

Chapter 2

Electromagnetics of Metals and Theory Fundamentals

Abstract In this chapter, we focus on describing the classical electromagnetic theory to expound the basic fundamentals of small discrete particles. With this theory, we can finally derive the mechanism and property of plasmonic particles like gold, silver, copper, etc. Here, we first lead in the Maxwell's equations. They will make it easier to understand the interaction of electromagnetism. Then, we introduce some fundamental parameters, such as the refractive index and the relative parameters, to make the analysis clearly. These quantities will be used in the simplest plane-wave solution and surface plasmon polariton (SPPS) equation which are the intermediate processes that can lead us to the final answer. In order to explain the mechanism clearly, we do not want to twist in the objective factor, so the light we use here is a monochromatic parallel beam, and dipole excitation is considered as the most important factor. And the light containing the general properties of optics can ignore plenty of special cases.

Keywords Maxwell's equation • Plane wave • Refractive index • Relative parameters • Dipole excitation • Adsorption and scattering

2.1 Maxwell's Equations

In space, the physical electromagnetic field is generated by moving electrically charged objects. When the objects move, the electric and magnetic fields change at the same time. So, it can be easily realised that we can use these two vectors, E and B , to represent electromagnetic field, called the electric vector and the magnetic induction, respectively.

As we know, when the charged objects move quickly, the charges can form the electric current. It is naturally to deduce the electric current density j , the electric displacement D , and the magnetic vector H . Unless otherwise stated, the particles used here are noble metals.

These are the original quantities that can finally derive Maxwell's equations with the space and time derivatives [1].

$$\text{curl } H - \frac{1}{c} D' = \frac{4\pi}{c} j \quad (2.1)$$

$$\text{curl } E + \frac{1}{c} B' = 0 \quad (2.2)$$

$$\text{div } D = 4\pi \rho \quad (2.3)$$

$$\text{div } B = 0 \quad (2.4)$$

It is worthwhile to note that the dot here shows differentiation with respect to time, and the physical property of medium at any point is continuous. The constant c in (2.1) and (2.2) is the velocity of light in vacuum and is approximately equal to 3×10^8 m/s.

From the derivation of (2.1), we can get [2]

$$\text{div } j = -\frac{1}{4\pi} \text{div } D' \quad (2.5)$$

Since $\text{div curl} \equiv 0$, and use (2.3), we can get

$$\frac{\partial \rho}{\partial t} + \text{div } j = 0 \quad (2.6)$$

When the charge is conserved at any point of the medium, it can be integrated under the condition that Gauss' theorem is fitted:

$$\frac{d}{dt} \int \rho \, dV + \int j \cdot n \, dS = 0 \quad (2.7)$$

The first integral is taking place throughout the volume, and the second one is bounded in the surface region, n denotes the unit outward normal. This equation implies that the total charge

$$e = \int \rho \, dV \quad (2.8)$$

The total charge e in Eq. (2.8) contained within the domain can only increase on account of the flow of electric current, and then, we can get

$$J = \int j \cdot n \, dS \quad (2.9)$$

The situation introduced here is dependent on the condition that the field quantities are independent to time. If time is discontinuous, what will happen? It can be imagined that the charged objects may move and appear anywhere. If there is no current ($j = 0$), the field is called a static field; if current exists ($j \neq 0$), the field is called a stationary field.

We use material equations (or constitutive relations) to define the relations of substances in the physical field. The relations that describe the behaviour of substances

under the influence of the field are called material equations (or constitutive relations). As we know, it is complicated and difficult to analyse. Here, we just discuss the relations when the field is time harmonic and the physical properties of it are independent of location, direction, and angle. So, it is easy to form the relations [3, 4]:

$$j = \sigma E \quad (2.10)$$

$$D = \varepsilon E \quad (2.11)$$

$$B = \mu H \quad (2.12)$$

Here, σ is called the specific conductivity, ε is known as the dielectric constant (or permittivity), and μ is called the magnetic permeability.

2.2 The Wave Equation

In order to interpret the relationship between the field vectors and the differential equations better, we focus our attention on the part where $j = 0$ and $\rho = 0$.

