15. Nanoparticle Optics in the Electrostatic Limit

In the previous chapter, we were restricted to nanospheres because a full solution of Maxwell's equation was needed. Such an analytic calculation is only possible for very simple geometries. However, if particles become sufficiently small so that the spatial variation of the electromagnetic field can be simplified, more complicated shapes can be applied. Hence, in this chapter, we adopt the "electrostatic limit" that is equivalent to ignoring the spatial variation of the incident electric field inside the particle.
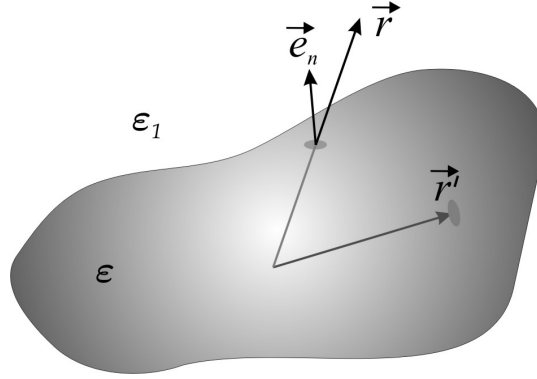

Figure 15.1 Geometry of metal nanoparticle having a dielectric constant ε embedded in a homogeneous medium with a dielectric constant ε_1.

We consider a nanoparticle such as the one depicted in Fig. 15.1 and apply the electrostatic method presented in Ref. [1]. In the electrostatic picture, an electric field only induces charges on the surface of the particle. Hence, the total electrostatic potential $\Phi(\vec{r})$ is the sum of an incident part $\Phi_0(\vec{r})$ and the contribution generated by the surface charges. If the surface charge density is $\sigma(\vec{r})$, the potential is given by

$$\Phi(\vec{r}) = \Phi_0(\vec{r}) + \frac{1}{4\pi\varepsilon_0} \oint \frac{\sigma(\vec{r}')}{|\vec{r} - \vec{r}'|} dS',$$

where the integral is over the entire surface of the particle. We can now use this to compute the electric field via the relation $\vec{\mathcal{E}}(\vec{r}) = -\nabla\Phi(\vec{r})$. In particular, we wish to compute the electric field on the surface. In this situation, case has to be taken because the normal component is discontinuous. The normal component is given by $\mathcal{E}_n(\vec{r}) = -\vec{e}_n \cdot \nabla\Phi(\vec{r})$, where $\vec{e}_n$ is the outward unit normal vector at position $\vec{r}$. The discontinuity means that the normal component just outside the particle $\mathcal{E}_n^{out}$ is related to the one just inside $\mathcal{E}_n^{in}$ via the relation

$$\mathcal{E}_n^{out}(\vec{r}) - \frac{\sigma(\vec{r})}{2\varepsilon_0} = \mathcal{E}_n^{in}(\vec{r}) + \frac{\sigma(\vec{r})}{2\varepsilon_0}.$$

Using these relations, we find that

$$\mathcal{E}_n^{out/in}(\vec{r}) = \vec{e}_n \cdot \vec{\mathcal{E}}_0 + \frac{1}{4\pi\varepsilon_0} \oint \sigma(\vec{r}')g(\vec{r},\vec{r}')dS' \pm \frac{\sigma(\vec{r})}{2\varepsilon_0},$$

where + and – go with the fields outside and inside the particle, respectively. Also, $\vec{\mathcal{E}}_0$ is the (constant) incident field and g denotes the so-called Green's function

$$g(\vec{r},\vec{r}') = -\vec{e}_n \cdot \nabla \frac{1}{|\vec{r}-\vec{r}'|} = \vec{e}_n \cdot \frac{\vec{r}-\vec{r}'}{|\vec{r}-\vec{r}'|^3}. \tag{1}$$

