Nonradiative Energy Losses of Plasmon-Polariton in a Metallic Nano-chain Deposited on a Semiconductor Substrate

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Received: 22 June 2018 / Accepted: 7 August 2018 / Published online: 3 September 2018
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Abstract

Propagation of plasmon-polariton in a metallic nano-chain in a dielectric surroundings is almost undamped and irradiation-less and such nano-chains are considered as quasi-perfect wave-guides for plasmon-polaritons. If, however, a chain is deposited on a semiconductor substrate or embedded in a semiconductor surroundings, plasmon-polaritons are strongly quenched due to the energy transfer from plasmon oscillations to band electrons in the semiconductor medium via the near-field coupling channel. For the reverse direction of this energy transfer the balance of the thermal losses of plasmon-polariton can be achieved. By a control of a dielectric spacing between the metallic nano-chain and the semiconductor substrate (and a type of the deposition), various regimes for coupling of two systems can be organized. We present the exact solution for propagation of strongly damped plasmon-polaritons in metallic nano-chain due to coupling of plasmons with band electrons in the semiconductor substrate.

Keywords Plasmon-polariton · Metallic nano-chain · Semiconductor substrate

Introduction

Experimental and theoretical investigation of plasmon oscillations in metallic nanoparticles and metallic nano-arrays has a growing significance for applications in nanophotonics and plasmonics. Metallic surface modifications in nano-scale of solar cells exhibit growth of photo-voltaic efficiency due to plasmon mediation of sun light energy harvesting [1–6]. Periodic structures of metallic nanoparticles are considered as plasmon wave-guides with low damping [7–9]. Propagation of plasmon-polaritons in metallic nano-chains [10–12] is prospective for sub-diffraction light circuits for new generation of opto-electronics via light signal transformation into plasmon-polariton with much shorter wavelength [13–15]. Plasmon-polaritons do not interact with photons due to the large incommensurability in momentum for the same energy and this prevents radiation losses of plasmon-polaritons. Nevertheless, when metallic nano-chains are placed on a semiconductor substrate or

embedded in a semiconductor surroundings, then the strong coupling of plasmon oscillations in each metallic nanocomponent causes the plasmon-polariton energy outflow to the semiconductor electron system resulting in strong damping of the collective plasmon modes. On the other hand, the same near-field coupling may be used in opposite direction to supply energy to plasmon-polariton from the semiconductor substrate where the inverse electron occupation of semiconductor band system may be attained, e.g., by application of a lateral current. This might be convenient to balance the dissipation of plasmon-polariton energy caused by electron scattering in metallic components and provide a perfectly undamped plasmon-polariton propagation in metallic chains. For description of near-field coupling of plasmon-polariton in a metallic nano-chain with the semiconductor substrate, one can utilize the Fermi golden rule to derive the related damping rate.

Let us recall that plasmon properties in metallic nanoparticles depend on a nanoparticle size. For metallic ultrasmall clusters of size 1–3 nm for radius the dominating are quantum effects as, e.g., the spill-out of electrons beyond the jellium rim [16–19] lowering electron density in such small clusters. Plasmon oscillation energy is thus red-shifted as proportional to the square-root of the electron density. Damping of plasmons in this size-scale is caused by their decay into electron-hole pairs

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(Landau damping) [18]. Nevertheless, for larger metallic nanoparticles, both the spill-out and the Landau damping are of lowering significance as proportional to the inverse of the nanoparticle radius. Damping of plasmons for particles of size of several tens nm is linked to their pronounced radiative properties [16, 17, 20]. For nanoparticles of noble metals (gold, silver, and copper), their surface plasmon resonances overlap with the visible light spectrum.

Irradiation of surface plasmons in nanoparticles manifests itself in their collective specific propagation in metallic nano-chains [21–23]. A long range propagation of plasmon-polariton signal along these structures has been demonstrated; e.g., in [24], it has been reported observation of 5 μm range propagation in gold nanoparticles with averaged radius $a = 50$ nm aligned in the equidistant chain with separation between neighboring spheres $d = 200$ nm. In series of papers [10, 25–28], practically not damped propagation of plasmon-polaritons modes in gold and silver nano-chains has been demonstrated over distances ~ 0.5 μm . Plasmon-polaritons are referred to hybridization of plasmons with photons resulting in lowering of their group velocity below $0.1 \times c$ [10, 26, 28]. The related momentum incommensurability at the same energy of photons and plasmon-polaritons causes that the latter do not irradiate energy and propagate along metallic nano-chains over large distances [11, 24].

In the present paper, we describe the propagation of plasmon-polaritons in a metallic nano-chain deposited on a semiconductor substrate or embedded in a semiconductor medium including a coupling of plasmons with semiconductor band system in near-field-zone and related energy transfer between plasmon-polaritons and semiconductor electrons. Energy outflow from plasmon-polaritons to the semiconductor band system enhances damping of plasmon-polaritons, whereas an opposite direction of the energy flow may be utilized to cover plasmon-polariton Joule losses caused by electron scattering in metallic components. First, we will analyze the surface dipole-type plasmons in a single metallic nanosphere (within the formerly formulated RPA model [29, 30]) including damping effects, in particular of the Lorentz friction of plasmons resulting in the far-field-zone radiation and the additional energy outflow via channel of near-field-zone coupling of dipole plasmons to electrons in a substrate semiconductor. Next, we will describe collective surface plasmons excitations in a nano-chain of metallic particles, i.e., plasmon-polaritons, taking into account all channels for energy losses. The propagation of damped plasmon-polaritons will be analyzed for longitudinal and transverse polarizations of plasmon oscillations with respect to the propagation direction and for variety of geometry and size and material details of the whole system configuration.

Plasmon Oscillations in a Single Metallic Nanosphere Including Their Damping

A metallic nanosphere is conventionally modeled as the spherical static positive jellium with electrically balanced electron liquid which can locally fluctuate in density resulting in regular charge oscillations: the surface plasmons—when oscillations have a translational character with the electrical local imbalance occurring on the sphere surface only, and the volume plasmons—of compressional character along the radius of a nanosphere. It is interesting that the energy of nanosphere volume plasmons for particular modes is always greater than the bulk plasmon energy $\hbar\omega_p = \hbar\sqrt{\frac{e^2 n_e}{m\epsilon_0}}$ (m is the mass of electron, e is the electron charge, n_e is the density of free electrons in a metal, ϵ_0 is the dielectric constant), whereas the energy of surface plasmon modes is lower than $\hbar\omega_p$ [29]. The latter property makes noble metal (Au, Ag, Cu) nanoparticles attractive for applications as their surface plasmon resonances overlap with the visible light spectrum.

Fluctuations of electron local density in the nanosphere of surface and volume parts [29]

$$\delta\rho(\mathbf{r}, t) = \begin{cases} \delta\rho_1(\mathbf{r}, t), & \text{for } r < a, \\ \delta\rho_2(\mathbf{r}, t), & \text{for } r \geq a, \quad (r \rightarrow a+), \end{cases} \quad (1)$$

satisfy the equations derived in the framework of random phase approximation (RPA) [29]:

$$\frac{\partial^2 \delta\rho_1(\mathbf{r}, t)}{\partial t^2} = \frac{2}{3} \frac{\epsilon_F}{m} \nabla^2 \delta\rho_1(\mathbf{r}, t) - \omega_p^2 \delta\rho_1(\mathbf{r}, t), \quad (2)$$

and

$$\begin{aligned} \frac{\partial^2 \delta\rho_2(\mathbf{r}, t)}{\partial t^2} = & -\frac{2}{3m} \nabla \cdot \left\{ \left[\frac{3}{5} \epsilon_F n_e + \epsilon_F \delta\rho_2(\mathbf{r}, t) \right] \frac{\mathbf{r}}{r} \delta(r-a) \right\} \\ & - \left[\frac{2}{3} \frac{\epsilon_F}{m} \frac{\mathbf{r}}{r} \cdot \nabla \delta\rho_2(\mathbf{r}, t) + \frac{\omega_p^2}{4\pi} \frac{\mathbf{r}}{r} \cdot \nabla \int d^3 r_1 \frac{1}{|\mathbf{r} - \mathbf{r}_1|} \right. \\ & \times (\delta\rho_1(\mathbf{r}_1, t) \Theta(a - r_1) + \delta\rho_2(\mathbf{r}_1, t) \Theta(r_1 - a)) \left. \right] \delta(r-a), \end{aligned} \quad (3)$$

where Θ is the Heaviside step function defining the static jellium $n_e(\mathbf{r}) = n_e \Theta(a - r)$ and a is the nanosphere radius. The analysis and solution of the above equations have been performed in details in [29], resulting in determination of plasmon self-mode spectra, both for the volume and surface modes.

This RPA treatment did not account, however, for plasmon damping. The damping of plasmons can be included in a phenomenological manner, by adding the term, $-\frac{2}{\tau_0} \frac{\partial \delta\rho(\mathbf{r}, t)}{\partial t}$, to the r.h.s. of both Eqs. 2 and 3, taking advantage of their oscillatory form [29]. The damping ratio

$\frac{1}{\tau_0}$ accounts for electron scattering losses (eventually Joule heat losses in metal material of a nanosphere) [25],

$$\frac{1}{\tau_0} \simeq \frac{v_F}{2\lambda_b} + \frac{Cv_F}{2a}, \quad (4)$$

where C is the constant of unity order, v_F is the Fermi velocity in the metal, λ_b is the electron mean free path, the same as in the bulk metal (including scattering of electrons on other electrons, on impurities and on phonons in the metallic nanoparticle [25]); e.g., for Au, $v_F = 1.396 \times 10^6$ m/s and $\lambda_b \simeq 53$ nm (at room temperature); the latter term in the formula (4) accounts for scattering of electrons on the boundary of the nanoparticle, whereas the former one corresponds to scattering processes similar as in bulk. The other effects, as the so-called Landau damping (especially important in small clusters [19, 31]), corresponding to decay of plasmon for high energy particle-hole pair, are of lowering significance for nano-sphere radii larger than 2–3 nm [31] and are completely negligible for radii larger than 5 nm (we will consider here the large nanospheres with radii ≥ 5 nm). Note that the similarly lowering role with the radius growth plays also electron liquid spill-out effect [16, 18], though it was of primary importance for small clusters [16, 20].

