma_s) + 2\epsilon_m. \qquad (2)$$

Here $\gamma_s \sim v_F/R$ characterizes the SP damping by intraband *e*-*h* excitations due to the surface scattering, and ω_p is the plasmon frequency of the conduction (*s*-*p*) electrons. The SP frequency, ω_{sp}, is determined by $\epsilon'_{\mathrm{sp}}(\omega_{\mathrm{sp}}) = 0$.

Equation (1) describes the linear absorption by large metal clusters. When the electron gas is in the quasiequilibrium with the lattice, the temperature dependence of $\alpha(\omega)$ also determines the time evolution of the differential absorption measured by pump-probe spectroscopy. This is the case for time delays between the pump and the

probe optical pulses longer than ~ 1 ps [10–12]. Since for electron temperature T much smaller than the Fermi energy E_F, the intraband contribution to $\epsilon_{sp}(\omega)$ is nearly T independent, the SP dynamics comes mainly from the T dependence of the *interband* dielectric function $\epsilon_d(\omega)$. The latter is typically approximated by its bulk expression calculated for noninteracting electrons [1]. In such a model, the SP dynamics is essentially size independent.

Here we point out that in small particles, there is a size-dependent contribution to $\epsilon_d(\omega)$ that arises from an interband d-hole scattering mechanism, absent in bulk metals. This many-body effect originates from the fact that the collective surface excitations strongly modify the dynamically screened e-e interactions inside nanoparticles, as we demonstrate below.

The screened Coulomb potential at point $\mathbf{r}$ arising from an electron at point $\mathbf{r}'$ inside a spherical particle, $U_\omega(\mathbf{r}, \mathbf{r}')$, is determined by the equation [13]

$$U_\omega(\mathbf{r}, \mathbf{r}') = U(\mathbf{r} - \mathbf{r}')$$
$$+ \int d\mathbf{r}_1 \, d\mathbf{r}_2 \, U(\mathbf{r} - \mathbf{r}_1) \Pi_\omega(\mathbf{r}_1, \mathbf{r}_2) U_\omega(\mathbf{r}_2, \mathbf{r}'), \quad (3)$$

where $U(\mathbf{r} - \mathbf{r}')$ is the unscreened Coulomb potential and $\Pi_\omega(\mathbf{r}_1, \mathbf{r}_2)$ is the polarization operator. The latter includes contributions from the conduction and d band, as well as from the surrounding medium, $\Pi_\omega = \Pi_\omega^c + \Pi_\omega^d + \Pi_\omega^m$. For simplicity, we assume here step density profiles, $n_i(\mathbf{r}) = \bar{n}_i \theta(R - r)$, $i = c, d$, where $\bar{n}_c$ ($\bar{n}_d$) is the average density of the conduction (d) electrons. For the high frequencies of interest, Π_ω^c can be expanded in $1/\omega$, yielding to lowest order [14] $\Pi_\omega^c(\mathbf{r}, \mathbf{r}_1) = -(1/m\omega^2)\nabla[n_c(\mathbf{r})\nabla\delta(\mathbf{r} - \mathbf{r}_1)]$. The d-band contribution to the right-hand side (rhs) of Eq. (3) can be found from the relation

$$-e^2 \int d\mathbf{r}_1 \, \Pi_\omega^d(\mathbf{r}, \mathbf{r}_1) U_\omega(\mathbf{r}_1, \mathbf{r}') = \nabla \mathbf{P}_\omega^d(\mathbf{r}, \mathbf{r}'), \quad (4)$$

where $\mathbf{P}_\omega^d(\mathbf{r}, \mathbf{r}') = -\chi_d(\omega)\nabla U_\omega(\mathbf{r}, \mathbf{r}')$ is the d-band polarization vector ($\mathbf{P}_\omega^d = 0$ outside the nanoparticle) and $\chi_d = (\epsilon_d - 1)/4\pi$ is the interband susceptibility. Π_ω^m can be obtained from a similar relation (with $\mathbf{P}_\omega^m = 0$ inside the nanoparticle). After some algebra, Eq. (3) takes the form

