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Second Harmonic Generation from the surface of spherical particles in Nonlinear Rayleigh-Gans-Debye Model with the dispersion

V. N. Kapshai[1], S. A. Viarbitskaya[2], P. van der Meulen[3], T. Hansson[3]

В классической нелинейной модели Рэлея-Ганса-Дебая (NLRGD) для описания генерации второй гармоники от поверхности сферической частицы предполагается, что показатели преломления частицы и окружающей среды одинаковы и дисперсия незначительна. Мы обобщаем данную модель на случай значительной дисперсии материалов и демонстрируем необходимость такого учета, сравнивая результаты обобщенной модели NLRGD и нелинейной модели Вентцеля-Крамерса-Бриллюэна (WKB).
Ключевые слова: генерация второй гармоники, сферическая частица, дисперсия.

The classical nonlinear Rayleigh-Gans-Debye (NLRGD) model of the Second Harmonic Generation from the surface of spherical particles assumes that the refractive indices of the particle and the surrounding medium are similar and the dispersion is negligible. We extend the model to include the dispersion of materials and demonstrate that dispersions should be taken into account in the case of dispersive materials, by comparing the results of the generalized NLRGD model with nonlinear Wentzel-Kramers-Brillouin (WKB) model.
Keywords: second harmonic generation, spherical particle, dispersion.

1. Introduction. Second harmonic generation (SHG) from the surface of spherical isotropic centrosymmetric particles was first observed about 15 years ago [1]–[3]. Since then it has been used by various authors for the experimental study of various physical and chemical processes occurring on the surface of small particles suspended in liquid solutions [4], [5]. Theoretical formulations of the SHG from spherical particles presented in the literature include several different approaches: nonlinear Rayleigh-Gans-Debye (NLRGD) model [6]–[12], nonlinear Wentzel-Kramers-Brillouin (NLWKB) model [13], [14], nonlinear Mie theory [8], [15], [16]. Nonlinear Mie theory has the advantage of being based on the exact solution of the problem of linear light scattering, but it is very difficult to analyze the theoretical curves and experimental data, since the fields, both of the first and the second harmonic (SH) are expressed through the infinite series of spherical vectors. On the other hand the NLRGD and the NLWKB models are catching because they are easy to implement and analyze; at the same time they are adequate, if certain conditions hold [17].

The NLRGD model is analogous to the linear RGD model [18]: the field inside the particle, leading to the nonlinear polarization, is assumed to be only slightly different from the incident wave, which is a good approximation, if the refractive indices of the particle (n_p) and the environment (n_m) are approximately equal and the particle size is small compared to the wavelength of incident radiation. Mathematically, these assumptions can be written in the following form:

$$\left\{ |\eta-1|, |\rho|, \right\} << 1; \quad \left(\eta = n_p / n_m; \quad \rho = 4k_\omega a(\eta-1) \right), \tag{1}$$

where a is the particle radius, k_ω – the amplitude of the wave vector $\vec{k}_\omega$, characterizing the incident wave. In the usual formulation of the NLRGD model the dependence of the refractive index on the frequency is ignored, it is considered that $2k_\omega = k_{2\omega}$, where $k_{2\omega}$ is the amplitude of the SH wave vector $\vec{k}_{2\omega}$, i.e. the value $\xi = n^{2\omega} / n^{\omega}$ is equal to one for the particle and for the environment.

Analytical solution of the SHG problem in the approximation (1) was considered earlier by various groups of authors [6]–[12], [17]. At a careful analysis of various answer options in the

NLRGD model existing in the literature [6]–[12], we observed that the results of the calculations performed by different authors differ from one another considerably and in a nontrivial way. This led us to conduct our own research of the model. Analytical and numerical comparison of our results with the formulas obtained in [6]–[12] showed their difference from all the variants [6]–[12]. It turned out that the difference of our results from the results of studies [6], [7], [9]–[12] is, so to say, radical. On the other hand the results of [8] differ from ours by the lack of a simple but principally important factor $(qa)^{-1}$. This factor is extremely important both in terms of studying the dependence of all quantities on the radius of the spherical particle, and from the point of view of the Rayleigh limit. Taking this into account in this paper, we generalize the NLRGD-model to the case of dispersion, i.e. when $\xi \neq 1$.