We put B from (2.2) into (2.12). After the deformation of the equation, it gives [2]

$$\text{curl} \left(\frac{1}{\mu} \text{curl} E \right) + \frac{1}{c} \text{curl} H' = 0 \quad (2.13)$$

Take the differential quotient to time of (2.1); substitute E for D using (2.11). Then, it gives

$$\text{curl} \left(\frac{1}{\mu} \text{curl} E \right) + \frac{\varepsilon}{c^2} E'' = 0 \quad (2.14)$$

Be aware of the identities $\text{curl} uv = u \cdot \text{curl} v + (\text{grad} u) \times v$ and $\text{curl} \text{curl} = \text{grad} \text{div} - \nabla^2$ (2.14) becomes [5]

$$\nabla^2 E - \frac{\varepsilon \mu}{c^2} E'' + (\text{grad} \ln \mu) \times \text{curl} E - \text{grad} \text{div} E = 0 \quad (2.15)$$

With the help of the identity, $\text{div} uv = u \cdot \text{div} v + v \cdot \text{grad} u$ (2.3) becomes

$$\varepsilon \cdot \text{div} E + E \cdot \text{grad} \varepsilon = 0 \quad (2.16)$$

After collating (2.15), it gives

$$\nabla^2 E - \frac{\varepsilon \mu}{c^2} E'' + (\text{grad} \ln \mu) \times \text{curl} E + \text{grad}(E \cdot \text{grad} \ln \varepsilon) = 0 \quad (2.17)$$

We can also get the similar answer if we substitute H for B using (2.12) and (2.13) gives

$$\nabla^2 H - \frac{\varepsilon \mu}{c^2} H'' + (\text{grad} \ln \varepsilon) \times \text{curl} H + \text{grad}(H \cdot \text{grad} \ln \mu) = 0 \quad (2.18)$$

It is worth mentioning that if the medium is homogeneous, i.e. $\text{grad } \log \varepsilon = \text{grad } \ln \mu = 0$ (2.17) and (2.18) become

$$\nabla^2 E - \frac{\varepsilon \mu}{c^2} E'' = 0 \quad (2.19)$$

$$\nabla^2 H - \frac{\varepsilon \mu}{c^2} H'' = 0 \quad (2.20)$$

The equations prove that the electromagnetic waves surely exist, and they are standard equations of wave motion. And we can get the velocity in the medium

$$v = \frac{c}{\sqrt{\varepsilon \mu}} \quad (2.21)$$

Compare (2.21) with $n = \frac{c}{v}$, we can get [6]

$$n = \sqrt{\varepsilon \mu} \quad (2.22)$$

For the most transparent substance, μ is practically equal to unity, n is the refractive index. That is why we consider ε as a constant normally. When we take the atomic structure of matter into account, ε is not an immutable characteristic of the material. It will be discussed in the next section.

2.3 Scattering from Inhomogeneous Media

Scattering is a physical process in which light is deflected haphazardly as a result of collisions. Here, we shall confine our attention to the part that the relationship between media and the incident wave is linear. When the physical property is time independent, it is called static scattering.

At first, we will take two extreme media into consideration. One is conducting medium, the other is nonconducting medium.

For the conducting one, we assume that it is not related to V , the space-dependent part in Eq. (2.17) can be extracted from the complex electric field, deform it in the monochromatic electromagnetic field, we can get [7]

$$\nabla^2 E(r, \omega) + k^2 \varepsilon(r, \omega) E(r, \omega) + \text{grad} [E(r, \omega) \cdot \text{grad } \ln \varepsilon(r, \omega)] = 0 \quad (2.23)$$

As we know, the medium is isotropic and nonmagnetic. So, the time-dependent part can be defined as

$$E = E_0 e^{-i\omega t} \quad (2.24)$$

(Not to explain in the following analysis), substitute (2.24) for E in (2.23), we can get

$$k^2 = \frac{\omega^2}{c^2} \left(1 + i \frac{\sigma}{\varepsilon_0 \omega} \right) \quad (2.25)$$

We define $1 + i\frac{\sigma}{\epsilon_0\omega}$ as the complex permittivity $\epsilon_r(\omega)$. It establishes a relationship between the specific conductivity and the dielectric constant. In order to get ϵ , we now introduce the free-electron gas (FEG) model. It is a special quantum mechanics model that describes the property of Fermi systems in the ideal gas. It ignores the interaction between centron and electron, electron and electron, and assumes that the electrons can move freely in the background full of protons.

