Contribution of dipolar interactions to third-order nonlinear dielectric susceptibility of nanocomposites

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We consider an ensemble of identical semiconductor nanoparticles randomly embedded into dielectric matrix. The nanoparticles are polarized by the laser irradiation having linear polarization. The contribution of dipole–dipole interactions to third-order dielectric susceptibility is calculated by using mean random field method. It is shown that this contribution always has a negative sign, and it can be comparable with the values of optical nonlinearity observed experimentally. © 2010 Optical Society of America

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In recent years there has been considerable interest in studying optical properties of nanocomposites containing, in particular, semiconductor particles. Nonlinear optical characteristics of such the systems are enhanced in comparison with bulk materials. Specifically, nanocomposites can be utilized as optical limiters, sensors, light emitters, etc.

Concentrations of the nanoparticles in the host medium can be as much as tens of percent when the interparticle coupling effects come into prominence, especially the dipole–dipole interactions. Existing theories usually neglect this effect. Some authors numerically treat the contribution of dipolar interactions to optical properties of nanocomposites containing metallic particles [1]. This approach requires much computation and has less generalization. In this Letter, we make an attempt to close this gap.

In our model we consider the steady-state ensemble of identical spherical nanoparticles randomly embedded into dielectric matrix that are polarized by laser irradiation. The incident light is assumed to have linear polarization. The particles are thought of as being polarized dipoles keeping their polarization for a while. We suppose that the dipole moments have equal magnitudes with two equiprobable opposite directions. The model suggests that some number of nanoparticles are polarized with constant dipole moment at every instant. These approximations are assumed to be valid for the case of nanocomposites containing semiconductor quantum dots [2]. These particles could be excited, and the lifetime of this state is much larger than the period of optical field alteration. The modeled ensemble can be treated as an Ising system in this approach.

The absolute value of the induced dipole electric moment p of a particle in our model is assumed to be proportional to the amplitude of electric field of the incident irradiation E_{in} ,

$$p = \varepsilon_m \alpha v E_{\rm in},\tag{1}$$

where α is dimensionless polarizability of the particle, v is its volume, and ε_m is a dielectric function of matrix. Dipole moment **p** may have two opposite randomly selected directions. One can estimate α , using classic theory, as

$$\alpha = \frac{3}{4\pi} \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m},\tag{2}$$

where ε_p is a dielectric function of the particle.

Further, we calculate the random electric field induced on the test particle by other polarized particles through the dipolar interaction. The field of induced dipole of the *l*th particle located by radius-vector \mathbf{R}_l at test particle is

$$\mathbf{E}_l = \frac{3(\mathbf{R}_l \cdot \mathbf{p})\mathbf{R}_l - \mathbf{p}R_l^2}{\varepsilon_m R_l^5}.$$

It is known that the probability function of random field $\mathbf{E} = \sum_{l} \mathbf{E}_{l}$ in such a system is Cauchy–Lorentzian or Gaussian depending on volume concentration *c* of nanoparticles in the sample [3].

For $c \rightarrow 0$ the distribution function over dipolar interaction fields *E* is Cauchy–Lorentzian [3,4]:

$$W_L = \frac{B_L}{\pi (B_L^2 + E^2)},$$
 (3)

where

$$B_L = \frac{8\pi^2}{9\sqrt{3}} cv\alpha E_{\rm in}.\tag{4}$$

At higher concentrations for finite particles the distribution function turns into Gaussian [3]:

$$W_{G} = \frac{\exp(-(E/B_{G})^{2})}{\sqrt{\pi}B_{G}}$$
(5)

with variance

$$B_G = \sqrt{\frac{32\pi cv}{15(2r)^3}} \alpha E_{\rm in},\tag{6}$$

where r is the radius of the particle. The threshold concentration of transition to Gaussian distribution was estimated in [5] as 0.1. It should be underlined that

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the mean random field on the test particle is zero owing to the symmetry of the problem.

The energy of interaction of dipole induced on the test particle with the random field is -pE, so one can arrive at the partition function per particle using relation

$$Z = \int \exp(-pE/k_B T)W(E)dE,$$
(7)

where W(E) is the distribution function (3) or (5), k_B is the Boltzmann constant, and *T* is the temperature. Free energy of the ensemble is

$$F = -k_B T \frac{c}{v} \ln Z.$$

The nonlinear cubic dielectric susceptibility of the isotropic medium $\chi^{(3)}$ is defined by relation between $E_{\rm in}$ and macroscopic polarization *P*:

$$P = \chi^{(1)} E_{\rm in} + \chi^{(3)} |E_{\rm in}|^2 E_{\rm in}, \qquad (8)$$

where $\chi^{(1)}$ is linear susceptibility of the system. For monochromatic irradiation and nonabsorbing medium *P* can be calculated using the thermodynamic relation [6]

$$P = -\frac{\partial \langle F \rangle_t}{\partial E_{\rm in}},\tag{9}$$

where $\langle \rangle_t$ denotes time averaging. One can obtain thirdorder susceptibility $\chi^{(3)}$ by solving Eqs. (8) and (9).