The homogeneous (2) and (3) determine self-frequencies of plasmon modes. One can write out also the dual inhomogeneous equations with the explicit driving factor. This factor would be the time-dependent electric field, e.g., the electric component of the incident e-m wave (laser beam or sun-light in photovoltaic applications [32]). The resonant light wavelength with surface plasmon in the metallic nanosphere (Au, Ag, Cu) is of order of 500 nm and highly exceeds the nanosphere size (with radius 5–50 nm); thus, the dipole-approximation regime conditions are satisfied. Hence, the driving field $\mathbf{E}(t)$ of e-m wave almost homogeneous over the nanosphere (which corresponds to the dipole approximation) can only excite the dipole surface mode in the electron liquid of the metallic nanosphere. The dipole type mode may be described by the function $Q_{1m}(t)$ with $l = 1$ and $m = -1, 0, 1$ being the angular momentum numbers related to spherical symmetry of the metallic nanoparticle. The function $Q_{1m}(t)$ satisfies the equation,

$$\begin{aligned} & \frac{\partial^2 Q_{1m}(t)}{\partial t^2} + \frac{2}{\tau_0} \frac{\partial Q_{1m}(t)}{\partial t} + \omega_1^2 Q_{1m}(t) \\ &= \sqrt{\frac{4\pi}{3}} \frac{en_e}{m} \left[E_z(t) \delta_{m,0} + \sqrt{2} (E_x(t) \delta_{m,1} + E_y(t) \delta_{m,-1}) \right], \end{aligned} \quad (5)$$

where $\omega_1 = \frac{\omega_p}{\sqrt{3\varepsilon}}$ (it is a dipole surface plasmon Mie-type frequency [33], ε is the dielectric susceptibility of the

nanosphere surroundings). The electron density fluctuations can be written as follows [29],

$$\delta\rho(\mathbf{r}, t) = \begin{cases} 0, & r < a, \\ \sum_{m=-1}^1 Q_{1m}(t) Y_{1m}(\Omega), & r \geq a, \quad r \rightarrow a+, \end{cases} \quad (6)$$

where $Y_{lm}(\Omega)$ is the spherical function with $l = 1$. The plasmon oscillations given by Eq. 6 define the dipole $\mathbf{D}(t)$,

$$\begin{cases} D_x(t) = e \int d^3r x \delta\rho(\mathbf{r}, t) = \frac{\sqrt{2\pi}}{\sqrt{3}} e Q_{1,1}(t) a^3, \\ D_y(t) = e \int d^3r y \delta\rho(\mathbf{r}, t) = \frac{\sqrt{2\pi}}{\sqrt{3}} e Q_{1,-1}(t) a^3, \\ D_z(t) = e \int d^3r z \delta\rho(\mathbf{r}, t) = \frac{\sqrt{4\pi}}{\sqrt{3}} e Q_{1,0}(t) a^3. \end{cases} \quad (7)$$

The dipole $\mathbf{D}(t)$ satisfies thus the equation (by virtue of Eq. 5),

$$\left[\frac{\partial^2}{\partial t^2} + \frac{2}{\tau_0} \frac{\partial}{\partial t} + \omega_1^2 \right] \mathbf{D}(t) = \frac{a^3 4\pi e^2 n_e}{3m} \mathbf{E}(t) = \varepsilon a^3 \omega_1^2 \mathbf{E}(t). \quad (8)$$

The damping term in the above equation includes energy dissipation due to electron scattering in metallic nanosphere, i.e., electron-electron, electron-phonon, electron-admixture scattering, as well contribution of the boundary scattering effect [25]. There is, however, also an important channel of plasmon damping caused by irradiation losses, not included into formula for τ_0 . The radiative losses of plasmon energy in the dielectric surroundings can be expressed by the Lorentz friction [34], i.e., by the fictitious electric field slowing down the motion of charges,

$$\mathbf{E}_L = \frac{2\sqrt{\varepsilon}}{3c^3} \frac{\partial^3 \mathbf{D}(t)}{\partial t^3}. \quad (9)$$

Thus, one can rewrite (8) including the Lorentz friction term,

$$\left[\frac{\partial^2}{\partial t^2} + \frac{2}{\tau_0} \frac{\partial}{\partial t} + \omega_1^2 \right] \mathbf{D}(t) = \varepsilon a^3 \omega_1^2 \mathbf{E}(t) + \varepsilon a^3 \omega_1^2 \mathbf{E}_L, \quad (10)$$

or more explicitly, for the case when $\mathbf{E} = 0$,

$$\left[\frac{\partial^2}{\partial t^2} + \omega_1^2 \right] \mathbf{D}(t) = \frac{\partial}{\partial t} \left[\frac{2}{\tau_0} \mathbf{D}(t) + \frac{2}{3\omega_1} \left(\frac{\omega_p a}{c\sqrt{3}} \right)^3 \frac{\partial^2}{\partial t^2} \mathbf{D}(t) \right]. \quad (11)$$

Applying now the perturbation procedure for solving of Eq. 11 and treating the r.h.s of this equation as the perturbation, one obtains in zeroth step of perturbation

$\left[\frac{\partial^2}{\partial t^2} + \omega_1^2\right] \mathbf{D}(t) = 0$, from which $\frac{\partial^2}{\partial t^2} \mathbf{D}(t) = -\omega_1^2 \mathbf{D}(t)$. Therefore, within the first step of the perturbation, one can substitute the latter formula to the r.h.s. of Eq. 11, i.e.,

$$\left[\frac{\partial^2}{\partial t^2} + \frac{2}{\tau} \frac{\partial}{\partial t} + \omega_1^2\right] \mathbf{D}(t) = 0, \quad (12)$$

where

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{\omega_1}{3} \left(\frac{\omega_p a}{c\sqrt{\epsilon}}\right)^3. \quad (13)$$

In this way, we have included the Lorentz friction into the total attenuation rate $\frac{1}{\tau}$. This is justified for not extreme large nanospheres, i.e., when the second term in Eq. 13, proportional to a^3 , is sufficiently small to fulfill the perturbation procedure constraints. For nanospheres with radius 10–30 nm, this approximation is fulfilled and was verified experimentally for Au and Ag nanospheres [30, 35]. Inclusion of the Lorentz friction explains an experimentally observed red-shift of resonance surface plasmon frequency with growing a . Indeed, the solution of Eq. 12 is of the form $\mathbf{D}(t) = \mathbf{A}e^{-t/\tau} \cos(\omega'_1 t + \phi)$, where $\omega'_1 = \omega_1 \sqrt{1 - \frac{1}{(\omega_1 \tau)^2}}$, which gives the experimentally observed red-shift of the plasmon resonance due to $\sim a^3$ growth of plasmon damping caused by irradiation. The Lorentz friction term in Eq. 13 dominates plasmon damping in a dielectric surroundings for $a \geq 12$ nm (for Au and Ag) due to this a^3 dependence. The plasmon damping grows rapidly with a and results in pronounced red-shift of resonance frequency in good coincidence with the experimental data for $10 < a < 30$ nm (Au and Ag) [30]. Taking into account that $\frac{1}{\tau_0}$ scales as $\frac{1}{a}$, while the Lorentz friction contribution as a^3 for $10 < a < 30$ nm, in this region for size of metallic particles one encounters the cross-over of the attenuation rate with respect to a . The minimum of damping is achieved at

$$a^* = \left(\frac{9}{2} \sqrt{\epsilon} \frac{v_{FC}^3}{\omega_p^4}\right)^{1/4}, \quad (14)$$

and for $a < a^*$, the damping ratio grows with lowering a approximately as $\sim \frac{1}{a}$, while for $a > a^*$, this ratio grows with rising a as proportional to a^3 . The value of a^* can be estimated for Au, Ag and Cu—cf. Table 1.

Table 1 Radius of the nanosphere corresponding to the minimal value of surface plasmon damping in dielectric surroundings

$n = \sqrt{\epsilon}$	a^*		
	Au	Ag	Cu
$n = 1$ vacuum	8.4	8.44	6.46
$n = 1.4$ water	9.137	9.18	9.202
$n = 2$	9.989	10.037	10.04

Radiative Properties of Plasmon-Polaritons in the Metallic Nano-chain Embedded in the Dielectric Medium

When a metallic nanosphere is an element of the chain of similar nanospheres equidistantly distributed along a line, one has to take into account that except of the irradiation losses in a particular nanosphere, the simultaneous income of energy takes place from radiation of other nanospheres when in the total chain the collective plasmon excitation (plasmon-polariton) propagates.

The interaction between nanospheres in the chain can be considered as of dipole-type coupling. The minimal separation of nanospheres in the chain is $d = 2a$ (d is the measure of distance between neighboring sphere centers) and the dipole approximation of plasmon interaction in the nanosphere-chain is sufficiently accurate for $d > 3a$, when multipole interaction contribution can be neglected. Various numerical large-scale calculations of e-m field distribution in such systems were done including dipole and also multipole interactions between plasmonic oscillations in metallic components [21–23]. The model of interacting dipoles [36, 37] was developed earlier for investigation of stellar matter [38, 39] and next, it has been adopted to metal particle systems [40, 41]. The numerical studies beyond the dipole model [21, 23] indicated that the dipole model is sufficiently accurate when the particle separation is not lower than particle dimensions, when the multipole contribution to interaction are small [42].

The oscillating dipole $\mathbf{D}(t)$ located in the point $\mathbf{r}$ causes in the other place $\mathbf{r}_0$ (assuming the vector $\mathbf{r}_0$ is fixed to the end of $\mathbf{r}$) the electric field in the form as follows (including relativistic retardation of electromagnetic signals) [34, 43]:

$$\begin{aligned} \mathbf{E}(\mathbf{r}, \mathbf{r}_0, t) = & \frac{1}{\epsilon} \left(-\frac{\partial^2}{v^2 \partial t^2} \frac{1}{r_0} - \frac{\partial}{v \partial t} \frac{1}{r_0^2} - \frac{1}{r_0^3} \right) \mathbf{D}(\mathbf{r}, t - r_0/v) \\ & + \frac{1}{\epsilon} \left(\frac{\partial^2}{v^2 \partial t^2} \frac{1}{r_0} + \frac{\partial}{v \partial t} \frac{3}{r_0^2} + \frac{3}{r_0^3} \right) \mathbf{n}_0 (\mathbf{n}_0 \cdot \mathbf{D}(\mathbf{r}, t - r_0/v)), \end{aligned} \quad (15)$$

where $\mathbf{n}_0 = \frac{\mathbf{r}_0}{r_0}$ and $v = \frac{c}{\sqrt{\epsilon}}$. The above formula includes the terms corresponding to the near-field-zone (denominator with r_0^3), medium-field-zone (denominator with r_0^2) and far-field-zone (denominator with r_0) contributions to dipole field. Equation 15 allows for writing out the dynamical equation for plasmon oscillations at each nano-sphere of the chain, which can be numbered by integer l (d denotes the separation between nano-spheres in the chain, a is the nanosphere radius, the vectors $\mathbf{r}$ and $\mathbf{r}_0$ are collinear, if the origin of coordinate system is associated with one of the nano-spheres in the chain).