However, we also know that the normal components are related via the dielectric constants, i.e. $\varepsilon_1 \mathcal{E}_n^{out}(\vec{r}) = \varepsilon \mathcal{E}_n^{in}(\vec{r})$. This means that with a bit of rearrangement, Eq. (3) can be reformulated as

$$\sigma(\vec{r}) = 2\varepsilon_0 \lambda \vec{e}_n \cdot \vec{\mathcal{E}}_0 + \frac{\lambda}{2\pi} \oint \sigma(\vec{r}')g(\vec{r},\vec{r}')dS', \tag{2}$$

where $\lambda = (\varepsilon - \varepsilon_1)/(\varepsilon + \varepsilon_1)$. This formulation is very convenient because it allows us to compute the distribution of surface charges from a single equation.

15.1 Cylindrical nanoparticles

The framework above applies to nanoparticles of completely general shape. It even works for collections of nanoparticles if the surface is taken as the sum of surfaces. In practice, however, Eq. (15.2) is difficult to solve in the general case. Fortunately, many important cases are much simpler. In particular, many relevant nanoparticle geometries have cylindrical symmetry, i.e. they have a rotational symmetry axis as illustrated in Fig. 15.2. In this case, the general problem can be reduced significantly.
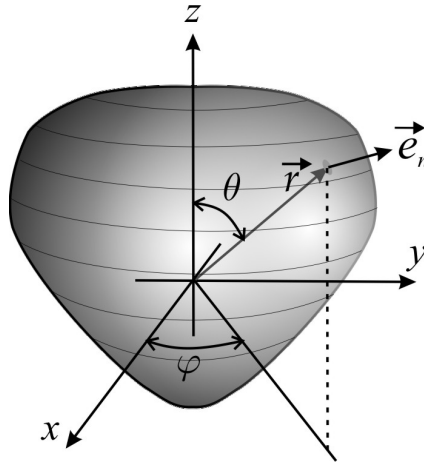

Figure 15.2 Cylindrically symmetric nanoparticle.

Using the geometry of Fig. 15.2, we can without loss of generality choose to keep the incident field $\vec{\mathcal{E}}_0$ in the (x,z)-plane. The x- and z-axes are the horizontal (h) and vertical (v) directions, respectively, and so we decompose $\vec{\mathcal{E}}_0 = \mathcal{E}_0^h \vec{e}_x + \mathcal{E}_0^v \vec{e}_z$. Due to the superposition principle we can, in fact, treat the horizontal and vertical cases separately. We then benefit significantly from the simple angular dependence of these cases.

In a cylindrical geometry, we may express the geometrical vectors using polar angles in a simple manner, Hence,

$$
\begin{aligned}
\vec{r} &= r(\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta) \\
\vec{e}_n &= (n_x\cos\varphi, n_x\sin\varphi, n_z) \\
\vec{r}' &= r'(\sin\theta'\cos\varphi', \sin\theta'\sin\varphi', \cos\theta')
\end{aligned}
\qquad (3)
$$

where r, n_x, n_z are all function of θ and r' is a function of θ'. It follows that $\vec{e}_n \cdot \vec{\mathcal{E}}_0$ is $\mathcal{E}_0 n_x \cos\varphi$ and $\mathcal{E}_0 n_z$ in the horizontal and vertical cases, respectively. It is then readily shown that the surface charge follows exactly the same dependence on the angle φ. Due to the symmetry, the surface area element dS must be independent of φ and we may write $dS' = S(\theta')d\theta'd\varphi'$. We will return to the θ dependence later. We also need the following relations to reduce the Green's function:

$$
\begin{aligned}
\vec{e}_n \cdot (\vec{r} - \vec{r}') &= n_z(r\cos\theta - r'\cos\theta') + n_x(r\sin\theta - r'\sin\theta'\cos(\varphi-\varphi')) \\
|\vec{r} - \vec{r}'|^2 &= r^2 + r'^2 - 2rr'\cos\theta\cos\theta' - 2rr'\sin\theta\sin\theta'\cos(\varphi-\varphi')
\end{aligned}
\qquad (4)
$$