2. Nonlinear Rayleigh-Gans-Debye model taking into account the dispersion. Consider an electromagnetic plane wave incident along the axis Z and polarized along the axis X. In order to characterize the polarization of the SH field, it is convenient to define the scattering plane, containing the axis Z (the wave vector of the incident wave $\vec{k}_\omega$) and the SH wave vector $\vec{k}_{2\omega}$. In this case, if we consider the SH field in the direction determined by the polar angle θ and azimuthal angle φ, then the situation is physically equivalent to the one, where the incident wave is linearly polarized in the plane of the azimuthal angle $-\varphi$, and the scattering plane is the plane *XZ*. We will consider this as the case (Fig. 1). In this case the polarization vector of the incident wave is

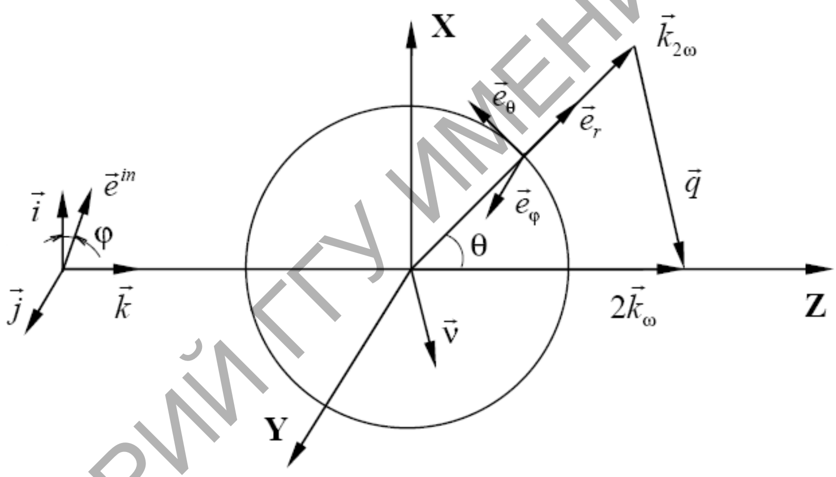

Fig. 1 – Geometry of the SHG process in the NLRGD model.
Cartesian and spherical coordinate systems that define the geometry of the SH radiation

$$\vec{e}^{\,in} = (\cos\varphi; \quad -\sin\varphi; \quad 0).$$

Thus, the polarization of the incident fundamental wave in the general case has two components, perpendicular (s) and parallel (p) to the scattering plane. We define that these polarization directions coincide with the unit vectors $\vec{i}$ and $\vec{j}$ of the chosen Cartesian coordinate system. For the SH field we assume that the s- and p- components are the components directed along the unit vectors $\vec{e}_\varphi$ and $\vec{e}_\theta$ of the spherical system. Cartesian components of these vectors can be written as

$$\begin{cases} \vec{e}_r = (\sin\theta; \quad 0; \quad \cos\theta); \\ \vec{e}_\theta = (\cos\theta; \quad 0; \quad -\sin\theta); \\ \vec{e}_\varphi = (0; \quad 1; \quad 0). \end{cases}$$

Taking into account the dispersion in the nonlinear RGD-theory we define the scattering vector $(\vec{v}^2 = 1)$

$$\vec{q} = q\,\vec{v} = 2\vec{k}_{\omega} - \vec{k}_{2\omega} = -2k^{\omega}(\xi\sin\theta\,\vec{i} + (\xi\cos\theta - 1)\vec{k}); \quad q = |\vec{q}| = 2k^{\omega}\sqrt{1+\xi^2 - 2\xi\cos\theta}\,. \qquad (2)$$

The corresponding expression for the scattering vector in the usual formulation of the NLRGD model can be obtained from (4) upon substitution $\xi = 1$. Generated SH field can be found in the Green function method as

$$\vec{E}(\vec{r}) = \frac{(2\omega)^2}{c^2}\int_V \frac{\exp(ik_{2\omega}|\vec{r}-\vec{x}|)}{|\vec{r}-\vec{x}|}\vec{P}^{2\omega}(\vec{x})d\vec{x}\,. \qquad (3)$$