For the case of a Lorentzian distribution function the integration in Eq. (7) could be limited by $\pm E_{\text{max}}$:

$$E_{\max} = 2p/\varepsilon_m (2r)^3, \tag{10}$$

which is the maximum value of dipolar interaction field from the possible closest particle. The partition function for Lorentzian distribution is

$$Z = \frac{i}{2\pi} \{ [\text{Ei}_{1}(a+ib) - \text{Ei}_{1}(-a-ib)]e^{-ib} + [\text{Ei}_{1}(-a+ib) - \text{Ei}_{1}(a-ib)]e^{ib} \},\$$

$$a = \frac{a^{2}v^{2}E_{\text{in}}^{2}}{4r^{3}k_{B}T}, \qquad b = \frac{a^{2}vE_{\text{in}}^{2}}{k_{B}T}, \qquad (11)$$

where Ei₁ is the exponential integral. Expanding $\partial F/\partial E_{\rm in}$ into a series in terms of $E_{\rm in}$ and retaining the lowest-order term, we obtain $\chi^{(3)}$:

$$\chi^{(3)} = \frac{8\pi^2 \epsilon_m^2 \alpha^4 v c^2}{27k_B T} \left\{ \frac{16c\pi^2}{9} + \frac{\sqrt{3}v}{(2\arctan\frac{32\pi^2 c r^3}{9\sqrt{3}v} - \pi)r^3} \right\}.$$
(12)

Applying again $c \to 0$ we have

$$\chi^{(3)} = -\frac{8\pi\epsilon_m^2 v^2 \alpha^4 c^2}{9\sqrt{3} r^3 k_B T}.$$
 (13)

The formula (12) was obtained under assumption of polarization of the test particle parallel to selected direction. The particle can be also polarized in the opposite

direction. In this case we change sign of exponential argument in Eq. (7). Further manipulations lead to the same results, so time averaged $\chi^{(3)}$ is given by Eq. (12). For c > 0.1, dipolar contribution to nonlinear Kerr

For c > 0.1, dipolar contribution to nonlinear Kerr dielectric susceptibility is readily obtainable:

$$\chi^{(3)} = -\frac{4\pi\epsilon_m^2 v^2 \alpha^4 c^2}{15r^3 k_B T}.$$
 (14)

The relation between $\chi^{(3)}$ and nonlinear refractive index n_2 is

$$n_2 = rac{4\pi}{n_0} \chi^{(3)}$$

where n_0 is the linear refractive index.

It should be emphasized that dipolar induced n_2 always has negative sign. This results from the randomizing nature of dipole–dipole interactions in the ensemble. Figure 1 shows $\chi^{(3)}$ calculated using Eqs. (12) and (14) as functions of volume concentration of nanoparticles.

The contribution of interparticle interactions can be comparable with other contributions to nonlinear part of refractive index. For instance, the third-order susceptibility measured for SiO₂-TiO₂ films doped with PbS quantum dots with 25 mol.% concentration at 1.064 μ m wavelength in picosecond regime was about -1×10^{-10} esu [7]. The calculations using Eqs. (2) and (14) yield $\chi^{(3)} = -1.4 \times 10^{-10}$ esu for nanoparticles with values derived from [7]: $r = 1.4 \times 10^{-7}$ cm, $\varepsilon_m = 2.28$, $\varepsilon_p = 19.23$, $\alpha = 0.17$, T = 300 K, c = 0.18. The third-order nonlinear susceptibility observed for silica glasses containing ZnSe nanocrystals at 3% concentration was -4.6×10^{-12} esu [8]. The formula (12) with parameters based on data from [8] $(r = 2.7 \text{ nm}, \alpha = 0.11, c = 0.03)$ gives -6×10^{-12} esu.

Decrease in $\chi^{(3)}$ with gain of nanoparticle concentrations was observed in [7–9]. It could be connected with growing strength of dipole interactions in ensemble. The dependence of $\chi^{(3)}$ on the concentration observed in [9] and in [7] with picosecond pulses was explicitly nonlinear. It may be justified on the basis of interparticle interactions whose contribution to $\chi^{(3)}$ is expected to vary as c^2 .



Fig. 1. (Color online) Reduced dipolar contribution to thirdorder susceptibility of ensemble versus volume concentration of spherical nanoparticles calculated using Lorentzian and Gaussian distribution functions [Eqs. (12) and (14)].

It should be stressed that $\chi^{(3)}$ depends strongly on polarizability α which changes for quantum dots owing to confinement effect. For example, the polarizability values of CdSe quantum dots measured at terahertz or static electric fields lie in the range 0.4 [10] to 3.6 [11]. Also, not all the nanoparticles may be polarized simultaneously; in this instance nonpolarized nanoparticles should be excluded from concentration *c*.

The dielectric susceptibility of the medium in the first approximation varies inversely as temperature similarly to paramagnets. It is to be noted that α also can depend on temperature.

From this it can be concluded that interparticle dipolar interactions contribute significantly to the third-order dielectric susceptibility of nanocomposites containing semiconductor quantum dots. This contribution always leads to self-defocusing optical nonlinearity of the system.

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