

#### **Solutions**

# A single spherical silver nanoparticle

Volume of the nanoparticle: $V = \frac{4}{3}\pi R^3 = 4.19 \times 10^{-24} \text{ m}^3$ . Mass of the nanoparticle: $M = V \rho_{Ag} = 4.39 \times 10^{-20} \text{ kg}$ . Number of ions in the nanoparticle: $N = N_A \frac{M}{M_{Ag}} = 2.45 \times 10^5$ . Charge density $\rho = \frac{eN}{V} = 9.38 \times 10^9 \text{ Cm}^{-3}$ , charge density $\rho = en$ .	0.7	
Electrons' concentration $n = \frac{N}{V} = 5.85 \times 10^{28} \text{ m}^{-3}$ . Total charge of free electrons $Q = eN = 3.93 \times 10^{-14} \text{ C}$ . Total mass of free electrons $m_0 = m_e N = 2.23 \times 10^{-25} \text{ kg}$ .		
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## The electric field in a charge-neutral region inside a charged sphere

For a sphere with radius *R* and constant charge density  $\rho$ , for any point inside the sphere designated by radius-vector  $\mathbf{r} = r\mathbf{e}_r$  (r < R) Gauss's law yields directly  $4\pi r^2 \varepsilon_0 \mathbf{E}_+ = \frac{4}{3}\pi r^3\rho \,\mathbf{e}_r$ , where  $\mathbf{e}_r$  is the unit radial vector pointing away from the center of the sphere. Thus,  $\mathbf{E}_+ = \frac{\rho}{3\varepsilon_0}\mathbf{r}$ . Likewise, inside another sphere of radius  $R_1$  and charge density  $-\rho$  the field is  $\mathbf{E}_- = \frac{-\rho}{3\varepsilon_0}\mathbf{r}'$ , where  $\mathbf{r}'$  is the radius-vector of the point in the coordinate system with the origin in the center of this sphere. Superposition of the two charge configurations gives the setup we want with  $\mathbf{r}' = \mathbf{r} - \mathbf{x}_d$ . So inside the charge-free region  $|\mathbf{r} - \mathbf{x}_p| < R_1$  the field is  $\mathbf{E} = \mathbf{E}_+ + \mathbf{E}_- = \frac{\rho}{3\varepsilon_0}\mathbf{r} + \frac{-\rho}{3\varepsilon_0}(\mathbf{r} - \mathbf{x}_d)$  or  $\mathbf{E} = \frac{\rho}{3\varepsilon_0}\mathbf{x}_d$  with pre-factor  $A = \frac{1}{3}$ 

## The restoring force on the displaced electron cloud

With  $\mathbf{x}_{p} = x_{p} \, \mathbf{e}_{x}$  and  $x_{p} \ll R$  we have from above that approximately the field induced inside the particle is  $\mathbf{E}_{ind} = \frac{\rho}{3\varepsilon_{0}} \mathbf{x}_{p}$ . The number of electrons on the particle's border that produced  $\mathbf{E}_{ind}$  is negligibly smaller than the number of electrons inside the particle, so  $\mathbf{F} \cong Q\mathbf{E}_{ind} = (-\mathbf{e}N)\frac{\rho}{3\varepsilon_{0}}\mathbf{x}_{p} = -\frac{4\pi}{9\varepsilon_{0}}R^{3}e^{2}n^{2}\mathbf{x}_{p}\mathbf{e}_{x}$  (note the antiparallel attractive force is proportional to the displacement that it is similar to Hooke's law). The work done on the electron cloud to shift it is  $W_{el} = -\int_{0}^{x_{p}}F(x') \, dx' = \frac{1}{2}\left(\frac{4\pi}{9\varepsilon_{0}}R^{3}e^{2}n^{2}\right)x_{p}^{2}$ 

#### The spherical silver nanoparticle in an external constant electric field

	Inside the metallic particle in the steady state the electric field must be equal to 0. The		
2.4	induced field (from 2.2 or 2.3) compensates the external field: $E_0 + E_{ind} = 0$ , so	0.6	



 $x_{\rm p} = \frac{3\varepsilon_0}{\rho} E_0 = \frac{3\varepsilon_0}{en} E_0.$ Charge displaced through the *yz*-plane is the total charge of electrons in the cylinder of radius *R* and height  $x_p: -\Delta Q = -\rho \pi R^2 x_p = -\pi R^2 ne x_p.$ 