The integration in (5) is performed only across a thing layer of thickness d_0 on the sphere surface, so $d\vec{x} = d_0 \cdot a^2 d\Omega$. Induced polarization of the sphere $\vec{P}^{2\omega}(\vec{x})$ is taken as

$$P_{\mathrm{i}}^{2\omega}(\vec{x}) = \chi_{ijk}(\vec{x})E_j(\vec{x})E_k(\vec{x})\,, \qquad (4)$$

where $\vec{E}(\vec{x})$ is the field at the point $\vec{x}$, which in the RGD-approximation is replaced by the incident wave field

$$\vec{E}^{in}(\vec{x}) = \vec{e}^{\,in}E_0\exp(i\,\vec{k}_{\omega}\vec{x})\,. \qquad (5)$$

In the far field zone the scattered field behaves like a harmonic outgoing spherical wave: the substitution of (4) and (5) into (3) leads to the following expression for the components of the SH field:

$$E_i(\vec{r}) = \frac{(2\omega)^2}{c^2}\frac{\exp(ik_{2\omega}r)}{r}d_0 a^2 E_0^2 e_j^{in} e_k^{in}\int_{4\pi}\exp(i\vec{q}\vec{x})\chi_{ijk}(\vec{x})d\Omega_{\vec{x}}\,. \qquad (6)$$

The most general expression for the susceptibility tensor, in our case can be determined using the methods described in [19], we yield ($\vec{x} = a\vec{n}$)

$$\chi_{ijk}(\vec{x}) = \chi_1\, n_i n_j n_k + \chi_2\, n_i\delta_{jk} + \chi_3\,(n_j\delta_{ik} + n_k\delta_{ij})\,. \qquad (7)$$

It is easy to see that on the surface of the particle

$$\chi_1 = \chi_{\perp\perp\perp} - \chi_{\perp\|\|} - 2\chi_{\|\|\perp}; \quad \chi_2 = \chi_{\perp\|\|}; \quad \chi_3 = \chi_{\|\|\perp}\,.$$

After substituting (7) into (6) the problem reduces to the calculation of integrals $(d\Omega_{\vec{x}} = d\Omega_{\vec{n}})$

$$J_k(\vec{q}a) = \int_{4\pi}\exp(i\vec{q}\vec{x})\, n_k\, d\Omega_{\vec{n}}; \quad J_{ijk}(\vec{q}a) = \int_{4\pi}\exp(i\vec{q}\vec{x})\, n_i n_j n_k\, d\Omega_{\vec{n}}\,.$$

This integration can be performed analytically and yields the following result:

$$J_k(\vec{q}a) = -iv_k F^{(1)}(qa);$$
$$J_{ijk}(\vec{q}a) = i\left(v_i\delta_{jk} + v_j\delta_{ik} + v_k\delta_{ij}\right)F_2(qa) + iv_i v_j v_k\left(-3F_2(qa) + F^{(3)}(qa)\right).$$

We use the following functions:

$$F^{(\beta)}(z) = 4\pi\frac{d^{\beta}}{dz^{\beta}}j_0(z); \quad F_2(z) = \frac{1}{z}\left(F^{(2)}(z) - \frac{1}{z}F^{(1)}(z)\right),$$

where $j_0(z)$ is a spherical Bessel function.

As a result the SH field can be expressed as

$$\vec{E}(\vec{x}) = \frac{(2\omega)^2}{c^2}\frac{\exp(ik_{2\omega}|\vec{x}|)}{|\vec{x}|} d_0 a^2 E_0^2 \left[\vec{f}\right],$$

$$\left[\vec{f}\right] = \chi_1\left[\left(\vec{v} + 2\vec{e}^{in}(\vec{e}^{in}\vec{v})\right) iF_2(qa) + \vec{v}(\vec{e}^{in}\vec{v})^2\, i\left(-3F_2(qa) + F^{(3)}(qa)\right)\right] +$$
$$+\chi_2\left[\vec{v}\frac{1}{i}F^{(1)}(qa)\right] + \chi_3 2\left[\vec{e}^{in}(\vec{e}^{in}\vec{v})\frac{1}{i}F^{(1)}(qa)\right].$$

