ANISOTROPY OF ELECTRICAL PROPERTIES OF A LAYER OF SPHERICAL PARTICLES LOCATED NEAR A SUBSTRATE

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Abstract

In this paper, we study the effects of a semi-infinite matrix disperse system on the external electromagnetic radiation in the electrostatic approximation. With the help of our previous technique, we obtain general expressions for the multipole expansion coefficients of the electric potential for a sphere accounting for the interaction between ambient particles and the substrate. The polarizability tensor and resonant frequencies of a single sphere show anisotropy due to the influence of a substrate.

1. Introduction

Interest in matrix disperse systems (MDS) is stimulated, first of all, by the possibility of manufacturing materials with predicted optical properties. At the same time, the properties of MDS may strongly differ from those of the materials used for the formation of MDS [1]. In the theoretical studies MDS are usually considered as infinite systems.

In this work, we take into account the effects of an MDS interface. Namely, the MDS is considered as a half space dielectric matrix with a plane interface separating it from another half space homogeneous dielectric. The matrix is filled with spherical inclusions of different diameters located near the substrate forming a layer of randomly or regularly arranged particles. The results [2] obtained for the monolayer of spheres on a dielectric substrate can be obtained from our model as a particular case. Basically, this work is a generalization of [2,3,4].

2. Basic equation

We consider the semi-infinite MDS consisting of dielectric spheres of different diameters embedded in a homogeneous dielectric (ambient) as shown in Fig. 1. Another half space is filled with another homogeneous dielectric (substrate). The system is placed in the electric field proportional to $e^{i\omega t}$. Let $\varepsilon_a(\omega), \varepsilon_s(\omega)$ and $\varepsilon_i(\omega)$ be the dielectric functions of the ambient, substrate and the i^{th} sphere, respectively, and R_i be the radius of the i^{th} sphere.

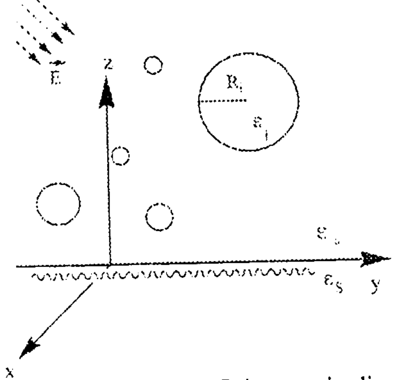

Fig. 1. Geometry of the semi-infinite matrix disperse system

Let the wavelength of the external electromagnetic field be much larger than radii of the spheres and the distances between them. In other words, we use the electrostatic approximation. In such a case resulting electric field is caused by the interaction of the external field with the MDS and the substrate and its potential satisfies the Laplace equation

$$\Delta\psi(\vec r) = 0 \tag{1}$$

in the regions I - inside MDS (out of spheres), II - inside the spheres, III - inside the substrate, and standard boundary conditions

$$(\psi_i = \psi_j)_{\sigma_{ij}}, \left(\varepsilon_i \frac{\partial \psi_i}{\partial n_i} = \varepsilon_j \frac{\partial \psi_j}{\partial n_j}\right)_{\sigma_{ij}}, \tag{2}$$

where ε_i is dielectric function of the matter filling out the i^{th} region (i=*I, II, III*),

$_i$ is the resulting field potential in the i^{th} region,

σ_{ij} denotes the common bound surface of the regions i and j.

Using ideas of the image and multipole expansion methods of solving of electrostatic problems we seek a solution of the problem (1,2) in the following form:

$$\psi^I = \psi^I_{ext} + \sum_i \psi^I_{i-th\,spere} + \psi^I_{substrate} = -\vec E_o \vec r + \sum_{ilm} A_{ilm} F_{lm}(\vec\rho_i) + \sum_{ilm} A'_{ilm} F_{lm}(\vec\rho_i') \tag{3}$$

$$\psi_i^{II} = \sum_{lm} B_{ilm} G_{lm}(\vec\rho_i); \tag{4}$$

$$\psi^{III} = \psi^{III}_{ext} + \psi^{III}_0 + \sum_{ilm} C_{ilm} F_{lm}(\vec\rho_i'); \tag{5}$$

$$\psi^I_{ext} = -\vec E_0 \vec r = -(E_{ox}x + E_{oy}y + E_{oz}z) \tag{6}$$

$$\psi^{III}_{ext} = -\vec E_0' \vec r = -(aE_{ox}x + bE_{oy}y + cE_{oz}z)$$

where $F_{lm}(\vec r) \equiv r^{-l-1} Y_{lm}(\vec r)$; $G_{lm}(\vec r) \equiv r^l Y_{lm}(\vec r)$;

