# ON THE THEORY OF DEPOLARIZED LIGHT SCATTERING BY BROWNIAN PARTICLES IN AN EXTERNAL ELECTRIC FIELD

**A.V. KYRYLYUK, A.V. ZATOVSKY**

**I.I. Mechnikov Odesa National University**
*(2, Dvoryans'ka Str., Odesa 65026, Ukraine),*

UDC 533.723+535.337


The influence of an external electric field on the spectrum of depolarized light scattering by a dilute suspension of anisotropic ellipsoidal particles in a simple liquid was considered. The wing of the Rayleigh line has a non-Lorentzian shape in the electric field and has a fine structure as additional local maxima in the spectrum. The position of these maxima can be controlled by changing the value of the constant electric field.

In the last years, a considerable attention has been paid to the study of the influence of an external electric field on the rotary Brownian motion of foreign particles embedded into a liquid [1—5]. Changes in the character of the thermal motion of Brownian particles are vividly seen in different spectroscopic experiments. Theoretical description of the results of spectroscopic investigations is based upon the method of time-correlation functions (CFs) of various molecular variables [6].

In the present work, we study the spectra of depolarized light scattering by a dilute suspension of Brownian particles with uniaxial symmetry in an external electric field. The wing of the Rayleigh scattering line for dilute suspensions of foreign particles can be considered to be caused by the rotational motion of particles, and changes in the scattering spectra can be referred to the orientation of particles in an external electric field. The foreign particles are modeled as rigid ellipsoids of revolution, which have anisotropic electric characteristics and acquire only an induced dipole moment. As in [7], the memory effects are explicitly taken into account and the rotary motion of foreign particles is regarded as a non-Markovian stochastic process. It is shown that, in the presence of an external field, the spectrum of depolarized light scattering has a fine structure and it is of a non-Lorentzian type. The position of the additional lines in the scattering spectrum can be controlled by changing the value of the field.

Let the vertically polarized (along the $z$-axis) incident light propagate along the $y$-axis of the laboratory frame $(x, y, z)$, and let the horizontally polarized scattered light (in the $xy$-plane) be detected along the $x$-axis. Under the chosen scattering geometry, the spectral density of scattered light is proportional to the Fourier representation of the CF for the components of the symmetric traceless polarizability tensor of a particle

$$I^{VH}(\omega) \sim \langle \alpha_{xz}(t)\alpha^*_{xz}(t)\rangle_\omega, \tag{1}$$

where the angular brackets denote the averaging over the thermal motion. The constant electric field is assumed to be oriented along the $z$-axis. Instead of Cartesian components of the polarizability tensor, we introduce the independent components of the second-rank spherical tensor $\alpha_\lambda(\lambda = 0, \pm 1, \pm 2)$ [8] in a standard way. The orientation of the molecular frame $(x', y', z')$ with respect to the laboratory one is determined by the Euler angles $\vec{\beta}(\vartheta, \psi, \varphi)$. Under rotation of the particle, this spherical tensor transforms as

$$\alpha_\mu(t) = \sum_{\nu=-2}^{2} D^{(2)}_{\mu\nu}\left(\vec{\beta}(t)\right)\alpha'_\nu(0), \tag{2}$$

where $D^{(l)}_{\mu\nu}$ is the generalized spherical function (Wigner rotation function). Thus, the spectral density $I^{VH}(\omega)$ of scattered light is expressed as

$$I^{VH}(\omega) \sim \frac{1}{10}\left|\alpha'_0(0)\right|^2 \Psi^{(2)}_{10}(p), p = -i\omega + \frac{1}{\tau_{20}} + k^2 D, \tag{3}$$

where $\tau_{20}$ is the relaxation time of a particle orientation, $\vec{k}$ is the scattering vector, $D$ is the translational diffusion coefficient, and $\Psi^{(l)}_{\mu\nu}(\omega)$ is the Fourier representation of the CF normalized to unit

$$\Psi^{(l)}_{\mu\nu}(t) = \frac{\left\langle D^{(l)}_{\mu\nu}(t) D^{(l)*}_{\mu\nu}(0)\right\rangle}{\left\langle \left|D^{(l)}_{\mu\nu}(0)\right|^2\right\rangle}. \tag{4}$$

Due to the smallness of the anisotropy of translational diffusion, the translational Brownian motion of an ellipsoidal particle was represented by one translational diffusion coefficient $D = (2D_1 + D_3)/3$, which is calculated as the mean of the principal