Vectors $\vec{v}$ and $\vec{e}_{in}$ in this case can be written as

$$\vec{v} = \frac{1}{K}\left[\vec{e}_r(\cos\theta - \xi) - \vec{e}_\theta \sin\theta\right]; \quad K = \sqrt{1 - 2\xi\cos\theta + \xi^2},$$
$$\vec{e}^{in} = \left[\vec{e}_r \sin\theta\cos\varphi + \vec{e}_\theta \cos\theta\cos\varphi - \vec{e}_\varphi \sin\varphi\right],$$
$$(\vec{e}^{in}\vec{v}) = \left(\frac{-\xi\sin\theta\cos\varphi}{K}\right).$$

The following functions are used to obtain the final expression for the SH field in the NLRGD model:

$$\begin{cases} F_s(z) = \dfrac{3}{z^2}\left[\left(1 - \dfrac{1}{3}z^2\right)\sin z - z\cos z\right]; \\ F_p(z) = \dfrac{3}{z^3}\left[\left(1 - \dfrac{1}{2}z^2\right)\sin z - \left(z - \dfrac{1}{6}z^3\right)\cos z\right]; \\ F_d(z) = \dfrac{1}{z}\left[\left(-\dfrac{1}{z}\right)\sin z + \cos z\right] = \dfrac{2}{z}\left[F_p(z) - F_s(z)\right]. \end{cases}$$

Finally, the SH field is expressed in terms of functions $F_s(z)$ and $F_p(z)$ only, because

$$F_2(z) = 4\pi\cdot\frac{1}{z}F_s(z); \quad F^{(3)}(z) = (-2)\cdot 4\pi\cdot\frac{1}{z}F_p(z); \quad F^{(1)}(z) = 4\pi\cdot F_d(z).$$

Thus, the SH field has the form

$$\vec{E}(\vec{x}) = \frac{(2\omega)^2}{c^2}\frac{\exp(ik_{2\omega}r)}{r} d_0 a^2 E_0^2\left(\frac{1}{qa}\right)\left[\Theta(\theta,\varphi)\vec{e}_\theta + \Phi(\theta,\varphi)\vec{e}_\varphi\right],$$

where we use the notations

$$\Theta(\theta,\varphi) = \frac{\sin\theta}{K}\left\{\left[-\cos\theta\,\Gamma_1(\theta) + \sin^2\theta\frac{\xi}{K^2}\Gamma_2(\theta)\right]\xi\cos^2\varphi + \Gamma_3(\theta)\right\};$$
$$\Phi(\theta,\varphi) = \frac{\sin\theta}{K}\Gamma_1(\theta)\xi\cos\varphi\sin\varphi,$$
$$\Gamma_1(\theta) = 2\left[\left(\chi_{\perp\perp\perp} - \chi_{\perp\parallel\parallel}\right)F_s(qa) - 2\chi_{\parallel\parallel\perp}F_p(qa)\right];$$
$$\Gamma_2(\theta) = (\chi_{\perp\perp\perp} - \chi_{\perp\parallel\parallel} - 2\chi_{\parallel\parallel\perp})(3F_s(qa) + 2F_p(qa));$$
$$\Gamma_3(\theta) = -\chi_{\perp\perp\perp}F_s(qa) - \chi_{\perp\parallel\parallel}\left[F_s(qa) - 2F_p(qa)\right] + 2\chi_{\parallel\parallel\perp}F_s(qa).$$