$\vec\rho_i \equiv \vec r - \vec r_i$; $\vec\rho_i' \equiv \vec r - \vec r_i'$;

$\vec r_i$ is a radius-vector of the center of the i^{th} sphere ; $\vec r_i'$ is a radius-vector of the i^{th} sphere center image and ψ_0^{III} is a constant contribution to the potential ψ^{III} related with a choice of radius-vector origin point. Note, that all the individual terms in (3,4,5) automatically satisfy equation (1), and (6) expresses the idea of force lines refraction on the boundary of different media.

The unknown coefficients $A_{lmi}, A'_{lmi}, B_{lmi}, C_{lmi}, a, b, c$ are obtained after applying the boundary conditions (2) to the expansions (3, 4, 5).

3. Boundary conditions on the substrate surface

1. Potential continuity condition on the surface σ_{I-III} take the form

$$(\vec{E}_0' - \vec{E}_0)\vec{r} - \psi_0^{III} + \sum_{ilm}\{A_{ilm}F_{lm}(\vec{\rho}_i) + A'_{ilm}F_{lm}(\vec{\rho}_i') - C_{ilm}F_{lm}(\vec{\rho}_i)\}\underset{\sigma_{I-III}}{=} 0 .$$

Different terms here have different arguments. It proves to be more convenient to reduce all the terms to a common argument, e.g. to $\vec{\rho}_i$. Using the fact, that for any point at the boundary surface σ_{I-III}

$$\vec{\rho}_i = (\rho_i, \theta_i, \varphi_i)$$
$$\vec{\rho}_i' = (\rho_i', \theta_i', \varphi_i') = (\rho_i, \pi - \theta_i, \varphi_i)$$

and using the relation [5]

$$Y_{lm}(\pi - \theta, \varphi) = (-1)^{l+m} Y_{lm}(\theta, \varphi)$$

we obtain

$$\Delta\vec{E}_0^{//}\vec{r}^{//} + \Delta\vec{E}_0^{\perp}\vec{r}^{\perp} - \psi_0^{III} + \sum_{ilm}\left\{A_{ilm} + (-1)^{l+m}A'_{ilm} - C_{ilm}\right\}F_{lm}(\vec{\rho}_i)\underset{\sigma_{I-III}}{=} 0 ,$$

where we have used decomposition $\vec{r} = \vec{r}^{//} + \vec{r}^{\perp}$ and analogous to it for $\Delta\vec{E} \equiv \vec{E}_0' - \vec{E}_0$. Obtained equation is equivalent to the set

$$\begin{cases} \Delta\vec{E}_0^{//} \cdot \vec{r}^{//} = 0 \\ \Delta\vec{E}_0^{\perp} \cdot \vec{r}^{\perp} - \psi_0^{III} = 0 \\ A_{ilm} + (-1)^{l+m}A'_{ilm} - C_{ilm} = 0 \end{cases} \qquad (7)$$

2. Potential derivative continuity condition on the surface σ_{I-III} in view of $\frac{\partial}{\partial n} = \frac{\partial}{\partial z}$ take the form

$$(c\varepsilon_s - \varepsilon_a)E_{oz} + \varepsilon_a\sum_{ilm}A_{ilm}\frac{\partial}{\partial z}F_{lm}(\vec{\rho}_i) + \varepsilon_a\sum_{ilm}A'_{ilm}\frac{\partial}{\partial z}F_{lm}(\vec{\rho}_i') - \varepsilon_s\sum_{ilm}C_{ilm}\frac{\partial}{\partial z}F_{lm}(\vec{\rho}_i)\underset{\sigma_{I-III}}{=} 0 .$$