$$\left(\epsilon_d - \frac{\omega_p^2}{\omega^2}\right) U_\omega(\mathbf{r}, \mathbf{r}') = U(\mathbf{r} - \mathbf{r}') + \left(\frac{\epsilon_d - \epsilon_m}{4\pi} - \frac{e^2 \bar{n}_c}{m\omega^2}\right)$$
$$\times \int d\mathbf{r}_1 \, \nabla_1 \frac{1}{|\mathbf{r} - \mathbf{r}_1|} \nabla_1 \theta(R - r_1)$$
$$\times U_\omega(\mathbf{r}_1, \mathbf{r}'), \quad (5)$$

with $\omega_p^2 = 4\pi e^2 \bar{n}_c/m$. We solved Eq. (5) by expanding U_ω in spherical harmonics, $Y_{LM}(\hat{\mathbf{r}})$. The solution reads [15]

$$U_\omega(\mathbf{r}, \mathbf{r}') = \frac{U(\mathbf{r} - \mathbf{r}')}{\epsilon(\omega)} + \frac{e^2}{R} \sum_{LM} \frac{4\pi}{2L + 1} \left(\frac{rr'}{R^2}\right)^L$$
$$\times Y_{LM}(\hat{\mathbf{r}}) Y_{LM}^*(\hat{\mathbf{r}}') \left[\frac{1}{\epsilon_L(\omega)} - \frac{1}{\epsilon(\omega)}\right], \quad (6)$$

where $\epsilon(\omega) = \epsilon_d(\omega) - \omega_p^2/\omega^2$. Here $\epsilon_L(\omega) = \epsilon_L'(\omega) + i\epsilon_L''(\omega)$ is an effective dielectric function, whose zeros, $\epsilon_L'(\omega) = \frac{L}{2L+1}[\epsilon_d'(\omega) - \omega_p^2/\omega^2] + \frac{L+1}{2L+1}\epsilon_m = 0$ determine the frequencies of the multipole collective surface excitations [1]. Note that $\epsilon_L''(\omega)$ contains a correction due to the damping of collective excitations by electron-hole pairs, which can be obtained by adding Im Π_ω^c to the rhs of Eq. (5).

Equation (6) represents a generalization of the plasmon pole approximation for spherical particles. The two terms in the rhs describe two distinct contributions. First is the usual bulklike screening of the Coulomb potential. The second, *size-dependent* contribution describes a new effective e-e interaction induced by the *surface*: the potential of an electron inside the nanoparticle excites collective surface modes, which in turn act as image charges that interact with the second electron. For frequencies close to that of the SP, it is sufficient to retain only the resonant dipole term, $L = 1$. The corresponding surface-induced e-e interaction potential is then

$$U_\omega^{sp}(\mathbf{r}, \mathbf{r}') = 3\frac{e^2}{R} \frac{\mathbf{r} \cdot \mathbf{r}'}{R^2} \frac{1}{\epsilon_{sp}(\omega)}, \quad (7)$$

where $\epsilon_{sp}(\omega) = 3\epsilon_1(\omega)$ is the same as in Eq. (2). Thus, for sufficiently small R, the dynamically screened Coulomb potential in the nanoparticle is dominated by the SP pole. This leads to the possibility of quasiparticle scattering accompanied by the emission of a SP.

In particular, consider the SP-mediated scattering of the d hole into the conduction band. This process is described by the Matsubara self-energy due to the potential (7) [13]

$$\Sigma_\alpha^d(i\omega) = -3\frac{e^2}{R^3} \sum_{\alpha'} \frac{1}{\beta} \sum_{i\omega'} \frac{|\mathbf{d}_{\alpha\alpha'}|^2}{\epsilon_{sp}(i\omega')} G_{\alpha'}^c(i\omega' + i\omega). \quad (8)$$