Therefore, the equation for the collective surface plasmon oscillation in the l^{th} sphere of the chain is as follows,

$$\begin{aligned} & \left[\frac{\partial^2}{\partial t^2} + \frac{2}{\tau_0} \frac{\partial}{\partial t} + \omega_1^2 \right] D_\alpha(l d, t) \\ &= \varepsilon \omega_1^2 a^3 \sum_{m=-\infty, m \neq l}^{m=\infty} E_\alpha \left(m d, t - \frac{|l-m|d}{c} \right) \\ &+ \varepsilon \omega_1^2 a^3 E_{L\alpha}(l d, t) + \varepsilon \omega_1^2 a^3 E_\alpha(l d, t). \end{aligned} \quad (16)$$

$$\begin{aligned} E_z(m d, t) &= \frac{2}{\varepsilon d^3} \left(\frac{1}{|m-l|^3} + \frac{d}{v|m-l|^2} \frac{\partial}{\partial t} \right) D_z(m d, t - |m-l|d/v), \\ E_{x(y)}(m d, t) &= -\frac{1}{\varepsilon d^3} \left(\frac{1}{|m-l|^3} + \frac{d}{v|m-l|^2} \frac{\partial}{\partial t} + \frac{d^2}{v^2|l-d|} \frac{\partial^2}{\partial t^2} \right) D_{x(y)}(m d, t - |m-l|d/v). \end{aligned} \quad (17)$$

Taking advantage of the chain periodicity, one can assume in analogy to Bloch states in 1D crystals with the reciprocal lattice of quasi-momentum,

$$\begin{aligned} D_\alpha(l d, t) &= D_\alpha(k, t) e^{-i k l d}, \\ 0 \leq k \leq \frac{2\pi}{d}. \end{aligned} \quad (18)$$

The above can be asserted in a more formal manner taking the Fourier picture of Eq. 16. As dipoles are localized on nanospheres in their centers, the system is discrete similarly as in the case of phonons in 1D crystal. One can thus apply the discrete Fourier transform (DFT) with respect to the positions, whereas the continuous Fourier transform (CFT) with respect to time. DFT is defined for a finite set of numbers, so one can consider the chain with $2N+1$ nanospheres, i.e., the chain of length $L = 2Nd$. Thus for any discrete characteristics $f(l)$, $l = -N, \dots, 0, \dots, N$ of the chain, like a dipole distribution, one deals with DFT

The first term of the r.h.s. in Eq. 16 describes the dipole coupling between nano-spheres in the chain and the next two terms correspond to contribution to plasmon attenuation due to the Lorentz friction (as described in the previous paragraph) and the driving field of an external electric field. The index α enumerates polarization, the longitudinal, $\alpha = z$, and the transverse, $\alpha = x(y)$, with respect to the chain orientation (assumed in z direction). According to Eq. 15 we have:

picture $f(k) = \sum_{l=-N}^N f(l) e^{i k l d}$, where $k = \frac{2\pi}{2Nd} n$, $n = 0, \dots, 2N$. Hence, $k d \in [0, 2\pi]$ due to periodicity of the equidistant chain. On the whole system, the Born-Karman boundary condition is imposed resulting in the above form of $k = \frac{2\pi}{2Nd} n$. In order to account for the infinite length of the chain, one can finally take the limit $N \rightarrow \infty$ which causes that the variable k is quasi-continuous, but still $k d \in [0, 2\pi]$.

The Fourier picture of Eq. 16, DFT for positions and CFT for time, is derived in the Appendix 1 and gives,

$$\begin{aligned} & \left(-\omega^2 - i \frac{2}{\tau_0} \omega + \omega_1^2 \right) D_\alpha(k, \omega) \\ &= \omega_1^2 \frac{a^3}{d^3} F_\alpha(k, \omega) D_\alpha(k, \omega) + \varepsilon a^3 \omega_1^2 E_{0\alpha}(k, \omega), \end{aligned} \quad (19)$$

with

$$\begin{aligned} F_z(k, \omega) &= 4 \sum_{m=1}^{\infty} \left(\frac{\cos(mkd)}{m^3} \cos(m\omega d/v) + \omega d/v \frac{\cos(mkd)}{m^2} \sin(m\omega d/v) \right) \\ &+ 2i \left[\frac{1}{3} (\omega d/v)^3 + 2 \sum_{m=1}^{\infty} \left(\frac{\cos(mkd)}{m^3} \sin(m\omega d/v) - \omega d/v \frac{\cos(mkd)}{m^2} \cos(m\omega d/v) \right) \right], \\ F_{x(y)}(k, \omega) &= -2 \sum_{m=1}^{\infty} \left(\frac{\cos(mkd)}{m^3} \cos(m\omega d/v) + \omega d/v \frac{\cos(mkd)}{m^2} \sin(m\omega d/v) - (\omega d/v)^2 \frac{\cos(mkd)}{m} \cos(m\omega d/v) \right) \\ &- i \left[-\frac{2}{3} (\omega d/v)^3 + 2 \sum_{m=1}^{\infty} \left(\frac{\cos(mkd)}{m^3} \sin(m\omega d/v) + \omega d/v \frac{\cos(mkd)}{m^2} \cos(m\omega d/v) \right) \right. \\ &\left. - (\omega d/v)^2 \frac{\cos(mkd)}{m} \sin(m\omega d/v) \right]. \end{aligned} \quad (20)$$

Fig. 1 The damping rate $Im\omega_{x(y)}(k)$, the self-frequency $Re\omega_{x(y)}(k)$ and the group velocity $v_{x(y)}(k)$ of plasmon polariton for transverse polarization in infinite chains of Au nanospheres with radius $a = 10$ nm and chain-separation $d = 3a$ for a vacuum surroundings (upper) and a semiconductor Si surrounding (lower)

The direct calculation of functions $ImF_z(k, \omega)$ and $ImF_{x(y)}(k, \omega)$ corresponding to the radiative damping for longitudinal and transverse plasmon-polariton polarizations, respectively, is explicitly done in the Appendix 1—(50) and (52). We have shown there that both these functions perfectly *vanish* when $0 < kd \pm \omega d/v < 2\pi$ (the corresponding region—the light cone—is indicated in Fig. 5). Outside this region, radiative damping expressed by $ImF_\alpha(k, \omega)$ functions is nonzero, which for longitudinal and transverse modes is illustrated in Figs. 6 and 7, correspondingly.

Plasmon-Polariton Self-modes in the Chain in the Dielectric Surroundings

The real part of the functions F_α renormalizes the self-frequency of plasmon-polaritons in the chain, whereas

the imaginary part renormalizes damping of these modes. $ReF_\alpha(k, \omega)$ and $ImF_\alpha(k, \omega)$ are functions of k and ω . Applying the perturbation method of solution, within the first order approximation one can put $\omega = \omega_1$ in ReF_α and also in the residual nonzero ImF_α outside the region $0 < kd \pm \omega_1 d/v < 2\pi$. Let us emphasize, however, that vanishing of $ImF_\alpha(k, \omega)$ inside the region $0 < kd \pm \omega d/v < 2\pi$ holds for any value of ω [44], thus also for exact (nonperturbative) solution as shown numerically in Figs. 1, 2, 3, and 4.

Upon the perturbation scheme, one can rewrite the dynamic (19) for plasmon-polariton modes in the chain in the following form:

$$\left(-\omega^2 - i \frac{2}{\tau_\alpha(k)} \omega + \omega_\alpha(k)^2\right) D_\alpha(k, \omega) = \varepsilon a^3 \omega_1^2 E_{0\alpha}(k, \omega), \quad (21)$$

Fig. 2 The damping rate $Im\omega_{x(y)}(k)$, the self-frequency $Re\omega_{x(y)}(k)$ and the group velocity $v_{x(y)}(k)$ of plasmon polariton for transverse polarization in infinite chains of Au nanospheres with radius $a = 5$ nm and chain-separation $d = 5a$ for a vacuum surroundings (upper) and a semiconductor (Si) surrounding (lower)

Fig. 3 The damping rate $Im\omega_{x(y)}(k)$, the self-frequency $Re\omega_{x(y)}(k)$ and the group velocity $v_{x(y)}(k)$ of plasmon-polariton for longitudinal polarization in infinite chains of Au nanospheres with radius $a = 10$ nm and chain-separation $d = 4a$ for a vacuum surroundings (upper) and a semiconductor (Si) surrounding (lower)

where the renormalized attenuation rate,

$$\frac{1}{\tau_\alpha(k)} = \begin{cases} \frac{1}{\tau_0}, & \text{for } 0 < kd \pm \omega_1 d/v < 2\pi, \\ \frac{1}{\tau_0} + \frac{a^3 \omega_1}{2d^3} ImF_\alpha(k, \omega_1), & \text{for } kd - \omega_1 d/v < 0 \text{ or } kd + \omega_1 d/a > 2\pi, \end{cases} \quad (22)$$

and the renormalized bare self-frequency (due to damping the true resonance is, however, red-shifted as for damped oscillator—not written here),

$$\omega_\alpha^2(k) = \omega_1^2 \left(1 - \frac{a^3}{d^3} ReF_\alpha(k, \omega_1) \right). \quad (23)$$

Equation 21 can be easily solved both for inhomogeneous and homogeneous (when $E_{0\alpha} = 0$) case. The general solution of Eq. 21 has a form of sum of the general solution of homogeneous equation and of single particular solution of inhomogeneous equation. The first one includes

Fig. 4 The damping rate $Im\omega_{x(y)}(k)$, the self-frequency $Re\omega_{x(y)}(k)$ and the group velocity $v_{x(y)}(k)$ of plasmon-polariton for longitudinal polarization in infinite chains of Au nanospheres with radius $a = 5$ nm

and chain-separation $d = 5a$ for a vacuum surroundings (upper) and a semiconductor (Si) surrounding (lower)

initial conditions and describes damped self-oscillations with frequency,

$$\omega'_\alpha = \sqrt{\omega_\alpha^2(k) - \frac{1}{\tau_\alpha^2(k)}}, \quad (24)$$

i.e., for each k and α ,

$$D'_\alpha(k, t) = A_{\alpha,k} e^{i(\omega'_\alpha t + \phi_{\alpha,k})} e^{-t/\tau_\alpha(k)}, \quad (25)$$

with constants $A_{\alpha,k}$ and $\phi_{\alpha,k}$ adjusted to the initial conditions.