ISSN 0503-1265. Ukr. J. Phys. 2004. V. 49, N 6

values of the translational diffusion tensor $D_1 = D_2 \neq D_3$. Since we investigate a dilute suspension of foreign particles, the translational and rotary motions of Brownian particles are considered independently. The action of the external electric field essentially influences the character of the rotary motion of particles in a suspension. The study of the orientational motion of an ellipsoidal particle is closely connected to its rotation, i.e., to the vector of the angular velocity. The vector of angular velocity of the particle can be viewed as the sum of two parts - the stochastic part of the angular velocity $\vec{\Omega}^r(t)$, which arises from the random Brownian motion, and the regular part $\vec{\Omega}^0(t)$ due to the action of a constant external electric field. The analysis of dynamic correlations for the orientational motion of ellipsoidal particles embedded into a liquid is carried out in terms of the time CFs of bilinear Wigner functions (4). The evolution of Wigner functions in time is governed by the following equation [8]:

$$\frac{d}{dt}D^{(l)}_{\mu\nu}(t) = -i\sum_{\lambda,\rho}\left[\Omega^0_\lambda(t) + \Omega^r_\lambda(t)\right] D^{(l)}_{\mu\rho}(t)\left\langle l\rho\left|I_\lambda\right|l\nu\right\rangle, \quad (5)$$

where $\langle \ldots |I| \ldots \rangle$ are matrix elements of the projections of the rotation operator on the coordinate axes of the molecular frame in units of $h$.

The regular part of the angular velocity of an ellipsoidal particle in a constant electric field has been found from the solution of a boundary-value problem of electrodynamics and it has the following form [1]:

$$\vec{\Omega}^0(t) = -\sigma\left(\vec{n}\cdot\vec{E}\right)\left[\vec{n}\times\vec{E}\right], \quad (6)$$

where $\vec{n}$ is the unit vector oriented along the symmetry axis of an ellipsoid, and $\sigma$ determines electrical properties of the particle and the fluid. With the help of Eq. (6), one can easily obtain the expression for the angular velocity components via Wigner functions. We will formally integrate Eq. (5), put the result obtained in the right-hand side of the same equation, then we will multiply the obtained equation by $D^{(l)*}_{\mu\nu}(0)$, and make average over the thermal motion. In the equation obtained for CF (4), we use an approximate procedure of decomposition of a CF of the product of four Wigner functions into the sum of products of CFs of bilinear Wigner functions, which is analogous to the procedure employed for the unit vectors in [1]. By doing this, we retain higher correlations for the spherical harmonics. Taking into account the homogeneity of proceeding processes in time and regarding approximately the statistical properties of the stochastic part of the angular velocity as delta-correlated, we obtained finally the integro-differential equation for the time CFs (4),

$$\frac{d}{dt}\Psi^{(l)}_{\mu\nu}(t) = -\frac{l(l+1)-\nu^2}{3\tau_E^2}\int\limits_0^t dt'\Psi^{(2)}_{10}(t-t')\Psi^{(l)}_{\mu\nu}(t') -$$

$$-(\delta_{1,\mu}+\delta_{-1,\mu})\delta_{2,l}\delta_{0,\nu}\frac{l(l+1)-\nu^2}{3\tau_E^2}\times$$

$$\times\left[\int\limits_0^t dt'\Psi^{(l)}_{10}(t-t')\Psi^{(l)}_{1\nu}(t') - t\Psi^{(l)}_{1\nu}(t)\right] - \frac{1}{\tau_{l\nu}}\Psi^{(l)}_{\mu\nu}(t), \quad (7)$$

where $\tau_{l\nu}$ is the relaxation time of a particle orientation, and $\tau_E$ is the characteristic time of a change in the induced dipole moment in the external electric field, which are defined as

$$\frac{1}{\tau_{l\nu}} = l(l+1)\Theta_1 + \nu^2\left(\Theta_3 - \Theta_1\right), \quad (8)$$

$$\frac{1}{\tau_E} = \frac{\sigma E^2}{\sqrt{3}}\sqrt{\left\langle\left|D^{(2)}_{10}(0)\right|^2\right\rangle}. \quad (9)$$

Here, $\Theta_l$ are the principal values of the rotational diffusion tensor of an ellipsoid of revolution ($\Theta_1 = \Theta_2 \neq \Theta_3$).

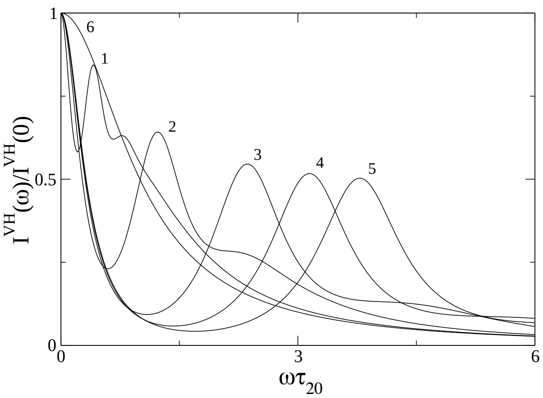
Note that Eq. (7) has been derived under the assumption of smallness of the characteristic relaxation time of the angular velocity $\tau_\Omega$ in comparison with the relaxation time of a particle orientation $\tau_{l\nu}$, $\tau_\Omega \ll \tau_{l\nu}$. Averaging over orientations and angular velocities of a particle was carried out independently.