Here $\mathbf{d}_{\alpha\alpha'} = \langle c, \alpha | \mathbf{r} | d, \alpha' \rangle = \langle c, \alpha | \mathbf{p} | d, \alpha' \rangle / im(E_\alpha^c - E_{\alpha'}^d)$ (we set $\hbar = 1$), where $|c, \alpha'\rangle$ ($|d, \alpha'\rangle$) and E_α^c (E_α^d) are the conduction (d-) band eigenstates and eigenenergies, respectively, and G_α^c is the Green function of noninteracting conduction electrons. For a quasicontinuous spectrum, the matrix element can be approximated by a bulklike expression, $\langle c, \alpha | \mathbf{p} | d, \alpha' \rangle = \delta_{\alpha\alpha'}\langle c | \mathbf{p} | d \rangle \equiv \delta_{\alpha\alpha'}\mu$, the corrections due to the surface scattering being $\sim R^{-1}$. After frequency summation, Im Σ_α^d takes the form

$$\text{Im} \, \Sigma_\alpha^d(E) = -\frac{9e^2\mu^2}{m^2(E_\alpha^{cd})^2 R^3} \text{Im} \frac{N(E_\alpha^c - E) + f(E_\alpha^c)}{\epsilon_{sp}(E_\alpha^c - E)}, \quad (9)$$

where $E_\alpha^{cd} = E_\alpha^c - E_\alpha^d$, and $f(E)$ and $N(E)$ are the Fermi and Bose distributions, respectively.

We see from Eq. (9) that the scattering rate of a d hole with energy E_α^d, $\gamma_h(E_\alpha^d) = \mathrm{Im}\,\Sigma_\alpha^d(E_\alpha^d)$, depends strongly on the nanoparticle size. Importantly, it exhibits a *peak* as the interband separation E_α^{cd} approaches the SP frequency ω_{sp}. The reason for such a sharp energy dependence is that the surface potential (7) induces only vertical (dipole) transitions, thus restricting the number of allowed final states.

Let us turn to the absorption spectrum. Consider an optically excited e-h pair with excitation energy ω close to the onset of interband transitions, Δ. As discussed above, the d hole can subsequently scatter into the conduction band by emitting a SP. Equation (9) indicates that for $\omega \sim \omega_{sp} \sim \Delta$, this process will be resonantly enhanced. In particular, this is the case in Cu and Au, where ω_{sp} and Δ are close to each other [6,8]. At the same time, the electron scatters in the conduction band via the usual two-quasiparticle process. For $\omega \sim \Delta$, the electron energy is close to E_F, and the scattering rate is $\gamma_e \sim 10^{-2}$ eV [16]. Using the bulk value of μ, $2\mu^2/m \sim 1$ eV near the L point [17], we find that γ_h exceeds γ_e for nanoparticles smaller than ~ 5 nm.

We now calculate the effect of the SP-assisted interband scattering on the absorption coefficient α. For noninteracting electrons, the interband susceptibility, $\chi_d(i\omega) = \tilde{\chi}_d(i\omega) + \tilde{\chi}_d(-i\omega)$, has the standard form

$$\tilde{\chi}_d(i\omega) = -\sum_\alpha \frac{e^2\mu^2}{m^2(E_\alpha^{cd})^2} \frac{1}{\beta} \sum_{i\omega'} G_\alpha^d(i\omega') G_\alpha^c(i\omega' + i\omega).$$

(10)

Since the d band is occupied for all energies, it is sufficient to include only the effect of d-hole scattering into $\tilde{\chi}_d(i\omega)$ [18]. Substituting $G_\alpha^d(i\omega') = [i\omega' - E_\alpha^d + E_F - \Sigma_\alpha^d(i\omega')]^{-1}$, with $\Sigma_\alpha^d(i\omega)$ given by Eq. (8), we obtain after the frequency summation

$$\tilde{\chi}_d(\omega) = \frac{e^2\mu^2}{m^2} \int \frac{dE^c\, g(E^c)}{(E^{cd})^2} \frac{f(E^c) - 1}{\omega - E^{cd} + i\gamma_h(\omega, E^c)},$$