For the inhomogeneous case, the particular solution is as follows:

$$D''_\alpha(k, t) = \varepsilon a^3 \omega_1^2 E_{0\alpha}(k) e^{i(\gamma t + \eta_{\alpha,k})} \frac{1}{\sqrt{(\omega_\alpha^2(k) - \gamma^2)^2 + \frac{4\gamma^2}{\tau_\alpha^2(k)}}}, \quad (26)$$

suitably to assumed single Fourier time-component of $E_{0\alpha}(k, t) = E_{0\alpha}(k) e^{i\gamma t}$, and $tg(\eta_{\alpha,k}) = \frac{2\gamma/\tau(\alpha,k)}{\omega(\alpha,k)^2 - \gamma^2}$ as for a driven oscillator. Let us emphasize that $E_{0\alpha}(k)$ is the real function for $E_{0\alpha}(ld)^* = E_{0\alpha}(ld) = E_{0\alpha}(-ld)$. An appropriate choice of the latter function, in practice a choice of the number of externally excited nanospheres in the chain, e.g., by suitably focused laser beam, allows for modeling of its Fourier picture $E_{0\alpha}(k)$. This gives the envelope of the wave packet if one inverts the Fourier transform in solution given by Eq. 26 back to the position variable. For the case of external excitation of only single nanosphere, the wave packet envelope includes homogeneously all wave vectors $k \in [0, 2\pi]$. The larger number of nanospheres is simultaneously excited the narrower in k wave packet envelope can be selected. For $E_{0\alpha}(ld)^* = E_{0\alpha}(ld) = E_{0\alpha}(-ld)$ the Fourier transform has the same properties, i.e., $E_{0\alpha}(k)^* = E_{0\alpha}(k) = E_{0\alpha}(-k)$ and the latter equality can be rewritten, due to the period $\frac{2\pi}{d}$ for k , as, $E_{0\alpha}(-k) = E_{0\alpha}(\frac{2\pi}{d} - k) = E_{0\alpha}(k)$ (to shift k to the equivalent positively-valued domain $k \in [0, 2\pi]$). The inverse Fourier picture of Eq. 26 (its real part) is,

$$D''_\alpha(ld, t) = \int_0^{2\pi/d} dk \cos(kld - \gamma t - \eta_{\alpha,k}) \varepsilon a^3 \omega_1^2 E_{0\alpha}(k) \times \frac{1}{\sqrt{(\omega_\alpha^2(k) - \gamma^2)^2 + \frac{4\gamma^2}{\tau_\alpha^2(k)}}}. \quad (27)$$

This integral can be rewritten by virtue of mean value theorem in the form,

$$D''_\alpha(ld, t) = \frac{2\pi}{d} \cos(k^*ld - \gamma t - \eta_{\alpha,k^*}) \varepsilon a^3 \omega_1^2 E_{0\alpha}(k^*) \times \frac{1}{\sqrt{(\omega_\alpha(k^*)^2 - \gamma^2)^2 + \frac{4\gamma^2}{\tau_\alpha^2(k^*)}}}. \quad (28)$$

The above expression describes the undamped wave motion with frequency γ and the velocity, amplitude, and phase shift determined by k^* . The energy losses are supplemented continuously by the driving force as for any steady state of the damped and driven oscillator. The amplitude attains its maximal value at the resonance, when

$$\gamma = \omega_\alpha(k^*) \sqrt{1 - \frac{2}{(\tau_\alpha(k^*)\omega_\alpha(k^*))^2}}. \quad (29)$$

In the chain being the subject of a persistent driving force in the form of the time-dependent external electric field applied to some number (even small number) of nanospheres, one deals with undamped wave packet propagation along the whole chain—the energy supply by a driving factor covers damping losses. These modes depending of particular shaping of the wave packet by specific choice of the chain excitation, may be responsible for experimentally observed long range practically undamped plasmon-polariton propagation [11, 24, 27, 28].

The self-modes of Eq. 25 are damped and their propagation depends on appropriately prepared initial conditions admitting nonzero values of $A_{\alpha,k}$. The resulting wave packet may embrace the wave-numbers k from some region of $[0, 2\pi]$. If only wave-numbers k , for which $0 < kd \pm \omega_1 d/v < 2\pi$ contribute to the wave packet, its damping is only of Ohmic-type (as is shown in the Appendix 1). The value of $\frac{1}{\tau_0}$ lowers with growing a (cf. Eq. 4)—thus for longer range of these damped excitations in the chain, the larger spheres are more suitable. The limiting value of $\frac{1}{\tau_0} = \frac{v_f}{2\lambda_B} \sim 10^{13}$ 1/s, which gives the maximal range of propagation for these modes of plasmon-polariton $\sim 0.1c\tau_0 \sim 10^{-6}$ m; for the group velocity of the wave packet, we assumed $\sim 0.1c$ as its maximum value (though depending on radius and separation of nanospheres in the chain). The group velocity calculated for both polarizations are presented in right panels of Figs. 1, 2, 3, and 4 (for accurate solution).

Though the presented above analysis is addressed to chains consisting of ideal nanospheres, the conclusions hold also for other shape particle chains and meet with experimental observations at least qualitatively. In [28], propagation of plasmon-polariton in nano-chain of silver rod-shaped particles (90:30:30 nm oriented with longer axis perpendicularly to the chain in order to enhance near-field coupling [27], with separation face to face, 70 nm) is evidenced by observing of luminescence of dye particle located in proximity to transmitting e-m signal but distantly from the point-like excitation source over the range of 0.5 μ m. The observed behavior has been supported by FDTD numerical simulations. Several samples of the chain were

fabricated by the electron beam lithography in the form of 2D matrix with sufficiently well-separated individual chains. The energy blue-shift of plasmon resonance for the nano-rods in the chain in comparison to the single particle is observed by ca. 0.1 eV (cf. Fig. 4 in [28]). This agrees with our estimation of reducing the radiation losses in the chain in comparison to strong Lorentz friction for single metallic nano-particle and related smaller red-shift of damped oscillations. The position of resonance maximum in the chain is located at higher energy for transverse mode than for the longitudinal one [26], which also agrees with theoretical predictions. In ref. [27], it is indicated that FDTD simulations give lower values of the group velocities for both polarizations and higher attenuation rates in comparison to these quantities previously estimated [25, 26] upon simplified point-dipole-model with near field-field interaction only and neglecting retardation effects. Let us note, however, that the simplified approach including only near-field contribution to electric field of interacting dipoles leads to an artifact, i.e., for some values of d and a chain parameters the instability of collective dynamics occurs [45]. This instability is completely removed by inclusion of medium- and far-field contributions to electric field of the dipole including relativistic retardation [44]. Nevertheless, the dipole interaction model even if including besides the near-field contribution also medium- and far-field ones and all retardation effects, still suffers from the absence of magnetic fields component needed for complete description of far-field wave propagation. As it is demonstrated in refs. [46, 47], for large separations in the chain, the scattering of e-m radiation dominates the signal behavior in metallic nano-chains which then acts as the Bragg grating for plasmon-polaritons. For ellipsoidal gold nanoparticles (210:80 nm) deposited on the top of silicon wave-guide, the change of regime from collective plasmon-polariton guiding to the Bragg scattering scenario takes place at distances between nanoparticles exceeding ca 1 μm [46]. This proves that the model of dipole coupling in the nano-chain works quite well in a wide region of chain parameters, in practice up to micron order for distances between metallic elements in the chain, which supports the qualitative argument that the Bragg grating regime is not efficient for sub-wave-length distances and justifies applicability of the model considered in the present paper. The SNOM measurements of near-field coupled plasmon modes in metallic nano-chain [10] interpreted within classical field-susceptibilities formalism in ref. [48] also supports the sufficient level of accuracy of dipole approximation for interaction in the chain for the considered here scale of nanosphere radii a of order of 10–30 nm and the chain separation d not exceeding $\sim 10 \times a$.

Damping of Surface Plasmons in a Single Metallic Nanoparticle Deposited on a Semiconductor Substrate

The interaction of band electrons with surface plasmon in the metallic nanoparticle deposited on the semiconductor top surface (or embedded in a semiconductor medium) causes the energy transfer resulting in an additional damping of plasmons. The perturbation of electron band system in the substrate semiconductor due to the presence of dipole surface plasmon oscillations in metallic nanosphere (with a radius a) deposited on the semiconductor surface (or emedded in) has the form of the potential of the e-m field of an oscillating dipole. The Fourier components of the electric $\mathbf{E}_\omega$ (the Fourier component of Eq. 15) and magnetic $\mathbf{B}_\omega$ fields produced in the distance $\mathbf{R}$ from the center of considered nanosphere with the dipole of surface plasmon with the frequency ω , have the form [34],

$$\mathbf{E}_\omega = \frac{1}{\varepsilon} \left\{ \mathbf{D}_0 \left(\frac{k^2}{R} + \frac{ik}{R^2} - \frac{1}{R^3} \right) + \hat{\mathbf{n}}(\hat{\mathbf{n}} \cdot \mathbf{D}_0) \left(-\frac{k^2}{R} - \frac{3ik}{R^2} + \frac{3}{R^3} \right) \right\} e^{ikR} \quad (30)$$

and

$$\mathbf{B}_\omega = \frac{ik}{\sqrt{\varepsilon}} [\mathbf{D}_0 \times \hat{\mathbf{n}}] \left(\frac{ik}{R} - \frac{1}{R^2} \right) e^{ikR}, \quad (31)$$

(ε is the dielectric permittivity). In the case of the spherical symmetry, the dipole of plasmon is considered as pinned to the center of the nanosphere, $\mathbf{D} = \mathbf{D}_0 e^{-i\omega t}$. In Eqs. 30 and 31, we used the notation for the retarded argument, $i\omega(t - \frac{R}{c}) = i\omega t - ikR$, $\hat{\mathbf{n}} = \frac{\mathbf{R}}{R}$, $\omega = ck$, momentum $\mathbf{p} = \hbar\mathbf{k}$. Because we consider the interaction with a closely adjacent layer of the substrate semiconductor, the terms with denominators R^2 and R we neglect as small in comparison to the term with R^3 denominator—this is the near-field-zone approximation (the magnetic field disappears and the electric field is of the form of a static dipole field [34]). Therefore, the related perturbation potential added to the system Hamiltonian attains the form,

$$w = e\psi(\mathbf{R}, t) = \frac{e}{\varepsilon R^2} \hat{\mathbf{n}} \cdot \mathbf{D}_0 \sin(\omega t + \alpha) = w^+ e^{i\omega t} + w^- e^{-i\omega t}. \quad (32)$$

The term $w^+ = (w^-)^* = \frac{e}{\varepsilon R^2} \frac{e^{i\alpha}}{2i} \hat{\mathbf{n}} \cdot \mathbf{D}_0$ describes emission, i.e., the case of our interest.