Again, reducing all the terms to argument $\vec{\rho}_i$ and using relation

$$\frac{\partial}{\partial z}F_{lm}(\pi - \theta, \varphi) = (-1)^{l+m-1}\frac{\partial}{\partial z}F_{lm}(\theta, \varphi) ,$$

which can be seen from [5]

$$\frac{\partial}{\partial z}[f(r)Y_{lm}(\theta,\varphi)] = \left[\frac{(l+1)^2 - m^2}{(2l+1)(2l+3)}\right]^{\frac{1}{2}}\left(\frac{\partial f}{\partial r} - \frac{l}{r}f\right)Y_{l+1,m}(\theta,\varphi) +$$
$$+\left[\frac{l^2 - m^2}{(2l-1)(2l+1)}\right]^{\frac{1}{2}}\left(\frac{\partial f}{\partial r} + \frac{l+1}{r}f\right)Y_{l-1,m}(\theta,\varphi) ,$$

we obtain equation

$$(c\varepsilon_s - \varepsilon_a)E_{oz} + \sum_{ilm}[\varepsilon_a A_{ilm} + \varepsilon_a(-1)^{l+m-1}A'_{ilm} - \varepsilon_s C_{ilm}]\frac{\partial}{\partial z}F_{lm}(\vec{\rho}_i)\underset{\sigma_{I-III}}{=} 0$$

or equivalent set

$$\begin{cases} c\varepsilon_s - \varepsilon_a = 0 \\ \varepsilon_a A_{ilm} + \varepsilon_a (-1)^{l+m-1} A'_{ilm} - \varepsilon_s C_{ilm} = 0 \end{cases} \tag{8}$$

3. The solution of eq. (7,8) is

$$\begin{cases} a = 1 \\ b = 1 \\ c = \dfrac{\varepsilon_a}{\varepsilon_s} \\ \psi_0^{III} = \left(\dfrac{\varepsilon_a}{\varepsilon_s} - 1\right) E_{0z} h_0 \\ A'_{ilm} = (-1)^{l+m} \dfrac{\varepsilon_a - \varepsilon_s}{\varepsilon_a + \varepsilon_s} A_{ilm} \\ C_{ilm} = \dfrac{2\varepsilon_a}{\varepsilon_a + \varepsilon_s} A_{ilm} \end{cases} \tag{9}$$

where h_0 is the height of the global origin over the substrate.

4. Boundary conditions on the sphere surface and equation for A_{ilm}

1. On the surface of j^{th} sphere the potential continuity condition take the form

$$-\vec{E}_0 \cdot \vec{r} + \sum_{ilm} A_{ilm} F_{lm}(\vec{\rho}_i) + \sum_{ilm} A'_{ilm} F_{lm}(\vec{\rho}'_i) - \sum_{lm} B_{jlm} G_{lm}(\vec{\rho}_j) \underset{\sigma_{I-II_j}}{=} 0 .$$

Applying representations $\vec{r} = \vec{r}_j + \vec{\rho}_j$ and $\vec{\rho}_i = \vec{\rho}_j - (\vec{r}_i - \vec{r}_j)$, well-known addition theorem [6] for spherical harmonics

$$F_{lm}(\vec{r} - \vec{R}) = \sum_{l_1 m_1} T_{lm}^{l_1 m_1} F_{LM}(\vec{R}) G_{l_1 m_1}(\vec{r}) , \qquad (r<R)$$

where
$$T_{lm}^{l_1 m_1} \equiv (-1)^{l+m_1} \left[4\pi \frac{(2l+1)}{(2l_1+1)(2L+1)} \cdot \frac{(L+M)!(L-M)!}{(l+m)!(l-m)!(l_1+m_1)!(l_1-m_1)!} \right]^{\frac{1}{2}} ,$$
$$L \equiv l + l_1 , \qquad M \equiv m - m_1 ,$$

