Comment on "Silver nanoparticle array structures that produce remarkably narrow plasmon line shapes" [J. Chem. Phys. 120, 10871 (2004)]

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Recently, Zou, Janel, and Schatz (referred to as ZJS below) have described remarkably narrow plasmon resonances in linear arrays of silver nanospheres.[1] Without questioning the novelty and significance of these results, I would like to point out that the above-referenced paper contains two incorrect statements.

The first statement is about my previous work. Namely, ZJS write that in a previous study[2] I have considered "…infinite one-dimensional arrays in the quasistatic approximation." In fact, there was no quasistatic approximation made in Ref. 2. The approximation that was made was the *dipole approximation*. These two approximations are distinctly different. For example, even in the electrostatic limit, the dipole approximation is grossly inaccurate for two touching conducting spheres excited by a constant external electric field parallel to the axis connecting the spheres' centers.[3] On the other hand, electromagnetic interaction of small impurities in a crystal or of dye molecules in large molecular aggregates[4] cannot be understood within the quasistatics, although the dipole approximation may be very accurate in this case.

Perhaps, the source of confusion is that in Sec. II A of Ref. 2 I wrote "The object under investigation is a linear infinite chain with step *a* consisting of pointlike dipole units (monomers)…." Also, in the Introduction of Ref. 2, I have suggested that the physical system to which the considered model is applicable is a molecular aggregate. Later, in Sec. V, I have considered a particular example in which the polarizability of a dipole, α, was given by the quasistatic polarizability of a small sphere with the appropriate radiative correction. However, the theoretical formalism of Ref. 2 did not put any restrictions on α. And, regardless of the form of α, the interaction of dipoles was described with full account of retardation effects.

In fact, ZJS also work in the dipole approximation, although they validate their results by comparison with a more general *T*-matrix solutions. The situation is somewhat more complicated, however, because ZJS use, in addition, an approximation proposed by Doyle in 1989 (Ref. 5) in the context of effective-medium theory of the so-called extended Maxwell–Garnett composites, i.e., composites in which inclusions are not small compared to the wavelength. More specifically, Doyle has studied electromagnetic properties of a homogeneous host with randomly distributed spherical inclusions. The essence of the approximation is to consider only dipole-dipole interactions of the inclusions but to assign

them dynamic dipole polarizability α. The latter is given by formula (2) below; it is defined as the linear coefficient between the amplitude of incident plane wave and the total dipole moment of polarizable sphere of arbitrary size (assuming, the sphere is isolated) and, in that sense, is exact. It can be seen that the Doyle's approach only concerns the choice of α within the dipole approximation. Thus, it is fully consistent with the general formalism developed in Ref. 2.

It should be noted that the accuracy and limits of applicability of the Doyle's approximation have not been systematically investigated. In one critical study of extended Maxwell–Garnett composites[6] Ruppin has shown that the Doyle's approximation is consistent with the asymptotes obtained in the limit of small volume fraction of inclusions, and, in that limit, allows one to consider inclusions with size parameters of at least $x \sim 0.5$. Thus, the Doyle's approximation can be useful for moderate size parameters. However, if the spherical inclusions are in close proximity of each other, the secondary scattered waves incident upon each of them are no longer plane waves. But the dynamic polarizability used by Doyle is exact only with respect to incident plane waves. Besides, coupling of higher multipole modes excited in spherical inclusions can become significant. Therefore, it is quite obvious that the use of Doyle's approximation does not fix, in principle, the deficiencies of the dipole approximation.

The second statement concerns the possibility of cancellation of the imaginary part of denominator in the expression $P = \alpha E_0 / (1 - \alpha S)$ [Eq. (5), or, in a more specific form, Eq. (7) of Ref. 1]. This is discussed on p. 10874 of Ref. 1. ZJS consider the case when the incident wave vector is perpendicular to a linear chain of polarizable dipoles with the period D. The polarization of the incident wave is also perpendicular to the chain. It is stated that the resonance width, which is related in Ref. 1 to the imaginary part of the denominator of the above equation, vanishes when $\gamma \lesssim 8\pi^3 A / D^3$, where γ and A are parameters which specify the polarizability of an isolated sphere. Namely, ZJS use the formula $\alpha = -A / (\omega - \omega_p + i\gamma)$, where ω is frequency of incident radiation, ω_p is the surface plasmon frequency and γ is the relaxation parameter. Assuming that the result $\text{Im} S = -8\pi^3 / D^3$, which is given in Ref. 1 for λ slightly larger than the interparticle distance D, is correct, one immediately can see that the cancellation takes place exactly at $\gamma = 8\pi^3 A / D^3$. For smaller values of γ, the imaginary part of

the denominator becomes, in fact, negative. Such result clearly contradicts conservation of energy and is unphysical. It was obtained in Ref. 1 due to several mistakes which are discussed below.