In the monochromatic electromagnetic field [8], motion of electrons can be shown as

$$mv' = eE \quad (2.26)$$

Compare with (2.24), we can get

$$v = \frac{-eE}{im\omega} \quad (2.27)$$

Since $j = nev$, substitute j for v , it becomes

$$j = -\frac{ne^2}{im\omega}E \quad (2.28)$$

The comparison of (2.10) and (2.28) gives

$$\sigma = -\frac{ne^2}{im\omega} \quad (2.29)$$

Put σ into Eq. (2.25), we can get

$$\epsilon_r(\omega) = 1 - \frac{ne^2}{\epsilon_0 m \omega^2} = 1 - \frac{\omega_p^2}{\omega^2} \quad (2.30a)$$

$$\omega_p^2 = \frac{ne^2}{\epsilon_0 m} \quad (2.30b)$$

For the nonconducting one, we can also get the similar answer from Lorenz model in the dielectric. The electron theory assumes that:

First, the charges in the atoms or molecules are spread in the surface under the quasi-elastic force.

Second, dielectric will be polarised under the effect of incident light, following forced vibration of charged particle.

Third, atomic nucleus is considered to be immobile, and the charges vibrate at the inherent vibration frequency.

Since the restoring force $f = -m\omega_0^2 r$, we can easily infer the equation of electron forced vibration

$$mr'' = -eE - fr - gr' \quad (2.31)$$

Here, eE is the electric field force, fr is the quasi-elastic force, gr' is the damping force. And we lead in two quantities, eigentone $\omega_0 = \sqrt{f/m}$, damping factor $\gamma = \sqrt{g/m}$, to make the equation easy to settle (2.31) becomes

$$r'' + \gamma r' + \omega_0^2 r = -\frac{eE_0 e^{-i\omega t}}{m} \quad (2.32)$$

We then can get the solution of Eq. (2.32)

$$r(t) = \frac{(-e)}{m} \frac{E_0 e^{-i\omega t}}{(\omega_0^2 - \omega^2) - i\gamma\omega} \quad (2.33)$$

From the definition of the electric dipole moment and polarisation, we can get

$$p = qr \quad (2.34)$$

$$P = Np = -Ne r \quad (2.35)$$

Put (2.33) into (2.35), we can get

$$P = \frac{Ne^2}{m} \frac{E_0 e^{-i\omega t}}{(\omega_0^2 - \omega^2) - i\gamma\omega} \quad (2.36)$$

Since $p = \varepsilon_0 \chi E$, then

$$\chi = \omega_p^2 \frac{1}{(\omega_0^2 - \omega^2) - i\gamma\omega} \quad (2.37)$$

And the complex permittivity becomes [9]

$$\varepsilon_r(\omega) = 1 + \omega_p^2 \frac{1}{(\omega_0^2 - \omega^2) - i\gamma\omega} \quad (2.38)$$

To sum up, we can make the Eq. (2.38) simply when $\omega_p \gg \omega_0$, and this is the famous Drude model

$$\varepsilon_r(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \quad (2.39)$$