(11)

where $g(E^c)$ is the density of states in the conduction band, and we assumed a dispersionless d band with energy E^d. Here $\gamma_h(\omega, E^c) = \mathrm{Im}\,\Sigma^d(E^c - \omega)$ is the scattering rate of a d hole with energy $E^c - \omega$,

$$\gamma_h(\omega, E^c) = -\frac{9e^2\mu^2}{m^2(E^{cd})^2 R^3} f(E^c)\, \mathrm{Im}\,\frac{1}{\epsilon_{sp}(\omega)}.$$

(12)

FIG. 1. (a) Calculated differential transmission spectra for positive time delays with initial hot electron temperature $T_0 = 800$ K, $\epsilon_m = 2.25$, and $\gamma_s = 0.1$ eV. (b) Temporal evolution of the differential transmission for frequencies equal, above, and below the SP resonance. (c) Experimental temporal evolution of the pump-probe signal [6]. (d) Calculated differential transmission in the absence of interband d-hole scattering.
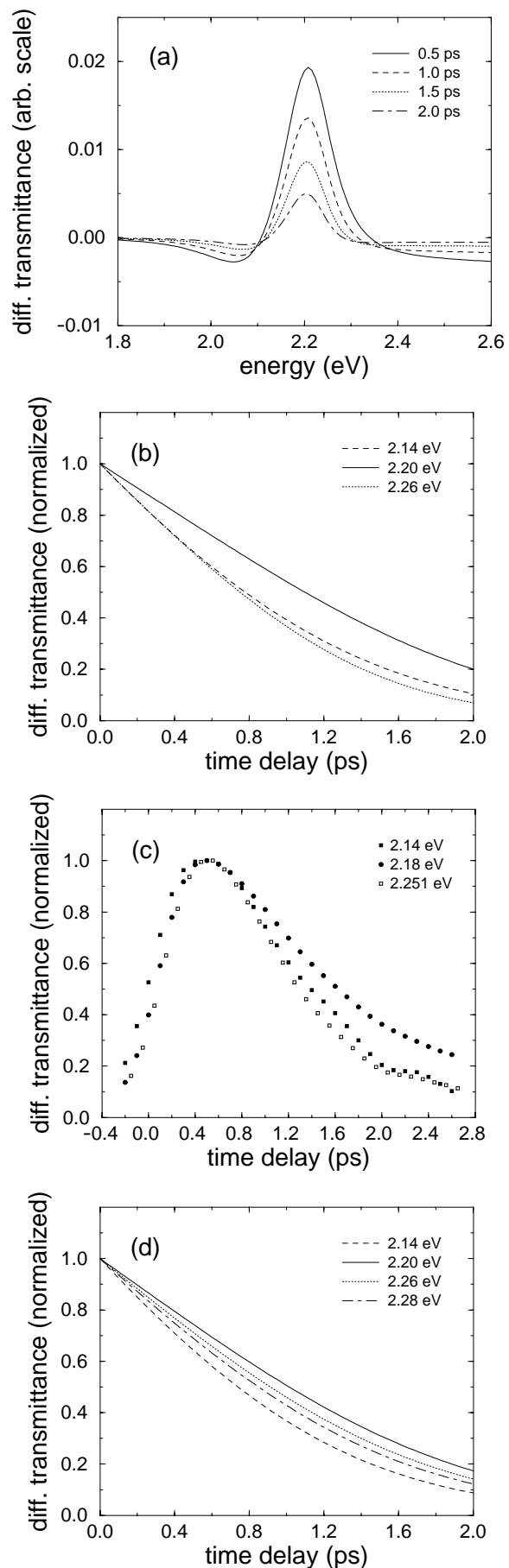
The comparison of Eqs. (12) and (1) shows that the scattering rate *depends on the frequency* in the same way as the absorption coefficient: both $\gamma_h(\omega, E^c)$ and $\alpha(\omega)$ exhibit a peak at $\omega = \omega_{sp}$. This implies that the d hole experiences *resonant scattering* into the conduction band as the optical field frequency approaches the SP frequency. We thus arrive at a self-consistent problem defined by Eqs. (1), (2), (11), and (12).