and taking into account that $\vec{\rho}_j \big|_{\sigma_{I-II_j}} = (R_j, \theta_j, \varphi_j)$, we obtain equation

$$\sum_{l_1 m_1} Y_{l_1 m_1}(\Omega_j) \left\{ A_{jl_1 m_1} R_j^{-l_1-1} + R_j^{l_1} \sum_{ilm} T_{lm}^{l_1 m_1} \left[A_{ilm} F'_{LM}(\vec{r}_i - \vec{r}_j) + A'_{ilm} F_{LM}(\vec{r}'_i - \vec{r}_j) \right] - B_{jl_1 m_1} R_j^{l_1} \right\} = \vec{E}_0 \cdot \vec{r}_j + (\vec{E}_0 . \vec{\rho}_j)_{\sigma_{I-II_j}}$$

where
$$F'_{lm}(\vec{r}_i - \vec{r}_j) \equiv \begin{cases} F_{lm}(\vec{r}_i - \vec{r}_j), \ i \neq j \\ 0, \ i = j \end{cases}$$

Interpreting this equation as multipole expansion, we can obtain expression for the coefficients $\{\ldots\}$ by using standard procedure $\int d\Omega \cdot Y_{lm}^{*} \cdot \ldots$, that leads to

$$\left\{ A_{jl_1 m_1} R_j^{-l_1-1} + R_j^{l_1} \sum_{ilm} T_{lm}^{l_1 m_1} \left[A_{ilm} F'_{LM}(\vec{r}_i - \vec{r}_j) + A'_{ilm} F_{LM}(\vec{r}'_i - \vec{r}_j) \right] - B_{jl_1 m_1} R_j^{l_1} \right\} = \sqrt{4\pi} \vec{E}_0 \vec{r}_j \delta_{00}^{l_1 m_1} + \frac{4}{3}\pi E_0 R_j \sum_{m=-1}^{1} \left[Y_{1m}^{*}(\vec{E}_0) \delta_{1m}^{l_1 m_1} \right]$$

While deriving last expression we have used relations [5]

$$\int Y_{lm}(\Omega) Y_{l'm'}^{*}(\Omega) d\Omega = \delta_{ll'} \delta_{mm'} \equiv \delta_{lm}^{l'm'} ,$$

$$\vec{a}\cdot\vec{b}=ab\cdot\cos\left(\vec{a}\,\hat{\cdot}\,\vec{b}\right)=\frac{4}{3}\pi ab\sum_{m=-1}^{1}Y_{1m}\left(\hat{\vec{a}}\right)Y^{*}_{1m}\left(\hat{\vec{b}}\right).$$

2. Potential derivative continuity condititon on the surface of j^{th} sphere in view of $\left.\frac{\partial}{\partial n}\right|_{\sigma_{I-II_j}}=\frac{\partial}{\partial\rho_j}$ and $\left.\rho_j\right|_{\sigma_{I-II_j}}=R_j$ take the form

$$\sum_{l_1m_1}\left\{\varepsilon_a(l_1+1)R_j^{-l_1-2}A_{jl_1m_1}+\varepsilon_j l_1R_j^{l_1-1}B_{jl_1m_1}-\varepsilon_a l_1R_j^{l_1-1}\sum_{ilm}T_{lm}^{l_1m_1}\left[A_{ilm}F'_{LM}\left(\vec{r}_i-\vec{r}_j\right)+A'_{ilm}F_{LM}\left(\vec{r}'_i-\vec{r}_j\right)\right]\right\}Y_{l_1m_1}\left(\Omega_j\right)=-\varepsilon_a(\vec{E}_0\cdot\hat{\vec{\rho}}_j)$$

Applying to this expression the same procedure as earlier, we obtain relation

$$\varepsilon_a(l_1+1)R_j^{-l_1-2}A_{jl_1m_1}+\varepsilon_j l_1R_j^{l_1-1}B_{jl_1m_1}-\varepsilon_a l_1R_j^{l_1-1}\sum_{ilm}T_{lm}^{l_1m_1}\left[A_{ilm}F'_{LM}\left(\vec{r}_i-\vec{r}_j\right)+A'_{ilm}F_{LM}\left(\vec{r}'_i-\vec{r}_j\right)\right]=-\frac{4}{3}\pi\varepsilon_a E_0\sum_{m=-1}^{1}\left[Y^{*}_{1m}\left(\vec{E}_0\right)\delta_{l_1m_1}^{1m}\right]$$