According to the Fermi golden rule (FGR) scheme, the inter-band transition probability is proportional to,

$$w(\mathbf{k}_1, \mathbf{k}_2) = \frac{2\pi}{\hbar} |\langle \mathbf{k}_1 | w^+ | \mathbf{k}_2 \rangle|^2 \delta(E_p(\mathbf{k}_1) - E_n(\mathbf{k}_2) + \hbar\omega), \quad (33)$$

where the Bloch states in the conduction and valence bands are assumed as planar waves (for simplicity), $\Psi_{\mathbf{k}} = \frac{1}{(2\pi)^{3/2}} e^{i\mathbf{k}\cdot\mathbf{R} - iE_{n(p)}(\mathbf{k})t/\hbar}$, $E_p(\mathbf{k}) = -\frac{\hbar^2 \mathbf{k}^2}{2m_p^*} - E_g$, $E_n(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m_n^*}$ (indices n, p refer to electrons from the conduction and valence bands, respectively, E_g is the forbidden gap).

The matrix element,

$$\langle \mathbf{k}_1 | w^+ | \mathbf{k}_2 \rangle = \frac{1}{(2\pi)^3} \int d^3 R \frac{e}{\varepsilon 2i} e^{i\alpha} \hat{\mathbf{n}} \cdot \mathbf{D}_0 \frac{1}{R^2} e^{-i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{R}}. \quad (34)$$

can be found analytically by a direct integration, which gives the formula ($\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2$),

$$\begin{aligned} \langle \mathbf{k}_1 | w^+ | \mathbf{k}_2 \rangle &= \frac{-1}{(2\pi)^3} \frac{e e^{i\alpha}}{\varepsilon} D_0 \cos \Theta(2\pi) \int_a^\infty dR \frac{1}{q} \frac{d}{dR} \frac{\sin qR}{qR} \\ &= \frac{1}{(2\pi)^2} \frac{e e^{i\alpha}}{\varepsilon} \frac{\mathbf{D}_0 \cdot \mathbf{q}}{q^2} \frac{\sin qa}{qa}. \end{aligned} \quad (35)$$

Next, we must sum up over all initial and final states in both bands. Thus, for the total interband transition probability, we have,

$$\delta w = \int d^3 k_1 \int d^3 k_2 [f_1(1 - f_2)w(\mathbf{k}_1, \mathbf{k}_2) - f_2(1 - f_1)w(\mathbf{k}_2, \mathbf{k}_1)], \quad (36)$$

where f_1, f_2 assign the temperature dependent distribution functions (Fermi-Dirac distribution functions) for initial and final states, respectively. For room temperatures $f_2 \simeq 0$ and $f_1 \simeq 1$, which leads to,

$$\delta w = \int d^3 k_1 \int d^3 k_2 \cdot w(\mathbf{k}_1, \mathbf{k}_2). \quad (37)$$

After some also analytical integration in the above formula, we arrive at the expression,

$$\begin{aligned} \delta w &= \frac{4}{3} \frac{\mu^2(m_n^* + m_p^*)2(\hbar\omega - E_g)e^2 D_0^2}{\sqrt{m_n^* m_p^*} 2\pi \hbar^5 \varepsilon^2} \int_0^1 dx \frac{\sin^2(xa\xi)}{(xa\xi)^2} \sqrt{1-x^2} \\ &= \frac{4}{3} \frac{\mu^2}{\sqrt{m_n^* m_p^*}} \frac{e^2 D_0^2}{2\pi \hbar^3 \varepsilon^2} \xi^2 \int_0^1 dx \frac{\sin^2(xa\xi)}{(xa\xi)^2} \sqrt{1-x^2}, \end{aligned} \quad (38)$$

$$\mathcal{A} = \beta \int_0^\infty \delta w \hbar \omega dt = \beta \hbar \omega \delta w \tau' / 2 = \begin{cases} \frac{2}{3} \frac{\beta \omega \tau' \mu \sqrt{m_n^* m_p^*} (\hbar\omega - E_g) e^2 D_0^2}{\hbar^4 \varepsilon^2}, & \text{for } a\xi \ll 1, \\ \frac{2}{3} \frac{\beta \omega \tau' \mu^{3/2} \sqrt{2} \sqrt{\hbar\omega - E_g} e^2 D_0^2}{a \hbar^3 \varepsilon^2}, & \text{for } a\xi \gg 1, \end{cases} \quad (40)$$

where τ' is the damping time-rate, β accounts for losses not included in the model, especially to reduce the energy transfer for a realistic deposition type on the top of

according to assumed band dispersions, m_n^* and m_p^* denote the effective masses of electrons and holes, $\mu = \frac{m_n^* m_p^*}{m_n^* + m_p^*}$ is the reduced mass, the parameter $\xi = \frac{\sqrt{2(\hbar\omega - E_g)(m_n^* + m_p^*)}}{\hbar}$. In limiting cases for a nanoparticle radius a , we finally obtain,

$$\delta w = \begin{cases} \frac{4}{3} \frac{\mu \sqrt{m_n^* m_p^*} (\hbar\omega - E_g) e^2 D_0^2}{\hbar^4 \varepsilon^2}, & \text{for } a\xi \ll 1, \\ \frac{4}{3} \frac{\mu^{3/2} \sqrt{2} \sqrt{\hbar\omega - E_g} e^2 D_0^2}{a \hbar^4 \varepsilon^2}, & \text{for } a\xi \gg 1. \end{cases} \quad (39)$$

In the latter case in Eq. 39, the following approximation was applied,

$$\int_0^1 dx \frac{\sin^2(xa\xi)}{(xa\xi)^2} \sqrt{1-x^2} \approx (for \ a\xi \gg 1) \frac{1}{a\xi} \int_0^\infty \times d(xa\xi) \frac{\sin^2(xa\xi)}{(xa\xi)^2} = \frac{\pi}{2a\xi},$$

whereas in the former one, $\int_0^1 dx \sqrt{1-x^2} = \pi/4$.

With regard to two limiting cases, $a\xi \ll 1$ or $a\xi \gg 1$, $\xi = \frac{\sqrt{2(\hbar\omega - E_g)(m_n^* + m_p^*)}}{\hbar}$, we see that $a \simeq$

$$1/\xi \simeq \begin{cases} > 2 \times 10^{-9} [m] \text{ for } \frac{\hbar\omega - E_g}{E_g} < 0.02 \\ < 2 \times 10^{-9} [m] \text{ for } \frac{\hbar\omega - E_g}{E_g} > 0.02 \end{cases}, \text{ and this}$$

range weakly depends on effective masses and E_g . Thus for nanoparticles with radii $a > 2$ nm, the first regime holds only close to E_g (less than the 2% distance to limiting E_g), whereas the second regime holds in the rest of the ω domain. For comparison, $a \simeq 1/\xi \simeq \begin{cases} > 0.5 \times 10^{-9} [m] \text{ for } \frac{\hbar\omega - E_g}{E_g} < 0.5 \\ < 0.5 \times 10^{-9} [m] \text{ for } \frac{\hbar\omega - E_g}{E_g} > 0.5 \end{cases}$, the first region widens considerably (to ca. 50% relative distance to E_g), but holds only for ultra-small size of nanoparticles ($a < 0.5$ nm). For larger nanospheres, e.g., with $a > 10$ nm, the second regime is thus dominating.

Assuming that the energy acquired by the semiconductor band system, $\mathcal{A}$, is equal to the output of plasmon oscillation energy (resulting in plasmon damping), one can estimate the corresponding damping rate of plasmon oscillations. Namely, at the lowering in time plasmon amplitude $D_0(t) = D_0 e^{-t/\tau'}$, one finds for a total transmitted energy,

semiconductor layer instead of the fully embedded case. Comparing the value of $\mathcal{A}$ given by the formula (40) with the energy loss of damping plasmon estimated in [29] (the

initial energy of the plasmon oscillations which has been transferred step-by-step to the semiconductor, $\mathcal{A} = \frac{D_0^2}{2\epsilon a^3}$, one can find,

$$\frac{1}{\tau'} = \begin{cases} \frac{4\beta\omega\mu\sqrt{m_n^*m_p^*}(\hbar\omega - E_g)e^2a^3}{3\hbar^4\epsilon}, & \text{for } a\xi \ll 1, \\ \frac{4\beta\omega\mu^{3/2}\sqrt{2}\sqrt{\hbar\omega - E_g}e^2a^2}{3\hbar^3\epsilon}, & \text{for } a\xi \gg 1. \end{cases} \quad (41)$$

By τ' , we denote here a large damping of plasmons due to energy transfer to the semiconductor highly exceeding the internal damping, characterized by τ_0 , due to scattering of electrons inside the metallic nanoparticle [29] ($\frac{1}{\tau_0} \ll \frac{1}{\tau'}$).