Writing the SH electric field in the form

$$\vec{E}(\vec{x}) = iM(a)F(\vec{x}); \quad M(a) = \frac{(2\omega)^2}{c^2}d_0 4\pi a^2 E_0^2,$$

and noting that the magnetic field is

$$\vec{H}(\vec{x}) = \frac{M(a)}{2\omega c} rot\vec{F}(\vec{r}) = \frac{M(a)}{2\omega c}\vec{G}(\vec{r}),$$

we find the components

$$G_\theta = \frac{1}{r\sin\theta}\frac{\partial}{\partial\varphi}F_r - \frac{1}{r}\frac{\partial}{\partial r}\left(rF_\varphi\right); \quad G_\varphi = \frac{1}{r}\frac{\partial}{\partial r}\left(rF\right)_r - \frac{1}{r}\frac{\partial}{\partial\theta}F_r .$$

Now, the energy flux density vector (the Poynting vector) of the SH can be found in the form

$$\vec{S} = \frac{1}{4\pi}\mathrm{Re}\left[\vec{E}\times\vec{H}\right] = \frac{1}{4\pi}\frac{M^2(a)}{2\omega c}\mathrm{Re}\, i\left[\vec{F}(\vec{x})\times\vec{G}^*(\vec{x})\right],$$

its radial component

$$S_r = \frac{1}{4\pi}\frac{\left(M(R)\right)^2}{2\omega c}\,\mathrm{Re}\, i\left(F_\theta G_\varphi^* - F_\varphi G_\theta^*\right),$$

to determine the energy flux of the SH.

3. Results. We have calculated the electric and magnetic fields of the SH, the Poynting vector, the angular energy distribution of the SH, its polarization dependence, and its particle radius dependence. Fig.2 shows examples of the angular dependence of the SH intensity in the *p*-in/*p*-out scattering configuration for various sizes of spherical polystyrene particles suspended in aqueous solution. Our interest in this system is motivated by the fact that it is one of the most commonly used for the study of the SHG from the surface of spherical particles [1]–[17]. Along the abscissa is the scattering angle (in degrees), along the vertical axis is the normalized SH intensity (the maximum of which is normalized to unity). The length of the incident fundamental wave was taken to be equal to 850 nm (the SH wavelength 425 nm), polystyrene particles ($n^\omega = 1.58, \quad n^{2\omega} = 1.62$) were weighed in water ($n^\omega = 1.33, \quad n^{2\omega} = 1.35$), which corresponds to the experiments described in [17]. Calculations showed that allowance for the dispersion is unimportant in the range of particle sizes, corresponding to conditions (1), namely for radii less than 250 nm [17]. The choice of the refractive index corresponding to either water or polystyrene influences the results more strongly. This, of course, is easy to understand, taking into account the considerable difference in the refractive indices of water and polystyrene as compared to the difference of indices for two different wavelengths – the fundamental and the second harmonic (either in the case of water or in the case of polystyrene). The conclusions of [17] are that for an optimal description of the SHG in an environment where the particle has a larger index of refraction than the surrounding medium, for "working" index of refraction index of the particle must be taken. For this reason, in subsequent calculations, we used the index of refraction of the particle as the main index for NLRGD.

In the cases where the value of $|\xi - 1|$ is approximately equal to or greater than 0.1, the dispersion in the numerical calculations should be taken into account. To demonstrate the latter, we have examined the hypothetical medium, having a large dispersion. In particular, we considered the case of the particle with $n_p^\omega = 1.60, \quad n_p^{2\omega} = 1.70\text{ - }2.00$ suspended in water. Calculations of the angular distributions of the SH for various sets of refraction indices and particle sizes are shown in Fig. 2. Together with the results of the NLRGD we present the results of calculations of the corresponding angular distributions in the NLWKB model; they can be taken as the closest to reality, according to [17]. Fig. 2 shows that the closest to the NLWKB angular dependence is calculated at $n^\omega = 1.60, \quad n^{2\omega} = 2.00$ (dashed lines). Thus, for small particles with high optical dispersion ($|\xi - 1| > 0.1$), the generalization of the NLRGD model given in this article, is necessary for an adequate theoretical description of the SHG.