The simplest case is that of vertical polarization, for which $\vec{e}_n \cdot \vec{\mathcal{E}}_0$ is independent of φ. We wish to prove that the surface charge is a function of θ only and so we write $\sigma(\vec{r}) = \sigma(\theta)$. The charge balance Eq.(15.2) therefore reduces to

$$
\text{Vertical:} \quad \sigma(\theta) = 2\varepsilon_0\lambda\mathcal{E}_0 n_z(\theta) + \lambda\int_0^\pi \sigma(\theta')G^{(v)}(\theta,\theta')S(\theta')d\theta', \qquad (5)
$$

where

$$
G^{(v)}(\theta,\theta') = \int_0^{2\pi} \frac{\vec{e}_n \cdot (\vec{r} - \vec{r}')}{2\pi|\vec{r} - \vec{r}'|^3} d\varphi'.
$$

Performing the integral using the geometrical relations we then find

$$
G^{(v)}(\theta,\theta') = \frac{1}{2\pi}\left\{\left[n_z(r\cos\theta - r'\cos\theta') + n_x r\sin\theta\right]F_{0,1}(x,y) - n_x r'\sin\theta'F_{1,1}(x,y)\right\}, \qquad (6)
$$

with $x = r^2 + r'^2 - 2rr'\cos\theta\cos\theta'$, $y = -2rr'\sin\theta\sin\theta'$ and introducing the functions

$$F_{m,n}(x,y) \equiv \int_0^{2\pi} \frac{\cos^m\varphi\, d\varphi}{(x + y\cos\varphi)^{(2n+1)/2}},$$

The first few of these functions are

$$F_{0,0}(x,y) = \frac{4}{\sqrt{x+y}} K\left(\frac{2y}{x+y}\right)$$

$$F_{0,1}(x,y) = \frac{4}{(x-y)\sqrt{x+y}} E\left(\frac{2y}{x+y}\right)$$

$$F_{1,0}(x,y) = \frac{4\sqrt{x+y}}{y} E\left(\frac{2y}{x+y}\right) - \frac{4x}{y\sqrt{x+y}} K\left(\frac{2y}{x+y}\right)$$

$$F_{1,1}(x,y) = \frac{4x}{y(y-x)\sqrt{x+y}} E\left(\frac{2y}{x+y}\right) + \frac{4}{y\sqrt{x+y}} K\left(\frac{2y}{x+y}\right)$$

$$F_{2,1}(x,y) = \frac{4y^2 - 8x^2}{y^2(y-x)\sqrt{x+y}} E\left(\frac{2y}{x+y}\right) - \frac{8x}{y^2\sqrt{x+y}} K\left(\frac{2y}{x+y}\right)$$

where K and E are elliptic integrals. Higher terms can be generated using $F_{m,n} = (F_{m-1,n-1} - xF_{m-1,n})/y$. The fact that these functions depend only on θ and θ' completes the proof.

For the horizontal case, we proceed in almost complete analogy but now the surface charge is found to follow the $\cos\varphi$ behaviour of $\vec{e}_n \cdot \vec{\mathcal{E}}_0$. Hence, we write $\sigma(\vec{r}) = \sigma(\theta)\cos\varphi$ in this case and using elementary mathematical manipulations (rewriting $\cos\varphi'$ as $\mathrm{Re}\left\{e^{i(\varphi-\varphi')}e^{-i\varphi}\right\}$ and doing the integral before taking the real part) find that

$$\text{Horizontal:} \quad \sigma(\theta) = 2\varepsilon_0\lambda\mathcal{E}_0 n_x(\theta) + \lambda\int_0^\pi \sigma(\theta')G^{(h)}(\theta,\theta')S(\theta')d\theta', \tag{7}$$

where

$$G^{(h)}(\theta,\theta') = \int_0^{2\pi} \frac{\vec{e}_n \cdot (\vec{r} - \vec{r}')\cos(\varphi - \varphi')}{2\pi|\vec{r} - \vec{r}'|^3} d\varphi'.$$

can be expressed as

$$G^{(h)}(\theta, \theta') = \frac{1}{2\pi}\left\{\left[n_z(r\cos\theta - r'\cos\theta') + n_x r\sin\theta\right]F_{1,1}(x,y) - n_x r'\sin\theta' F_{2,1}(x,y)\right\}. \qquad (8)$$