It is convenient to rewrite Eq. (5) of Ref. 1 as

$$P = \frac{E_0}{1/\alpha - S}. \tag{1}$$

Given the specific form $\alpha = -A/(\omega - \omega_p + i\gamma)$, this expression differs from Eq. (7) of Ref. 1 only by dividing the numerator and denominator by the real constant A. The quantity S here is the "dipole sum"—an eigenvalue of the electromagnetic state of the dipole chain which is excited by incident radiation. The imaginary part of the denominator of Eq. (1) defines total relaxation.

Note that $\text{Im}(1/\alpha)$ can contain two contributions which correspond to absorptive and radiative relaxation. Both are strictly negative. On the other hand, imaginary part of S has nothing to do with absorptive losses, since S does not depend on material properties. Thus, $\text{Im}S$ can only influence radiative relaxation and can be either positive or negative. In the first case, the radiative relaxation is increased compared to that of an isolated sphere, while in the latter case it is reduced. It is important to note that $1/\alpha$ and S satisfy the following general inequalities: $\text{Im}(1/\alpha) \leqslant -2k^3/3$ (Refs. 7 and 8) and $\text{Im}S \geqslant -2k^3/3$ (Ref. 9), where $k = 2\pi/\lambda$ is the wave number. Both inequalities follow from the very general consideration of energy conservation. At the very least, they show that the imaginary part of the denominator of Eq. (1) cannot become negative. The radiative relaxation is canceled if $\text{Im}S = -2k^3/3$ (this possibility is discussed below). If, in addition, $\text{Im}(1/\alpha) = -2k^3/3$, total relaxation is equal to zero. Physically, this cannot happen due to small absorption which is always present even in highly transparent materials, deviations from the dipole approximation, etc.

Let us rewrite the above inequalities for $\lambda \approx D$, which is the situation considered in Ref. 1. We obtain $\text{Im}(1/\alpha) \leqslant -16\pi^3/3D^3$ and $\text{Im}S \geqslant -16\pi^3/3D^3$. The result adduced in Ref. 1, namely, $\text{Im}S = -8\pi^3/D^3 \approx -k^3$, clearly contradicts the second inequality. This is due to two reasons. First, it is incorrect that the far-field term $\sum_{j \neq i}(k^2 e^{ikr_{ij}}/r_{ij})$ dominates the dipole sum S for $\lambda \approx D$, as is stated in Ref. 1. This would be only true for the *real part* of S. Second, even if only the far field term is used in the calculation of S, the result adduced in Ref. 1 is off by the factor of 2. The correct contribution to $\text{Im}S$ which comes from the far-zone term is $[\text{sgn}(D-\lambda)]4\pi^3/D^3$. The contribution which comes from the intermediate-zone term is $2\pi^3/3D^3$. The contribution from the near-zone term is zero. Thus, we have $\text{Im}S = -10\pi^3/3D^3$ for $D < \lambda$ and $\text{Im}S = 14\pi^3/3D^3$ for $D > \lambda$ (all calculations are done for $D - \lambda \ll D$). It can be seen that the inequality $\text{Im}S \geqslant -16\pi^3/3D^3$ is satisfied *strongly*. Therefore, not only the imaginary part of the denominator cannot become negative, but its exact cancellation is also impossible in the considered geometry. The smallest possible value of $\text{Im}(1/\alpha - S)$ is equal to $-2\pi^3/3D^3$. However, it is correct that the radiative relaxation is changed by a significant factor when $\lambda - D$ changes sign. Thus, $-[16\pi^3/3D^3 + \text{Im}S] = -10\pi^3/D^3$ for $\lambda < D$ and

$-[16\pi^3/3D^3 + \text{Im}S] = -2\pi^3/D^3$ for $\lambda > D$, a drop by the factor of 5. This can be practically important if radiative losses are dominant over absorptive losses.