For example, for nanospheres of Au deposited on the Si layer, we obtain for Mie self-frequency $\omega = \omega_1$,

$$\frac{1}{\tau'\omega_1} = \begin{cases} 44.092\beta \left(\frac{a[nm]}{l[nm]}\right)^3 \frac{\mu}{m} \frac{\sqrt{m_n^*m_p^*}}{m}, & \text{for } a\xi \ll 1, \\ 13.648\beta \left(\frac{a[nm]}{l[nm]}\right)^2 \left(\frac{\mu}{m}\right)^{3/2}, & \text{for } a\xi \gg 1, \end{cases} \quad (42)$$

for light(heavy) carriers in Si, $m_n^* = 0.19(0.98) m$, $m_p^* = 0.16(0.52) m$, m is the bare electron mass, $\mu = \frac{m_n^*m_p^*}{m_n^*+m_p^*}$ and $E_g = 1.14$ eV, $\hbar\omega_1 = 2.72$ eV. For these parameters and nanospheres with the radius a in the range of 5–50 nm, the lower case of Eq. 42 applies (at $\omega = \omega_1$). The parameter β fitted from the experimental data [3, 29] equals to ca 0.001.

$$\omega(k) = \sqrt{\omega_1^2 \left(1 - \frac{a^3}{d^3} \text{Re}F_\alpha(k, \omega_1)\right) - \left(\frac{1}{\tau_0} + \frac{1}{\tau'(\omega_1)} - \frac{a^3}{2d^3} \text{Im}F_\alpha(k, \omega_1)\right)^2},$$

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\tau'(\omega_1)} - \frac{a^3}{2d^3} \text{Im}F_\alpha(k, \omega_1). \quad (44)$$

where $\tau'(\omega_1)$ is given by Eq. 42. The exact solution of Eq. 43 is presented in Figs. 1, 2, 3, and 4 and exhibit minor corrections of perturbative solution, though the singularity points (indicated with circles) need to thorough exact solution to avoid the singular misbehavior of perturbative solution (cf. Appendix 2).

In Figs. 1, 2, 3, and 4, we present the numerical solution of the Eq. 43 for full domain of k for the real and imaginary parts of $\omega(k)$ with corresponds to the perturbation solution given by Eq. 44. The numerical solution of the nonlinear (43) is done by the Newton-type high accuracy method applied in 1000 points of the domain $kd \in [0, 2\pi]$ point by point (the derivative of $\text{Re}\omega(k)$ with respect to k , in order to find the group velocity, has been taken from the interpolated $\text{Re}\omega(k)$ function).

Because $\text{Im}F_\alpha(k, \omega) = 0$ in majority of the domain for k as shown in Appendix 1, one can expect that

Plasmon-Polariton Dynamics in the Metallic Chain Deposited on a Semiconductor Medium

Assuming that the metallic nano chain is deposited on (or embedded in), the semiconductor medium, plasmon oscillations at each nanoparticle of the chain are additionally damped due to energy transfer to the semiconductor band system as described above. Thus, Eq. 19 should be generalized to the form:

$$\left(-\omega^2 - i\left(\frac{2}{\tau_0} + \frac{2}{\tau'}\right)\omega + \omega_1^2\right)D_\alpha(k, \omega) = \omega_1^2 \frac{a^3}{d^3} F_\alpha(k, \omega) D_\alpha(k, \omega) + \epsilon a^3 \omega_1^2 E_{0\alpha}(k, \omega), \quad (43)$$

where τ' is given by Eq. 41. Equation 20 still holds.

The damping rate in the case of the complete embedded chain in the semiconductor medium does not depend on the polarization of plasmon oscillations and let us consider first this simplest case. Upon the perturbation scheme of solution of Eq. 43, we can consider the real part of the r.h.s. of this equation as the correction to the frequency of the plasmon-polariton whereas the imaginary part as the correction to the damping rate. In the explicit form, one can thus deal with a perturbative solution,

damping of plasmon-polariton k mode will go via the channels τ_0 and $\tau'(\omega_1)$ only and not via the Lorentz friction which is perfectly balanced by the radiation income of energy from other nanoparticles in the chain (cf. Appendix 1). The comparison of contributions of both active channels for plasmon-polariton damping is presented in Figs. 1, 2, 3, and 4 for different geometry and size parameters of the chain and for the longitudinal and transverse polarization of plasmon-polariton oscillations with respect to its propagation direction. In the case of a solution of nonhomogeneous (43), the stationary solution for k -mode corresponds to the usual damped driven oscillations, when the energy of the driving incident light is transferred to the semiconductor substrate in part whereas the rest is dissipated into the Joule heat in metal material of the chain. The energy transferred to the semiconductor may be transformed eventually into photo-current, reemitted as

light via exciton recombination, and also partly converted into the Joule heat via scattering of band electrons with phonons, defects and admixtures in the semiconductor medium.

If we deal with two channels of plasmon damping, thus the energy dissipation per time unit for these channels is equal to $\int_0^T \frac{dt}{T} \frac{2}{\tau_0} \left(\frac{\partial D_\alpha}{\partial t} \right)^2$ and $\int_0^T \frac{dt}{T} \frac{2}{\tau'} \left(\frac{\partial D_\alpha}{\partial t} \right)^2$, respectively. After averaging over the period of the stationary solution of the driven and damped oscillator, we arrive with the energy loss per time unit, $\frac{1}{\tau_0} \omega^2 A^2$ and $\frac{1}{\tau'} \omega^2 A^2$, where ω is the frequency of the driving force and $A = \frac{\varepsilon a^3 \omega_1^2 E_0}{\sqrt{(\omega_1^2 - \omega^2)^2 + 4\omega^2(1/\tau_0 + 1/\tau')^2}}$. This outflow of energy is compensated during each period T of driving force by the power of this force averaged over the period. Therefore, the ratio of energy losses via two channels equals to $(1/\tau_0)/(1/\tau')$. Because the part of energy transferred to the semiconductor surroundings (substrate) may not be converted into the Joule heat or irradiation, some deficit in energy balance might be occurred not exceeding, however the indicated above ratio. When this ratio, may of order of order 1/3 (for realistic value of the parameter β [32], cf. Figures 1, 2, 3, and 4) one could observe, e.g., an ostensible shortage in the energy balance on the level of ca. 75% of incoming energy.

Conclusions

We have focused attention on energy losses of plasmon-polaritons caused by coupling of collective plasmons with another charged system in near-field zone. Coupling of dipole plasmon mode with closely located band electrons in a semiconductor opens a very quick and thus effective channel for energy transfer, which results in strong damping of plasmon-polaritons in metallic nano-chains deposited on or embedded in a semiconductor surrounding/substrate. It should be emphasized that this channel of plasmon-polariton energy leakage is not of radiative type because it undergoes on the sub-diffraction scale with regard to wave-length of plasmon resonance. Depending on nanosphere radii in the chain different regimes for near-field coupling with semiconductor substrate occur. For ultra-small nanoparticles with radii 2–3 nm the dipole coupling with substrate electrons breaks translation invariance and lifts momentum conservation constraints imposed onto interband electron transitions in semiconductor. This highly enhances the indirect (not conserving momentum) interband transition probability resulting in strong damping of plasmon-polariton in a nano-chain. With increase of

nanoparticle size, this effect is gradually weakening and at ca. 5 nm for nanoparticle radius (Au or Ag) the interband transition probability again grows up but due to increase of dipole amplitude proportional to number of oscillating electrons. Again plasmon-polaritons are strongly damped in this scale for nanoparticle size. Damping of plasmon-polaritons due to near-field coupling with semiconductor surroundings typically three times exceeds Joule heat losses due to electron scattering in metallic nanoparticles, which means that relatively easy the latter energy dissipation can be balanced by inverted energy transfer from the surrounding/substrate semiconductor to metallic nano-chain resulting in arbitrary long range plasmon-polariton propagation in such a system. This effect might be of some significance for prospective opto-electronic plasmon-polariton circuit applications.

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Appendix 1: Calculation of Radiative Damping of Plasmon-Polariton in the Chain Located in a Dielectric Surroundings

Both sides of Eq. 16 can be multiplied by $\frac{e^{i(kld-\omega t)}}{2\pi}$, and next one can perform summation with respect to nanosphere positions and integration over t . Taking into account that,

$$\begin{aligned} & \frac{1}{2\pi} \int_{-\infty}^{\infty} \sum_{l=-N}^N D_\alpha \left(\pm md + ld; t - \frac{md}{v} \right) e^{-i(kld-\omega t)} \\ &= e^{i(\mp kmd + \omega \frac{md}{v})} D_\alpha(k, \omega), \end{aligned} \quad (45)$$

one obtains thus the following equation in Fourier representation (the discrete Fourier transform for nanosphere positions and the continuous Fourier transforms for time),

$$\begin{aligned} & \left(-\omega^2 - i \frac{2}{\tau_0} \omega + \omega_1^2 \right) D_\alpha(k, \omega) \\ &= \omega_1^2 \frac{a^3}{d^3} F_\alpha(k, \omega) D_\alpha(k, \omega) + \varepsilon a^3 \omega_1^2 E_{0\alpha}(k, \omega), \end{aligned} \quad (46)$$

where $k = \frac{2\pi n}{2Nd}$, $n = 0, 1, \dots, 2N$, i.e., $kd \in [0, 2\pi]$ due to periodicity of the chain with equidistant separation d of nanospheres, and the form of k is due to Born-Karman boundary condition with the period $L = 2Nd$. For $N \rightarrow \infty$

(infinite chain limit) k is a quasi-continuous variable. In Eq. 46,

$$\begin{aligned}
 F_z(k, \omega) &= 4 \sum_{m=1}^{\infty} \left(\frac{\cos(mkd)}{m^3} \cos(m\omega d/v) + \omega d/v \frac{\cos(mkd)}{m^2} \sin(m\omega d/v) \right) \\
 &\quad + 2i \left[\frac{1}{3} (\omega d/v)^3 + 2 \sum_{m=1}^{\infty} \left(\frac{\cos(mkd)}{m^3} \sin(m\omega d/v) - \omega d/v \frac{\cos(mkd)}{m^2} \cos(m\omega d/v) \right) \right], \\
 F_{x(y)}(k, \omega) &= -2 \sum_{m=1}^{\infty} \left(\frac{\cos(mkd)}{m^3} \cos(m\omega d/v) + \omega d/v \frac{\cos(mkd)}{m^2} \sin(m\omega d/v) - (\omega d/v)^2 \frac{\cos(mkd)}{m} \cos(m\omega d/v) \right) \\
 &\quad - i \left[-\frac{2}{3} (\omega d/v)^3 + 2 \sum_{m=1}^{\infty} \left(\frac{\cos(mkd)}{m^3} \sin(m\omega d/v) \omega d/v \frac{\cos(mkd)}{m^2} \cos(m\omega d/v) \right. \right. \\
 &\quad \left. \left. - (\omega d/v)^2 \frac{\cos(mkd)}{m} \sin(m\omega d/v) \right) \right]. \tag{47}
 \end{aligned}$$

Some summations in the above equations can be done analytically [49]:

Using the above formulae, one can show that if $0 < kd \pm \omega d/v < 2\pi$, then:

$$\begin{cases} \sum_{m=1}^{\infty} \frac{\sin(mz)}{m} = \frac{\pi-z}{2}, & \text{for } 0 < z < 2\pi, \\ \sum_{m=1}^{\infty} \frac{\cos(mz)}{m} = \frac{1}{2} \ln \left(\frac{1}{2-2\cos(z)} \right), \\ \sum_{m=1}^{\infty} \frac{\cos(mz)}{m^2} = \frac{\pi^2}{6} - \frac{\pi}{2}z + \frac{1}{4}z^2, & \text{for } 0 < z < 2\pi, \\ \sum_{m=1}^{\infty} \frac{\sin(mz)}{m^3} = \frac{\pi^2}{6}z - \frac{\pi}{4}z^2 + \frac{1}{12}z^3, & \text{for } 0 < z < 2\pi. \end{cases} \tag{48}$$

$$\begin{aligned}
 \text{Im} F_z(k, \omega) &= 2 \sum_{m=1}^{\infty} \left[\frac{\sin(m(kd + \omega d/v)) - \sin(m(kd - \omega d/v))}{m^3} \right. \\
 &\quad \left. - (\omega d/v) \frac{\cos(m(kd + \omega d/v)) + \cos(m(kd - \omega d/v))}{m^2} \right] + \frac{2}{3} (\omega d/v)^3 \\
 &= 2 \left[\frac{\pi^2}{6} (kd + \omega d/v) - \frac{\pi}{4} (kd + \omega d/v)^2 + \frac{1}{12} (kd + \omega d/v)^3 \right] \\
 &\quad - 2 \left[\frac{\pi^2}{6} (kd - \omega d/v) - \frac{\pi}{4} (kd - \omega d/v)^2 + \frac{1}{12} (kd - \omega d/v)^3 \right] \\
 &\quad - 2(\omega d/v) \left[\frac{\pi^2}{6} - \frac{\pi}{2} (kd + \omega d/v) + \frac{1}{4} (kd + \omega d/v)^2 \right] \\
 &\quad - 2(\omega d/v) \left[\frac{\pi^2}{6} - \frac{\pi}{2} (kd - \omega d/v) + \frac{1}{4} (kd - \omega d/v)^2 \right] + \frac{2}{3} (\omega d/v)^3 \equiv 0. \tag{49}
 \end{aligned}$$

However, if $kd - \omega d/v < 0$ or $kd + \omega d/v > 2\pi$ for some values of wave vector k , then a more general formula must be used (by usage of Heaviside step function one can extend

the formulae (48) to the second period of their left sides; note that for $d/a \in [2, 10]$, $a < 25$ nm the next periods over the second one are not reached for $kd \in [0, 2\pi)$). This

Fig. 5 The region (blue, $0 < kd \pm \omega_1 d/v < 2\pi$) in which the radiation losses vanish for infinite chains of Au nanospheres with radius $a = 10, 15, 20$ nm and chain-separation $d/a \in [3, 6]$ ($\omega = \omega_1, v = c$)

extended form for $ImF_z(k, \omega)$ is as follows (here, we use dimensionless variables $x = kd, y = d/a$):

$$\begin{aligned}
 ImF_z(k, \omega) = & \Theta(2\pi - x - \omega ya/v) 2 \left[\frac{\pi^2}{6} (x + \omega ya/v) - \frac{\pi}{4} (x + \omega ya/v)^2 + \frac{1}{12} (x + \omega ya/v)^3 \right] \\
 & \Theta(-2\pi + x + \omega ya/v) 2 \left[\frac{\pi^2}{6} (x + \omega ya/v - 2\pi) - \frac{\pi}{4} (x + \omega ya/v - 2\pi)^2 + \frac{1}{12} (x + \omega ya/v - 2\pi)^3 \right] \\
 & - \Theta(x - \omega ya/v) 2 \left[\frac{\pi^2}{6} (x - \omega ya/v) - \frac{\pi}{4} (x - \omega ya/v)^2 + \frac{1}{12} (x - \omega ya/v)^3 \right] \\
 & - \Theta(-x + \omega ya/v) 2 \left[\frac{\pi^2}{6} (x - \omega ya/v + 2\pi) - \frac{\pi}{4} (x - \omega ya/v + 2\pi)^2 + \frac{1}{12} (x - \omega ya/v + 2\pi)^3 \right] \\
 & - \Theta(2\pi - x - \omega ya/v) 2(\omega ya/v) \left[\frac{\pi^2}{6} - \frac{\pi}{2} (x + \omega ya/v) + \frac{1}{4} (x + \omega ya/v)^2 \right] \\
 & - \Theta(-2\pi + x + \omega ya/v) 2(\omega ya/v) \left[\frac{\pi^2}{6} - \frac{\pi}{2} (x + \omega ya/v - 2\pi) + \frac{1}{4} (x + \omega ya/v - 2\pi)^2 \right] \\
 & - \Theta(-x + \omega ya/v) 2(\omega ya/v) \left[\frac{\pi^2}{6} - \frac{\pi}{2} (x - \omega ya/v + 2\pi) + \frac{1}{4} (x - \omega ya/v + 2\pi)^2 \right] \\
 & - \Theta(x - \omega ya/v) 2(\omega ya/v) \left[\frac{\pi^2}{6} - \frac{\pi}{2} (x - \omega ya/v) + \frac{1}{4} (x - \omega ya/v)^2 \right] + \frac{2}{3} (\omega ya/v)^3.
 \end{aligned} \tag{50}$$

The function given by Eq. 50 is depicted in Fig. 6. The expression (50) allows to account for the inconsistency of periodic functions given by the sums of sines and cosines with the Lorentz friction term and not coincidence of arguments $kd \pm \omega d/v$ of trigonometric functions (out of the first period, which is sufficient for $d/a \leq 10, a < 25$ nm). In Fig. 5, we have plotted the solution of the equation

$(kd - \omega d/v)(kd + \omega d/v - 2\pi) = 0$, which determines the region for kd (denoted by x) versus d/a (denoted by y) inside which the exact cancellation of the Lorentz friction by radiative energy income from other nanospheres takes place. In Fig. 6, the comparison of this cancellation for various nanosphere diameters is presented, for longitudinal polarization of plasmon collective excitations.

Fig. 6 The function $ImF_z(k; \omega = \omega_1)$ for infinite chains of Au nanospheres with radius $a = 10, 15, 20$ nm and chain-separation $d = 3a, 4a, 5a$

The similar analysis can be done for transversal polarization, i.e., for $ImF_{x(y)}(k, \omega)$. This function is exactly zero only for the region for arguments $0 < kd - \omega d/v < 2\pi$ and $0 < kd + \omega d/v < 2\pi$, where one can write:

$$\begin{aligned}
 ImF_{x(y)}(k, \omega) &= - \sum_{m=1}^{\infty} \left[\frac{\sin(m(kd + \omega d/v)) - \sin(m(kd - \omega d/v))}{m^3} \right. \\
 &\quad - (\omega d/v) \frac{\cos(m(kd + \omega d/v)) + \cos(m(kd - \omega d/v))}{m^2} \\
 &\quad \left. - (\omega d/v)^2 \frac{\sin(m(kd + \omega d/v)) - \sin(m(kd - \omega d/v))}{m} \right] + \frac{2}{3}(\omega d/v)^3 \\
 &= - \left[\frac{\pi^2}{6}(kd + \omega d/v) - \frac{\pi}{4}(kd + \omega d/v)^2 + \frac{1}{12}(kd + \omega d/v)^3 \right] \\
 &\quad + \left[\frac{\pi^2}{6}(kd - \omega d/v) - \frac{\pi}{4}(kd - \omega d/v)^2 + \frac{1}{12}(kd - \omega d/v)^3 \right] \\
 &\quad + (\omega d/v) \left[\frac{\pi^2}{6} - \frac{\pi}{2}(kd + \omega d/v) + \frac{1}{4}(kd + \omega d/v)^2 \right] \\
 &\quad + (\omega d/v) \left[\frac{\pi^2}{6} - \frac{\pi}{2}(kd - \omega d/v) + \frac{1}{4}(kd - \omega d/v)^2 \right] \\
 &\quad - \frac{1}{2}(\omega d/v)^2 [\pi - kd - \omega d/v] - \frac{1}{2}[\pi - kd + \omega d/v] + \frac{2}{3}(\omega d/v)^3 \equiv 0.
 \end{aligned} \tag{51}$$

Nevertheless, outside the region $0 < kd \pm \omega d/v < 2\pi$, the value of $ImF_{x(y)}$ is not zero, as it is demonstrated in

Fig. 7, and can be accounted for by the formula ($x = kd$, $y = d/a$):

$$\begin{aligned}
 ImF_{x(y)}(k, \omega) &= -\Theta(2\pi - x - \omega ya/v) \left[\frac{\pi^2}{6}(x + \omega ya/v) - \frac{\pi}{4}(x + \omega ya/v)^2 + \frac{1}{12}(x + \omega ya/v)^3 \right] \\
 &\quad - \Theta(-2\pi + x + \omega ya/v) \left[\frac{\pi^2}{6}(x + \omega ya/v - 2\pi) - \frac{\pi}{4}(x + \omega ya/v - 2\pi)^2 + \frac{1}{12}(x + \omega ya/v - 2\pi)^3 \right] \\
 &\quad + \Theta(x - \omega ya/v) \left[\frac{\pi^2}{6}(x - \omega ya/v) - \frac{\pi}{4}(x - \omega ya/v)^2 + \frac{1}{12}(x - \omega ya/v)^3 \right] \\
 &\quad + \Theta(-x + \omega ya/v) \left[\frac{\pi^2}{6}(x - \omega ya/v + 2\pi) - \frac{\pi}{4}(x - \omega ya/v + 2\pi)^2 + \frac{1}{12}(x - \omega ya/v + 2\pi)^3 \right] \\
 &\quad + \Theta(2\pi - x - \omega ya/v)(\omega ya/v) \left[\frac{\pi^2}{6} - \frac{\pi}{2}(x + \omega ya/v) + \frac{1}{4}(x + \omega ya/v)^2 \right] \\
 &\quad + \Theta(x - \omega ya/v)(\omega ya/v) \left[\frac{\pi^2}{6} - \frac{\pi}{2}(x - \omega ya/v) + \frac{1}{4}(x - \omega ya/v)^2 \right] \\
 &\quad + \Theta(-2\pi + x + \omega ya/v)(\omega ya/v) \left[\frac{\pi^2}{6} - \frac{\pi}{2}(x + \omega ya/v - 2\pi) + \frac{1}{4}(x + \omega ya/v - 2\pi)^2 \right] \\
 &\quad + \Theta(-x + \omega ya/v)(\omega ya/v) \left[\frac{\pi^2}{6} - \frac{\pi}{2}(x - \omega ya/v + 2\pi) + \frac{1}{4}(x - \omega ya/v + 2\pi)^2 \right] \\
 &\quad + \Theta(2\pi - x - \omega ya/v) \frac{1}{2}(\omega ya/v)^2 [\pi - x - \omega ya/v] + \Theta(-2\pi + x + \omega ya/v) \frac{1}{2}(\omega ya/v)^2 [3\pi - x - \omega ya/v] \\
 &\quad - \Theta(x - \omega ya/v) \frac{1}{2}(\omega ya/v)^2 [\pi - x + \omega ya/v] - \Theta(-x + \omega ya/v)^2 [-\pi - x + \omega ya/v] + \frac{2}{3}(\omega ya/v)^3.
 \end{aligned} \tag{52}$$