15.2 Oblate Spheroids

As a relatively simple but still technologically important example we will consider oblate spheroids: "pancake" shaped particles obtained by flattening spheres along one direction. Such a particle is illustrated in Fig. 15.3.
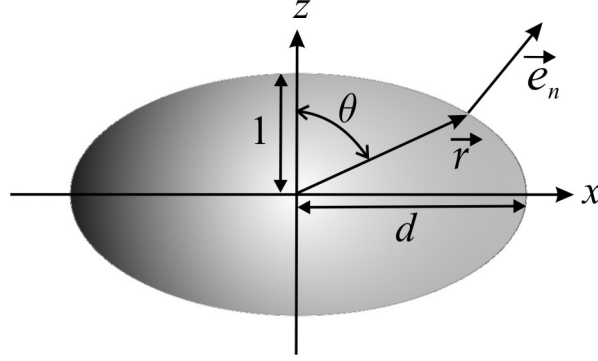

Figure 15.3 Cross section of an oblate spheroid.

The geometry of the spheroid is taken such that the thickness of the "pancake" is unity and the radius is d. Hence, all distances are actually measured in units of half the particle height. A particular point on the surface obeys the ellipse parameterization

$$1 = z^2 + \frac{x^2}{d^2} \quad \Rightarrow \quad 1 = r^2\cos^2\theta + \frac{r^2}{d^2}\sin^2\theta \quad \Rightarrow \quad r = \frac{d}{\sqrt{d^2\cos^2\theta + \sin^2\theta}}.$$

Also, the surface normal is calculated from the requirement that $\vec{e}_n \cdot (d\vec{r}/d\theta) = 0$. Hence, differentiating and ensuring normalization it is found that

$$n_x = \frac{\sin\theta}{\sqrt{d^4\cos^2\theta + \sin^2\theta}}, \quad n_z = \frac{d^2\cos\theta}{\sqrt{d^4\cos^2\theta + \sin^2\theta}}.$$

In general, the surface areal function $S(\theta)$ is to be calculated as $S(\theta) = r^3\sin\theta/\vec{e}_n \cdot \vec{r}$ and in the spheroid case we have $S(\theta) = d^2\sin\theta(\sin^2\theta + d^4\cos^2\theta)^{1/2}/(\sin^2\theta + d^2\cos^2\theta)^2$.

To solve equations like Eq.(15.5) and Eq.(15.7) numerically we need to discretize the angle θ. On the interval $\theta \in [0,\pi[$ we therefore select N discrete values θ_i with separations $\Delta_i = \theta_{i+1} - \theta_i$ (for $i = N$ we take $\Delta_N = \pi - \theta_i$). Hence, the equations are reformulated as

$$\sigma(\theta_i) \approx 2\varepsilon_0\lambda\mathcal{E}_0 n(\theta_i) + \lambda\sum_{j=1}^{N}\sigma(\theta_j)G(\theta_i,\theta_j)S(\theta_j)\Delta_j, \qquad (9)$$

where the appropriate Green's function and normal vector component should be chosen for the two polarizations. Equations of this sort are easily converted into a tractable form by introducing vectors

$$\vec{\sigma} = \begin{pmatrix} \sigma(\theta_1) \\ \sigma(\theta_2) \\ \vdots \\ \sigma(\theta_N) \end{pmatrix}, \quad \vec{e} = 2\varepsilon_0\mathcal{E}_0 \begin{pmatrix} n(\theta_1) \\ n(\theta_2) \\ \vdots \\ n(\theta_N) \end{pmatrix}.$$