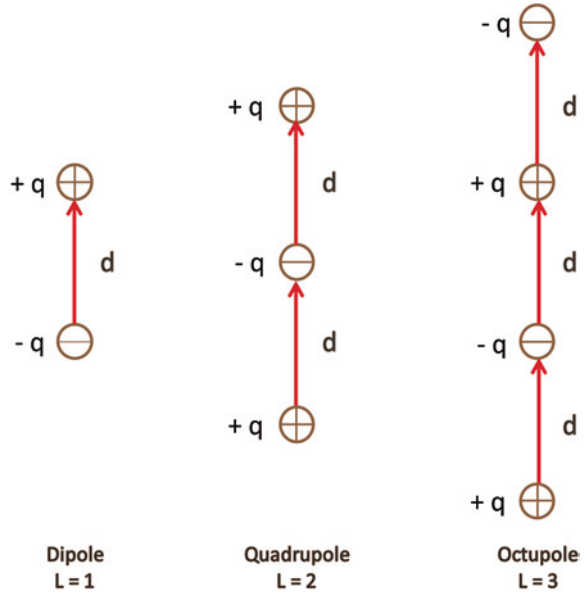
2.4 Localized Surface Plasmons

Localized surface plasmon resonance (LSPR) is different from surface polaritons, which can exist not only in the boundary of dielectric and metal, but also in the structures. LSPR frequency can be obtained by the Laplace equation.

Assuming that there is a metal particle in the vacuum, we can get its space distribution of potential through Laplace equation [10]:

$$\phi_1(r, \theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{\infty} a_{lm} r^l Y_{lm}(\theta, \varphi) \quad 0 < r \leq R \quad (2.40a)$$

Fig. 2.1 Different kinds of excitation



$$\phi_2(r, \theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-1}^{\infty} b_{lm} \frac{1}{r^{l+1}} Y_{lm}(\theta, \varphi) \quad r > R \quad (2.40b)$$

The boundary conditions: ϕ and $\varepsilon_i \frac{\partial \phi}{\partial x}$ are continuous when $r = R$. Sometimes we will consider the fact that there are other kinds of excitation like quadrupole, octupole, and so on (Fig. 2.1). We can also put them in the dipolar model. It shows

$$\omega_l = \omega_p \left(\frac{l}{2l+1} \right)^{0.5} \quad l = 1, 2, 3 \dots \quad (2.41)$$

In this book, our conclusion is based on the simple quasi-static approximation. It suggests that the particles we use here are much smaller than the wavelength of light. Dipole excitation is the most important one [11].

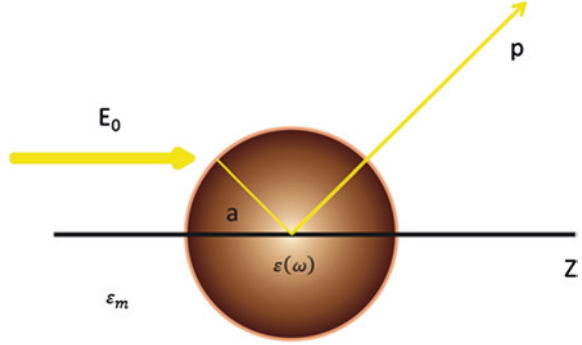
In the electrostatic approach, we can change the form of (2.40a, b) due to the azimuthal symmetry

$$\phi_1(r, \theta) = \sum_{l=0}^{\infty} \left[A_l r^l + B_l r^{-(l+1)} \right] P_l(\cos \theta) \quad (2.42)$$

Here, $P_l(\cos \theta)$ are the Legendre polynomials of order l , and θ is the angle between the position vector r at the line P and z -axis (Fig. 2.2).

In order to better understand the potentials, we excise (2.42) into ϕ_{in} and ϕ_{out} , defined as the function inside and outside the sphere, respectively, then we can get [12]

Fig. 2.2 Homogeneous metal particle in an electrostatic field



$$\phi_{\text{in}}(r, \theta) = \sum_{l=0}^{\infty} A_l r^l P_l(\cos \theta) \quad (2.43a)$$

$$\phi_{\text{out}}(r, \theta) = \sum_{l=0}^{\infty} \left[B_l r^l + C_l r^{-(l+1)} \right] P_l(\cos \theta) \quad (2.43b)$$

The boundary condition is $r \rightarrow \infty$, and then, the coefficient B_l can be determined. The requirement that $\phi_{\text{out}} \rightarrow -E_0 r \cos \theta$ as $r \rightarrow \infty$ demands that $B_l = -E_0$ and $B_l = 0$ for $l \neq 1$. The remained A_l , and C_l are defined by $r = a$. The equality of the normal components of the displacement field is

$$-\varepsilon_0 \varepsilon \frac{\partial \phi_{\text{in}}}{\partial r} \Big|_{r=a} = -\varepsilon_0 \varepsilon_m \frac{\partial \phi_{\text{out}}}{\partial r} \Big|_{r=a} \quad (2.44)$$