3. Two equations obtained from the boundary conditions on the surface of j^{th} sphere form the full set defining unknown coefficients A_{ilm} and B_{ilm} (note, that explicit form of A'_{ilm} as function of A_{ilm} was found earlier, see eq. (9)). After some transformations it can be reduced to the form

$$\begin{cases} B_{ilm}=f\left(A_{ilm}\right) \\ \sum\limits_{\substack{ilm\\ l\neq 0}}\left\{\delta_{jl_1m_1}^{ilm}+K_{jl_1m_1}^{ilm}\right\}A_{ilm}=V_{jl_1m_1}, \end{cases} \tag{10}$$

where

$$K_{jl_1m_1}^{ilm}\equiv\alpha_{jl_1}T_{l_1m_1}^{lm}\left\{F'_{LM}\left(\vec{r}_i-\vec{r}_j\right)+(-1)^{l+m}\frac{\varepsilon_a-\varepsilon_s}{\varepsilon_a+\varepsilon_s}F_{LM}\left(\vec{r}'_i-\vec{r}_j\right)\right\},$$

$$\alpha_{jl_1}\equiv\frac{l_1\left(\varepsilon_j-\varepsilon_a\right)}{l_1\varepsilon_j+(l_1+1)\varepsilon_a}R_j^{2l_1+1},$$

$$V_{jl_1m_1}=\frac{4}{3}\pi\alpha_{jl_1}E_0\sum_{m=-1}^{1}Y^{*}_{1m}\left(\hat{\vec{E}}_0\right)\delta_{m_1}^{m}\equiv\alpha_{jl_1}E_0\sqrt{\frac{2\pi}{3}}\left\{\sqrt{2}\cos\theta_0\delta_{l_1m_1}^{10}+\sin\theta_0e^{i\varphi_0}\delta_{l_1m_1}^{1-1}-\sin\theta_0e^{-i\varphi_0}\delta_{l_1m_1}^{11}\right.,$$

$$\vec{E}_0=\left(E_{0x},E_{0y},E_{0z}\right)=E_0(\sin\theta_0\cos\varphi_0,\sin\theta_0\sin\varphi_0,\cos\theta_0).$$

The explicit form of the function f in (10) is not needed for further consideration.

Second equation of (10) can be written in the matrix form $\left[\hat{1}+\hat{K}\right]\hat{A}=\hat{V}$ or $\hat{A}=\left[\hat{1}+\hat{K}\right]^{-1}\hat{V}$, that allows us to interpret the matrix $\hat{M}\equiv\left[\hat{1}+\hat{K}\right]^{-1}$, which connects external potential matrix V_{ilm} and multipole coefficients A_{ilm}, as the multipole polarizability matrix of the MDS spheres.

5. A single sphere near the substrate. The resonant frequencies

For the single sphere near the substrate, we can obtain the polarizability tensor in the dipole-dipole approximation by using (10):

$$\hat{\alpha}=\frac{4}{3}\pi R^3\varepsilon_a\left(\varepsilon-\varepsilon_a\right)\begin{pmatrix}\alpha_{II} & 0 & 0\\ 0 & \alpha_{II} & 0\\ 0 & 0 & \alpha_{\perp}\end{pmatrix}, \tag{11}$$

where $\alpha_i=\left[\varepsilon_a+L_i\left(\varepsilon-\varepsilon_a\right)\right]^{-1}$; $(i=II,\perp)$; $L_i=\frac{1}{3}\left(1+l_i\frac{\varepsilon_a-\varepsilon_s}{\varepsilon_a+\varepsilon_s}\right)$;

$$l_i = \frac{R}{h} \cdot \begin{cases} \frac{1}{8}, (i = //) \\ \frac{1}{4}, (i = \perp) \end{cases}$$

h is the distance between the sphere's center and the substrate.