Fig. 7 The function $\text{Im} F_{x(y)}(k; \omega = \omega_1)$ for infinite chains of Au nanospheres with radius $a = 10, 15, 20$ nm and chain-separation $d = 3a, 4a, 5a$

Fig. 8 Sums $\sum_{n=1}^{\infty} \frac{\sin(nx)}{n}$ (left), $\sum_{n=1}^{\infty} \frac{\cos(nx)}{n^2}$ (center), $\sum_{n=1}^{\infty} \frac{\sin(nx)}{n^3}$ (right), for $x \in (-1, 15)$

This function is plotted in Fig. 7. The discontinuity jump on the border between the regions with vanishing radiative damping and with nonzero radiative attenuation is caused by discontinuous function $\sum_{n=1}^{\infty} \frac{\sin(nz)}{n}$ (cf. Fig. 8) entering $\text{Im} F_{x(y)}$ but not $\text{Im} F_z$, cf. Equation 47.

Appendix 2: Exact Solution of Eq. 43—the Resolution of the Problem of Logarithmic Divergence of Far-Field-Zone Contribution

The imaginary part of the solution $\omega(k)$ of Eq. 43 defines plasmon-polariton attenuation, while the real part of $\omega(k)$ gives self-frequency of these oscillations (in the case of homogeneous equation, i.e., when $E_{0\alpha}(k, \omega) = 0$). The derivative of this self-frequency with respect to the wave vector k defines the group velocity of particular modes. Because of logarithmic singular term in the far-field transversal contribution to dipole interaction in the chain (cf. Equation 20),

$$\begin{aligned} & \sum_{m=1}^{\infty} \frac{\cos(m(x + \omega y a/v)) + \cos(m(x - \omega y a/v))}{m} \\ &= -\frac{1}{2} \ln[(2 - 2\cos(x + \omega y a/v))(2 - 2\cos(x - \omega y a/v))], \end{aligned} \quad (53)$$

one cannot apply the perturbation method for solution of dynamical equation, at least in the region close to the singularity. Note that within the perturbation approach one can substitute ω with ω_1 (Mie frequency) in r.h.s. of Eq. 43. This produces, however, the hyperbolic singularity in transversal group velocity resulted by virtue of Eq. 53. Moreover, within the perturbation approach, the logarithmic singularity occurs also for both polarizations, which is

noticeable if one takes the derivative with respect to k from the perturbative expressions for $\text{Re} \omega_{\alpha}(k)$. All these singularities occur in isolated points for which $k d \pm \omega_1 d/v = l\pi$ (l is an integer). Both hyperbolic and logarithmic divergences in perturbation formula for group velocities in this points would result in artificial local exceeding c by corresponding group velocities. To resolve the problem of this unphysical divergence, the exact solution of Eq. 43 must be found, because of divergence of the expression (53) the corresponding contribution cannot be treated still as perturbation. The exact solution of Eq. 43, found numerically, is plotted in Figs. 1, 2, 3, and 4, for both polarizations of plasmon-polaritons.

The exact solutions presented in Figs. 1, 2, 3, and 2 do not differ significantly from those obtained in the perturbation manner out of the singularity points, but the change suffices to remove out the logarithmic divergence from derivative of the self-frequencies. For the transverse polarization (Figs. 3 and 4), the difference is also not significant out of the singularity points. However, for the transverse polarization self-frequency in the case of exact solution, we deal with quenching of the logarithmic divergence (53) in contrary to the approximated its version (obtained within the perturbation approach). Instead of infinite singularity, we observe in the exact plot for the transverse polarization self-frequencies only relatively small minimum resulting then conveniently in finite group velocity (not greater than 5×10^7 m/s, for $a = 10$ – 20 nm). This quenched logarithmic singularity marked in Fig. 9 into small local minimum is presented in Fig. 10—right (on the left it is presented also the correction to the discontinuity step in the damping of transverse mode caused by logarithmic contribution to Eq. 43).

The exact solution of the dynamic (19) (and of Eq. 43) resolves thus the problem of risky logarithmic divergent contribution of transversal far-field part of dipole interaction

Fig. 9 The exact solution for self-frequency and damping rate of transverse mode of plasmon-polariton in the nano-chain (ω in ω_1 units; solution of Eq. 19 (similar as of Eq. 43) in 1000 points on the sector $[0, 2\pi]$; in plot of damping rate a local lowering below the Ohmic attenuation is marked; in the middle the plot for group

velocity of transverse mode is presented with hyperbolic-type singularities corresponding to logarithmic-type singularities of selfenergy (left); singularities are truncated what is visualized in marked regions in Fig. 10

of nano-spheres in the infinite chain and regularizes the final solution for corresponding characteristics of plasmon-polariton modes. In the vicinity of singularity points (in the domain for kd), the group velocity, though still well lower than light velocity, is, however, greater in comparison to group velocities in other regions of the k wave vector domain. This elucidates the former numerical observations [50] of long-range propagating mode for transversal polarization of plasmon-polariton in the nano-chain.

Even though the real part of the function F_z and thus perturbative $\omega_z(k)$ is given by a continuous function, the corresponding perturbative group velocity will have logarithmic singularity as the derivative of $\omega_z(k)$ with respect to k will contain the divergent sum $\sum_m (\cos(m(x + \omega_1 ya/v)) - \cos(m(x - \omega_1 ya/v)))/m$. The similar term is present also in perturbative formula for $\omega_{x(y)}(k)$. The origin

of these terms for both polarization is the medium-field-zone contribution to dipole interaction in the chain. In points $x \pm \omega_1 ya/v = p2\pi$, p integer, the logarithmic singularity produces an artifact of the group velocity v_z exceeding c . This precludes applicability of the perturbation solution approach, at least close to singularity points. Therefore, instead of putting $\omega = \omega_1$ in function F_α in r.h.s. of Eq. 16 (as was done for the perturbation method of solution of this equation), one must solve exactly the nonlinear (43). As was already mentioned above, this exact solution can be found numerically and both real and imaginary parts of ω can be determined in the whole region $kd \in [0, 2\pi]$ —in Figs. 1, 2, 3, and 4. For the longitudinal polarization of the group velocity, the exact solution is detailed on an example close to the singular point in Fig. 11. The exact solutions for v_z do not exhibit any singularities—the logarithmic singularity in perturbation term is quenched to only small

Fig. 10 Two level magnification of the scale of view on the truncated singularity region for transverse plasmon-polariton mode in the nano-chain for the exact solution of Eq. 19 (or similar of Eq. 43) ω in ω_1 units, v in m/s; vertical lines are artifact of numerical interpolation)(in

close vicinity of the singular point the solution has been found by the Newton-type method in 2000 points kd , point by point, for the sectors indicated in the figure)

Fig. 11 The exact solution for the group velocity v_z of longitudinal mode of plasmon-polariton in the nano-chain for $a = 10, 15$ nm and $d = 3a, 4a$, respectively, and the corresponding exact solutions for $\text{Re } \omega_z$ (left); exact solution of dynamic (19) (or of Eq. 43) removes the logarithmic singularity – the remaining local very narrow extremes are

local extrema similarly as it was demonstrated above for the transversal polarization.

The logarithmic-type singularity in the self-energy for transverse polarized plasmon-polaritons in the chain is the feature which essentially differentiates these modes from the longitudinally polarized ones. This singularity is caused by the sum of far-field-zone part of the electric field of all nanoparticle dipoles which influence a charge oscillations in each component of the chain and produces hyperbolic-type discontinuity in perturbative group velocity exclusively for transversal polarization. Besides this discontinuity the medium-field-zone component of electric interaction of dipoles additionally produces a logarithmic-type singularity in the perturbative group velocities for both polarizations (though any singularity in self-energies). We use here the terms logarithmic-type or hyperbolic-type singularities to distinguish the exact behavior of the group velocities obtained by the exact solution for self-energies for both polarizations, which are sharpened and truncated at c due to relativistic constraints imposed on the dynamic equation and manifesting themselves in the form of its solution. The retardation of electric signals prohibits the collective excitation group velocity to exceed the light velocity. This quenching concerns infinite singularities which occur in the perturbation expressions for self-energy and next in the perturbation formulae for group velocities at singular points. The relativistic invariance of dynamic equation for collective dipole plasmon oscillations in the chain prevents, however, exceeding the light velocity by the group velocity of particular plasmon-polariton modes. Thus, the exact solution of this equation inherently possesses also this property. Exact self-energies as solutions of nonlinear (43) have

truncated exactly at value of $|c|$ (for magnification in close vicinity of the singular point the solution has been found by the Newton-type method in 2000 points kd , point by point, for the sectors indicated in the bottom panels corresponding to marked fragments in the upper panels)

suitably regularized their dependence with respect to k , that their derivatives do not exceed c .

It is worth emphasizing for the sake of completeness of the description, that inclusion of magnetic field of dipoles does not modify this scenario, because the magnetic field contribution to self-energies is at least two order lower in comparison to electric field contribution due to the Fermi velocity of electrons being two order lower in comparison to light velocity, which significantly reduces the Lorentz force. Therefore, the magnetic field of the dipoles [34, 43],

$$B_\omega = ik(\mathbf{D}_\omega \times \mathbf{n}) \left(\frac{ik}{r_0} - \frac{1}{r_0^2} \right) e^{ikr_0}, \quad (54)$$

though contributing to the far-field and medium-field parts of plasmon-polariton self-energies, does not change significantly the similar terms caused by the electric field and causes only by two-orders lower corrections.

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