Next, we discuss the inequality $\text{Im}(1/\alpha) \leqslant -2k^3/3$. This inequality insures that the dipole contribution to the absorption cross section of a particle is not negative. It must hold even for nonabsorbing particles and, in particular, for $\gamma = 0$. In the case of a small particle, this inequality is satisfied if one uses the quasistatic polarizability with the inclusion of the radiative reaction correction: $\alpha = \alpha^{(\text{QS})}/(1 - 2ik^3\alpha^{(\text{QS})}/3)$. Here α is the polarizability with the radiative correction and $\alpha^{(\text{QS})} = R^3(\epsilon - 1)/(\epsilon + 2)$ is the quasistatic polarizability, R being the sphere radius. The importance of the radiative correction is discussed, for example, in Ref. 7, and the authors of Ref. 1 are also aware of it [see Ref. 10, Eqs. (16)–(18)]. The expression $\alpha = -A/(\omega - \omega_p + i\gamma)$ used in Ref. 1 does not contain the radiative correction. Therefore, its use (together with an incorrect expression for S) leads to unphysical results in the limit $\gamma \to 0$, such as the total cancellation of relaxation or negative relaxation. It should be also noted that the dynamic expression for α which ZJS used in numerical simulations (according to the Doyle's approximation) also satisfies the above inequality. Indeed, if we take

$$\alpha = \frac{3i}{2k^3} \frac{m\psi_1(mkR)\psi_1'(kR) - \psi_1(kR)\psi_1'(mkR)}{m\psi_1(mkR)\xi_1'(kR) - \xi_1(kR)\psi_1'(mkR)}, \tag{2}$$

where ψ_1 and ξ_1 are the Riccati–Bessel functions, $m = \sqrt{\epsilon}$ is the complex refractive index of the spheres, then the Taylor expansion of $\text{Im}(1/\alpha)$ in powers of the wave number reads

$$\text{Im}(1/\alpha) = -\frac{2k^3}{3} - \frac{3\,\text{Im}\,\epsilon}{R^3|\epsilon - 1|^2} - \frac{3k^2\text{Im}\,\epsilon}{5R|\epsilon - 1|^2}$$
$$- \frac{3k^4 R(8 + |\epsilon|^2 - 2\,\text{Re}\,\epsilon)\text{Im}\,\epsilon}{350|\epsilon - 1|^2} + O(k^6 R^3). \tag{3}$$

The expansion beyond the third order contains only even powers of k and it can be verified that each term in the expansion is nonpositive. The exact equality $\text{Im}(1/\alpha) = -2k^3/3$ takes place only for nonabsorbing materials with $\text{Im}\,\epsilon = 0$ (which do not occur in nature).

Finally, we discuss the possibility of exact cancellation of the radiative relaxation. Note that (i) only the *radiative part* of relaxation can be zero, (ii) the *total relaxation* is always nonzero due to nonzero absorption, but can become, in principle, arbitrarily small, and (iii) such cancellation cannot take place in the geometry considered in Ref. 1. Generally, there can be two reasons for cancellation of the radiative relaxation. The first is symmetry.[9] Within the dipole approximation, the cancellation takes place when the symmetry of a particular excitation mode is such that dipole radiation is forbidden. A nonzero radiative relaxation can still result from higher-multipole radiation, similarly to nonzero decay rates of excited atomic states whose decay is dipole forbidden. The second reason is when photon emission is prohibited by conservation laws, such as the light cone condition.[11] In a linear chain of dipole-polarizable particles the cancellation of radiative relaxation can take place when the incident wave vector is parallel to the chain. However, the radiative relaxation is always nonzero for normal incidence.

[1] S. Zou, N. Janel, and G. C. Schatz, J. Chem. Phys. **120**, 10871 (2004).
[2] V. A. Markel, J. Mod. Opt. **40**, 2281 (1993).
[3] I. E. Mazets, Tech. Phys. **45**, 8 (2000).
[4] D. Keller and C. Bustmante, J. Chem. Phys. **84**, 2961 (1986).
[5] W. T. Doyle, Phys. Rev. B **39**, 9852 (1989).
[6] R. Ruppin, Opt. Commun. **182**, 273 (2000).
[7] B. T. Draine, Astrophys. J. **333**, 848 (1988).
[8] V. A. Markel, J. Mod. Opt. **39**, 853 (1992).
[9] V. A. Markel, J. Opt. Soc. Am. B **12**, 1783 (1995).
[10] L. K. Kelly, E. Coronado, L. L. Zhao, and G. C. Schatz, J. Phys. Chem. **107**, 668 (2003).
[11] A. L. Burin, H. Cao, G. C. Schatz, and M. A. Ratner, J. Opt. Soc. Am. B **21**, 121 (2004).