as well as a matrix

$$\overset{\leftrightarrow}{G} = \begin{pmatrix} G(\theta_1,\theta_1)S(\theta_1)\Delta_1 & G(\theta_1,\theta_2)S(\theta_2)\Delta_2 & \cdots & G(\theta_1,\theta_N)S(\theta_N)\Delta_N \\ G(\theta_2,\theta_1)S(\theta_1)\Delta_1 & G(\theta_2,\theta_2)S(\theta_2)\Delta_2 & \cdots & G(\theta_2,\theta_N)S(\theta_N)\Delta_N \\ \vdots & \vdots & \ddots & \vdots \\ G(\theta_N,\theta_1)S(\theta_1)\Delta_1 & G(\theta_N,\theta_2)S(\theta_2)\Delta_2 & \cdots & G(\theta_N,\theta_N)S(\theta_N)\Delta_N \end{pmatrix}.$$

In terms of these quantities, the discretized equation reads as

$$\left\{\lambda^{-1}\overset{\leftrightarrow}{U} - \overset{\leftrightarrow}{G}\right\} \cdot \vec{\sigma} = \vec{e}, \quad \Rightarrow \quad \vec{\sigma} = \left\{\lambda^{-1}\overset{\leftrightarrow}{U} - \overset{\leftrightarrow}{G}\right\}^{-1} \cdot \vec{e}. \tag{10}$$

Thus, the unknown surface charges in vector $\vec{\sigma}$ are found by inverting a matrix and multiplying onto a known vector. Furthermore, it is realized that certain *eigenmodes* of the surface charge can be found whenever the determinant $\left|\lambda^{-1}\overset{\leftrightarrow}{U} - \overset{\leftrightarrow}{G}\right|$ vanishes. This is because this condition corresponds to a situation, in which a surface charge exists even with a vanishingly small incident field. This is clearly a mathematical abstraction but the significance is that in actual calculations, resonances in absorption or scattering cross sections may appear near these eigenmodes. From the form of the matrix it is also evident that eigenmodes are found whenever λ^{-1} is an eigenvalue of $\overset{\leftrightarrow}{G}$. In practice, the matrix $\overset{\leftrightarrow}{G}$ is slightly problematic because the diagonal elements diverge! By clever usage of the general properties of the Green's function, however, appropriate values of the diagonal elements can be found (see the exercise). If the dielectric constant of the metal nanoparticle is assumed to be of the lossless Drude form $\varepsilon(\omega) = \varepsilon_\infty - \omega_p^2/\omega^2$ the relation between eigenvalue and resonance frequency is given by

$$\omega = \frac{\omega_p}{\sqrt{\varepsilon_\infty + \varepsilon_0 \dfrac{\lambda+1}{\lambda-1}}}.$$