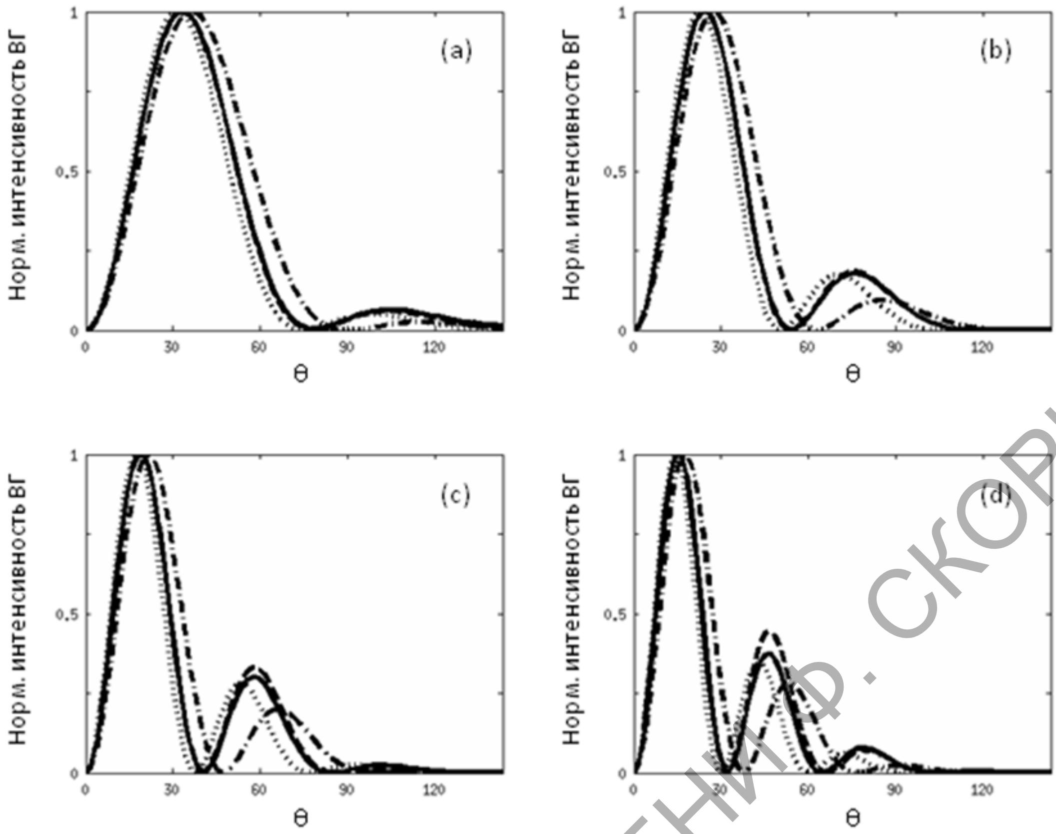

Fig. 2 – Angular dependence of the SH intensity in *p*-in/*p*-out polarization combination for various particle radii: (a) 0.05 mkm, (b) 0.10 mkm, (c) 0.15 mkm, (d) 0.20 mkm in the NLRGD with the dispersion at $n_m^{\omega} = 1.33$; $n_m^{2\omega} = 1.35$; $n_p^{\omega} = 1.60$; $n_p^{2\omega} = 2.00$ (NLWKB, solid lines), $n^{\omega} = 1.60$; $n^{2\omega} = 1.60$ (NLRGD, dot-dashed lines), $n^{\omega} = 2.00$; $n^{2\omega} = 2.00$ (NLRGD, dotted lines), $n^{\omega} = 1.60$; $n^{2\omega} = 2.00$ (NLRGD, dashed lines).

4. Conclusion. We have generalized the nonlinear Rayleigh-Gans-Debye model to the case of a large dispersion of materials and have obtained analytical expressions for calculations of the second harmonic generation from the surface of a small dielectric spherical particle. We have demonstrated the need to consider the dispersion of light by comparing the obtained angular dependence of the second harmonic intensity distribution with the same dependences, calculated in the nonlinear Wentzel-Kramers-Brillouin model.

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[1]Гомельский государственный
университет им. Ф. Скорины

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[2]Центр по развитию материалов и
структурных исследований,
Национальный центр научных исследований,
Тулуза, Франция

[3]Исследовательский центр АльбаНова,
Стокгольмский университет,
Стокгольм, Швеция