The main role of the SP-assisted d-hole scattering is to change the absorption line shape in the vicinity of the SP resonance. The SP width is determined by $\epsilon_d''(\omega) = 4\pi \tilde{\chi}_d''(\omega)$, which now, according to Eqs. (12) and (11), acquires a sharp frequency dependence for $\omega \sim \omega_{sp}$. It is also important that the effect of γ_h on $\epsilon_d''(\omega)$ increases with temperature. Indeed, the Fermi function in the rhs of Eq. (12) implies that γ_h is small unless $E^c - E_F \lesssim k_B T$. Since the main contribution to $\tilde{\chi}_d''(\omega)$ comes from energies $E^c - E_F \sim \omega - \Delta$, the scattering becomes efficient for temperatures $k_B T \gtrsim \omega_{sp} - \Delta$. The combined effect of the above ω and T dependence manifests itself strongly in the differential absorption dynamics, as illustrated below.

In Fig. 1 we show the results of our self-consistent numerical calculations of the differential transmission dynamics. We use the parameters of the experiment [6], performed on ~ 5 nm Cu nanoparticles, with the SP frequency, $\omega_{sp} \simeq 2.22$ eV, slightly above the onset of the interband transitions, $\Delta \simeq 2.18$ eV. Figure 1(a) shows the spectra at various time delays, calculated as the difference between $\alpha(\omega)$ at $T = 300$ K and $T(t)$, the pump-induced hot electron temperature. The latter was obtained from the two-temperature model with bulk Cu parameters [19] and initial temperature $T_0 = 800$ K. The d-hole scattering leads to a steeper ω dependence of the differential transmission for $\omega > \omega_{sp}$; its effect, however, is best seen in the time evolution as described below. We also included the effect of the intraband e-e scattering; for electron energy close to E_F, this can be achieved by adding the e-e scattering rate $\gamma_e(E^c) \propto [1 - f(E^c)](E^c - E_F)^2$ to γ_h in Eq. (11). The difference in $\gamma_e(E^c)$ for E^c smaller and larger than E_F leads to an asymmetric differential transmission line shape, in agreement with experiment [6].

In Fig. 1(b) we show the calculated time evolution of the differential transmission. The relaxation is slowest at $\omega = \omega_{sp}$, which can be attributed to the robustness of the SP mode; the corresponding relaxation time is 3.5 ps. More importantly, for short time delays, the relaxation is significantly faster below *and* above ω_{sp}, with a characteristic time of 1.4 ps. These results are consistent with the experimental data shown here for comparison in Fig. 1(c) (the experiment also revealed an initial nonequilibrium regime not addressed here). In contrast, in the absence of d-hole scattering [$\gamma_h = 0$ in Eq. (11)], the frequency dependence would be smooth *above* the resonance [see Fig. 1(d)]. Such a smooth dependence

originates from the line shape of the absorption peak: since $\omega_{sp} \sim \Delta$, the absorption is larger for $\omega > \omega_{sp}$ due to the interband transitions, and therefore the *relative* change in the absorption is smaller. This, however, changes with d-hole scattering turned on ($\gamma_h \neq 0$). To understand this difference, one should note that away from ω_{sp}, the relaxation characterizes the temperature-induced change in the SP *width*. The latter acquires an additional frequency dependence near the resonance, originating from that of $\gamma_h(\omega)$. This effect is enhanced above the resonance due to the similar frequency dependence of γ_h and α. Furthermore, the efficiency of this mechanism increases with T, as discussed above. This results in a strong frequency dependence of the relaxation (for $\omega > \omega_{sp}$) for shorter time delays, which correspond to higher T [see Fig. 1(b)].

In conclusion, we have shown that surface-induced electron-electron interactions in small metal particles lead to quasiparticle scattering mediated by collective surface excitations. In noble-metal particles, this size-dependent mechanism results in a surface-plasmon-assisted resonant scattering of d holes into the conduction band. The latter effect can be observed with ultrafast pump-probe spectroscopy. Our work points out the increasing role of many-body correlations with decreasing size, important for understanding the transition from boundary-constrained nanoscale materials to molecular clusters.

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