As an example, we now take Ag spheroids ($\varepsilon_\infty = 6$, $\hbar\omega_p = 9.3\,\text{eV}$) embedded in Si ($\varepsilon_1 = 12$). For a particular geometry, the spheroid is characterized by its ellipticity $e = \sqrt{1 - 1/d^2}$, which ranges between 0 for a sphere and 1 for a plane. In Fig. 15.4, results for the resonance wavelengths in this case are depicted.
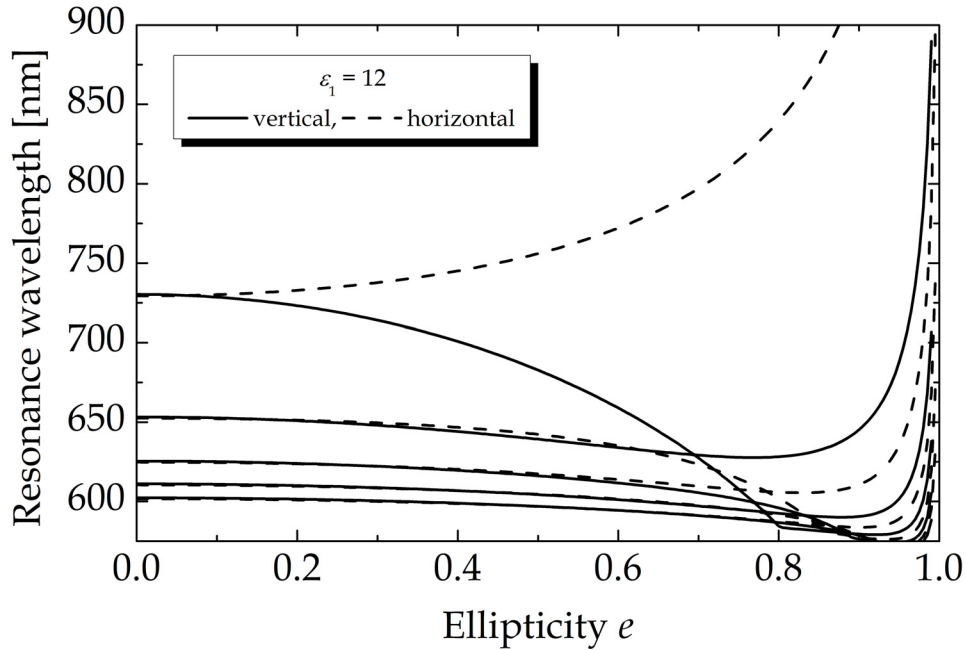

Figure 15.4 Resonance wavelengths of Ag spheroids embedded in Si. Solid and dashed curves illustrate vertical and horizontal resonances versus nanoparticle ellipticity.

The present technique can be extended in several directions. Primarily, based on solution of the inhomogeneous equation Eq.(15.10), the absorption cross section is calculated via

$$\sigma_{abs}(\omega) = \frac{\omega}{c\varepsilon_0\sqrt{\varepsilon_1}} \text{Im}\left\{\frac{p}{\mathcal{E}_0}\right\}, \tag{11}$$

where p is the induced dipole moment that is easily calculated using the formulas

$$\text{Vertical:} \quad \vec{p} = 2\pi\hat{z}\int_0^\pi \sigma(\theta)\frac{r^4(\theta)}{\vec{e}_n\cdot\vec{r}}\cos\theta\sin\theta d\theta$$

$$\text{Horizontal:} \quad \vec{p} = \pi\hat{x}\int_0^\pi \sigma(\theta)\frac{r^4(\theta)}{\vec{e}_n\cdot\vec{r}}\sin^2\theta d\theta \tag{12}$$

In addition, the nanoparticles positioned on a surface of embedded in thin layers can be handled by proper modifications to the Green's functions [2].

7

Exercise: Properties of the Green's function

a) Using Gauss' theorem, show that

$$\oint g(\vec{r},\vec{r}')dS = 4\pi \,.$$

b) Based on this result, show that the reduced Green's function for vertical polarization satisfies the condition

$$\int\limits_0^\pi G^{(v)}(\theta,\theta')S(\theta)d\theta = 1 \,.$$

This result can be used to handle the singularity of the Green's function. In a discetized version, it reads as

$$\sum_{i=1}^N G^{(v)}(\theta_i,\theta_j)S(\theta_i)\Delta_i = 1 \,.$$

It follows that the diagonal element must be

$$G^{(v)}(\theta_j,\theta_j) = \frac{1}{S(\theta_j)\Delta_j}\left\{1 - \sum_{i=1,i\neq j}^N G^{(v)}(\theta_i,\theta_j)S(\theta_i)\Delta_i\right\} \,.$$

For the horizontal case, unfortunately, no such simple result applies. Hence, special numerical handling of the diagonal terms is needed.

References

[1] I.D. Mayergoyz, D.R. Fredkin, and Z. Zhang, Phys. Rev. B72, 155412 (2005).
[2] J. Jung, T.G. Pedersen, T. Søndergaard, K. Pedersen, A. Nylandsted Larsen and B. Bech Nielsen "Electrostatic plasmon resonances of metal nanospheres in layered geometries", Accepted Phys. Rev. B.