Let us consider the case of Lorentz's dielectric functions and $\varepsilon_a = 1$ (vacuum):

$$\varepsilon(\omega) = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega}\ ; \qquad \varepsilon_s(\omega) = 1 + \frac{\omega_{ps}^2}{\omega_{0s}^2 - \omega^2 - i\gamma_s\omega}.$$

The resonant frequency is obtained by using the condition $\alpha_i(\omega_{res}) = \infty$. In our case it reduces to the following algebraic equation with respect to the frequency:

$$\omega^4 + a_3\omega^3 + a_2\omega^2 + a_1\omega + a_0 = 0, \tag{12}$$

where
$$a_3 = i(\gamma + \gamma_s)$$
$$a_2 = -\left(\omega_0^2 + \omega_{0s}^2 + \frac{1}{3}\omega_p^2 + \frac{1}{2}\omega_{ps}^2 + \gamma\gamma_s\right)$$
$$a_1 = -i\left(\gamma_s\omega_0^2 + \gamma\omega_{0s}^2 + \frac{1}{3}\gamma_s\omega_p^2 + \frac{1}{2}\gamma\omega_{ps}^2\right)$$
$$a_0 = \omega_0^2\omega_{0s}^2 + \frac{1}{3}\omega_{0s}^2\omega_p^2 + \frac{1}{2}\omega_0^2\omega_{ps}^2 + \frac{1}{6}(1 - l_i)\omega_p^2\omega_{ps}^2$$

A solution to (12) neglecting damping $(\gamma = \gamma_s = 0)$ is

$$\left(\omega_{1,2}^i\right)^2 = \frac{1}{2}\left\{y_1 + y_2 \pm \sqrt{(y_1 - y_2)^2 + 4l_i y_3}\right. \tag{13}$$

where
$$y_1 = \varpi_0^2 + \frac{\varpi_p^2}{3}; \quad y_2 = \varpi_{os}^2 + \frac{\varpi_{ps}^2}{2}; \quad y_3 = \frac{\varpi_p^2}{3} \cdot \frac{\varpi_{ps}^2}{2}.$$

Particularly, for a metallic sphere on the dielectric substrate from (13), using the inequality $\omega_{ps}/\omega_p << 1$, we obtain the following approximate expressions

$$\begin{cases} (\omega_{res}^{(1)})^2 = \frac{\varpi_p^2}{3} + l_i \frac{\varpi_{ps}^2}{2} \\ (\omega_{res}^{(2)})^2 = \omega_{0s}^2 + (1 - l_i)\frac{\varpi_{ps}^2}{2} \end{cases} \tag{14}$$

for the four (i=//,⊥) resonant frequencies. Note that $\varpi_p/\sqrt{3}$ is well-known surface plasmon frequency of a sphere and $\varpi_{ps}/\sqrt{2}$ is one of a substrate.

As we see, substrate changes the dipole moment of a sphere in such a way, that the four resonant frequencies arise in the absorption spectrum of a sphere. What causes arising of such number of the resonant frequencies? First, one pair of the frequencies is observed when the field direction is parallel to the substrate, while another one – when perpendicular, and these two pairs don't coincide in addition. In general case field has both the components and absorption spectrum has the four resonant frequencies respectively.

Second, under certain field direction (// or ⊥ to the substrate) the pair of frequencies arises due to an interaction between surface plasmons of the sphere and of the substrate. Under increasing of the distance between sphere and substrate this interaction vanishes and we obta well-known result: a single sphere and a single half-infinite substrate absorb radiation at the frequencies $\varpi_p/\sqrt{3}$ and $\varpi_{ps}/\sqrt{2}$ respectively.

6. Conclusion

We obtained the general expression for the resonant frequency of the model system, which is a dielectric sphere in vacuum on a dielectric substrate. The latter results in splitting and shifting of the resonant frequency depending on a direction of the external field according to (13). This allows one to suggest that layers of small particles on a substrate possess anisotropic electrodynamical properties.

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