The sought function $\Psi^{(2)}_{10}(\omega)$, which is necessary for the determination of the spectrum of depolarized scattering (3), can be found from the nonlinear differential equation of the first order

$$\frac{\Psi^{(2)}_{10}(0)}{\tau_E^2}\frac{\partial\Psi^{(2)}_{10}(\omega)}{\partial(i\omega)} + \left(-i\omega + \frac{1}{\tau_{20}}\right)\Psi^{(2)}_{10}(\omega) +$$

$$+\frac{3}{\tau_E^2}\left[\Psi^{(2)}_{10}(\omega)\right]^2 = \Psi^{(2)}_{10}(0), \quad (10)$$

which is obtained after making the Fourier transformation of Eq. (7) for $l = 2$, $\mu = 1$, and $\nu = 0$. Eq. (10) in dimensionless variables $\widetilde{\omega} \equiv \omega\tau_{20}$ and $\widetilde{\Psi}^{(2)}_{10} \equiv \Psi^{(2)}_{10}/\tau_{20}$ with the initial conditions $\mathrm{Im}\widetilde{\Psi}^{(2)}_{10}(0) = 0$ and $\mathrm{Re}\widetilde{\Psi}^{(2)}_{10}(0) = 1$ was solved by a numerical integration. In Figure, the spectra normalized to unit for depolarized light scattering $\widetilde{I}^{VH}(\widetilde{\omega}) \equiv I^{VH}(\omega)/I^{VH}(0)$ are shown for different values of the dimensionless electric field




Dependence of the light intensity normalized to unity (arbitrary units) on the dimensionless frequency $\tilde{\omega} \equiv \omega\tau_{20}$ for different values of the external electric filed (*1* — $G = 0.1$, *2* — 0.5, *3* — 1.5, *4* — 2.5, *5* — 3.5). The Lorentz line obtained without constant external field is represented as well (*6* — $G = 0$)

parameter $G \equiv (\tau_{20}/\tau_E)^2\Psi_{10}^{(2)}(0) \sim E^4$. We also show the scattering line without external field (curve *6*), which has the well-known Lorentz form with half-width $\Delta\omega = \frac{1}{\tau_{20}} + k^2D$ [1]. This curve is obtained from Eq. (10) in the limiting case $G = 0$.

From Figure, one can see that, in the presence of an external electric field, the spectrum of depolarized light scattering is not a Lorentzian, but it has a fine structure in the form of one or two maxima. By varying the external field, both the shape of the spectrum and the peak intensity of these additional maxima change. Upon increase in the electric field, the position of the maxima on the axis of frequencies shifts towards higher frequencies of the Rayleigh wing. The presence of an external electric field changes the character of the Brownian rotation of ellipsoidal particles, which results in the shape transformation of the wing of the Rayleigh line. As seen from Eq. (10), a change in the orientation of ellipsoids in a constant electric field is a highly nonlinear process, which complicates a more detailed analysis of the spectra. The strong dependence of the shape and spectral composition of the wing of the Rayleigh line on the electric field enables us to control changes in the scattering spectra by varying the external field.

The authors acknowledge A.Ya. Dzyublik for helpful discussions.


1. *Pokrovskii V.N.*//Uspekhi Fiz. Nauk.— 1972.— **14**.— P.737—746.
2. *Van der Zande B.M.I., Koper G.J.M., Lekkerkerker H.N.W.*//J. Phys. Chem. B.— 1999.— **103**.— P.5754—5760.
3. *Vojtylov V., Zernova T., Spartakov A. et al.*//Colloid. Surf. A.— 2002.— **209**.— P.123—129.
4. *Kalmykov Yu.P.*//Phys. Rev. E.— 2002.— **65**.— P.021101-1—021101-11.
5. *Titov S.V., Kalmykov Yu.P., Coffey W.T.*//J. Chem. Phys.— 2003.— **118**.— P.209—220.
6. *Burshtein A.I., Temkin S.I.* Spectroscopy of Molecular Rotation in Gases and Liquids.— Cambridge: Cambridge University Press, 1994.
7. *Zatovskii A.V., Salistra G.I.*//Ukr. Fiz. Zh.— 1973.— **18**, N 3.— P.435—439.
8. *Davydov A.S.* Excited States of Atomic Nuclei.— Moscow: Atomizdat, 1967 (in Russian).


Received 04.08.03

ДО ТЕОРІЇ ДЕПОЛЯРИЗОВАНОГО РОЗСІЯННЯ СВІТЛА БРОУНІВСЬКИМИ ЧАСТИНКАМИ У ЗОВНІШНЬОМУ ЕЛЕКТРИЧНОМУ ПОЛІ

*А.В.Кирилюк, О.В.Затовський*

Р е з ю м е

Розглянуто вплив зовнішнього електричного поля на спектр деполяризованого розсіювання світла суспензією анізотропних еліпсоїдальних частинок у простій рідині. Крило лінії Релея має не лорентцеву форму в електричному полі, а тонку структуру у вигляді додаткових локальних максимумів у спектрі, положення яких може бути контрольоване шляхом зміни величини постійного зовнішнього поля.