And the equality of the tangential components of the electric field is

$$-\frac{1}{a} \frac{\partial \phi_{\text{in}}}{\partial r} \Big|_{r=a} = -\frac{1}{a} \frac{\partial \phi_{\text{out}}}{\partial r} \Big|_{r=a} \quad (2.45)$$

The boundary mentioned before leads to $A_l = C_l = 0$ for $l \neq 1$, and then, we can calculate the evaluation of (2.43a, b)

$$\phi_{\text{in}} = -\frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m} E_0 r \cos \theta \quad (2.46a)$$

$$\phi_{\text{out}} = -E_0 r \cos \theta + \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} E_0 a^3 \frac{\cos \theta}{r^2} \quad (2.46b)$$

We can put the dipole moment p in (2.46b), it becomes

$$\phi_{\text{out}} = -E_0 r \cos \theta + \frac{pr}{4\pi \varepsilon_0 \varepsilon_m r^3} \quad (2.47)$$

$$p = 4\pi\epsilon_0\epsilon_m a^3 \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \quad (2.48)$$

According to (2.36), we can get

$$\chi = 4\pi a^3 \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \quad (2.49)$$

We can get the same functional form as the Clausius–Mossotti relation. The extinction cross section [13], C_{ext} is easily calculated as the sum of the absorption and scattering cross section via [2]

$$C_{\text{ext}} = C_{\text{abs}} + C_{\text{sca}} \quad (2.50)$$

where C_{abs} and C_{sca} are obtained from the polarisability χ in (2.49), it gives

$$C_{\text{sca}} = \frac{k^4}{6\pi} |\chi|^2 = \frac{8\pi}{3} k^4 a^6 \left| \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \right|^2 \quad (2.51a)$$

$$C_{\text{abs}} = klm[\chi] = 4\pi k a^3 lm \left[\frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \right] \quad (2.51b)$$

When the size of particles is much smaller than the incident wavelength ($a \ll \lambda$), the efficiency of absorption scales with a^3 and the scattering efficiency scales with a^6 . Also, the cross sections in (2.51a, b) can be applied in the expression of dielectric scatters. As $C_{\text{sca}} \propto a^6$, and that is why we cannot see the small particles in the camera like CCD, the background of scattering is too large to see small objects. We can also see that both absorption and scattering are enhanced when dipole excitation exists in the form of (2.51a, b). When we add a quasi-static limit in the dielectric function $\epsilon = \epsilon_1 + i\epsilon_2$, Eqs. (2.51a, b) becomes [14–16]

$$C_{\text{ext}} = 9 \frac{\omega}{c} \epsilon_m^{1.5} V \frac{\epsilon_2}{(\epsilon_1 + 2\epsilon_m)^2 + \epsilon_2^2} \quad (2.52)$$

Here, we know how to deal with a spherical nanoparticle. However, most of the nanoparticles are not sphere, like ellipsoid or spheroid. If we suppose that the nanoparticle is an ellipsoid with axes $a \leq b \leq c$, then we can get $\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1$. So, the expression of χ becomes

$L_{x,y,z}$ is called the depolarisation, which gives

$$\chi_{x,y,z} = \frac{4\pi abc(\epsilon_{Au} - \epsilon_m)}{3\epsilon_m + 3L_{x,y,z}(\epsilon_{Au} - \epsilon_m)} \quad (2.53)$$

$$L_x = \frac{1 - e^2}{e^2} \left(-1 + \frac{1}{2e} \ln \left(\frac{1+e}{1-e} \right) \right) \quad (2.54)$$

$$L_{y,z} = \frac{1 - L_x}{2} \quad (2.55)$$

It should be emphasised that the above equations are approximate calculation, which is based on the electromagnetic interactions on the dipolar model situated at the centres of each particle, other kinds of excitations like quadrupole, octupole effects are ignored. The incident wave and media should also be considered as linear. The subtle relationship between surface charges is still unclear, thus, the exploring of the theory for surface plasmon resonance is crucial in understanding the interaction between photons and electrons.

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