### The equivalent capacitance and inductance of the silver nanoparticle

	The electric energy $W_{\rm el}$ of a capacitor with capacitance <i>C</i> holding charges $\pm \Delta Q$ is $W_{\rm el} = \frac{\Delta Q^2}{2C}$ . The energy of such capacitor is equal to the work (see 2.3) done to separate the charges (see 2.4), thus $C = \frac{\Delta Q^2}{2W_{el}} = \frac{9}{4} \varepsilon_0 \pi R = 6.26 \times 10^{-19} \mathrm{F.}$	0.7
2.5b	Equivalent scheme for a capacitor reads: $\Delta Q = CV_0$ . Combining charge from (2.4) and capacitance from (2.5a) gives $V_0 = \frac{\Delta Q}{c} = \frac{4}{3}R E_0$ .	0.4

2.6a	The kinetic energy of the electron cloud is defined as the kinetic energy of one electron multiplied by the number of electrons in the cloud $W_{\text{kin}} = \frac{1}{2}m_ev^2N = \frac{1}{2}m_ev^2\left(\frac{4}{3}\pi R^3 n\right)$ . The current <i>I</i> is the charge of electrons in the cylinder of area $\pi R^2$ and height $v\Delta t$ divided by time $\Delta t$ (or simply the time derivative of charge $-\Delta Q$ ), thus $I = -e nv \pi R^2$ .	0.7
2.6b	The energy carried by current <i>I</i> in the equivalent circuit with inductance <i>L</i> is $W = \frac{1}{2}LI^2$ is, in fact, the kinetic energy of electrons $W_{\text{kin}}$ . Taking the energy and current from (2.6a) gives $L = \frac{4 m_e}{3\pi Rne^2} = 2.57 \times 10^{-14} \text{ H.}$	0.5

#### The plasmon resonance of the silver nanoparticle

2.7aFrom the LC-circuit analogy we can directly derive  $\omega_p = (LC)^{-1/2} = \sqrt{ne^2/3\varepsilon_0 m_e}$ .<br/>Alternatively it is possible to use the harmonic law of motion in (2.3) and get the same<br/>result for the frequency.0.52.7b $\omega_p = 7.88 \times 10^{15}$  rad/s, for light with angular frequency  $\omega = \omega_p$  the wavelength is<br/> $\lambda_p = 2\pi c/\omega_p = 239$  nm.0.4

## The silver nanoparticle illuminated with light at the plasmon frequency

The velocity of an electron  $v = \frac{dx}{dt} = -\omega x_0 \sin \omega t = v_0 \sin \omega t$ . The time-averaged kinetic energy on the electron  $\langle W_k \rangle = \langle \frac{m_e v^2}{2} \rangle = \frac{m_e}{2} \langle v^2 \rangle$ . During time  $\tau$  each electron hits an ion one time. So the energy lost in the whole nanoparticle during time  $\tau$  is  $W_{heat} = N \langle \frac{m_e v^2}{2} \rangle = \frac{4}{3} \pi R^3 n \langle \frac{m_e v^2}{2} \rangle$ . Time-averaged Joule heating power  $P_{heat} = \frac{1}{\tau} W_{kin} = \frac{1}{2\tau} m_e \langle v^2 \rangle \left(\frac{4}{3} \pi R^3 n\right)$ . The expression for current is taken from (2.6a), squared and averaged



$$\langle I^2 \rangle = (en \, \pi R^2)^2 \, \langle v^2 \rangle = \left(\frac{3Q}{4R}\right)^2 \langle v^2 \rangle.$$

The average time between the collisions is  $\tau \gg 1/\omega_{\rm p}$ , so each electron oscillates many times before it collides with an ion. The oscillating current  $I = I_0 \sin \omega t = \pi R^2 n e v_0 \sin \omega t$  produces the heat in the resistance  $R_{heat}$  equal to  $P_{heat} = R_{heat} \langle I^2 \rangle$ , that together with results from (2.8a) leads to  $R_{heat} = \frac{W_{\rm kin}}{\tau \langle I^2 \rangle} = \frac{2m_e}{3\pi n e^2 R \tau} = 2.46 \Omega$ .

For equivalent scattering resistance  $R_{\text{scat}} = \frac{P_{\text{scat}}}{\langle I^2 \rangle}$  and for harmonic oscillations we can average the velocity squared over one period of oscillations, so  $\langle v^2 \rangle = \frac{1}{2} \omega_p^2 x_0^2$ . 1.0 Together it yields  $R_{\text{scat}} = \frac{Q^2 x_0^2 \omega_p^4}{12\pi\epsilon_0 c^3} \frac{16R^2}{9Q^2 \langle v^2 \rangle} = \frac{8\omega_0^2 R^2}{27\pi\epsilon_0 c^3} = 2.45 \,\Omega.$ 

		Ohm's law for a <i>LCR</i> serious circuit is $I_0 = \frac{V_0}{\sqrt{(R_{heat} + R_{scat})^2 + (\omega L - \frac{1}{\omega C})^2}}$ . At the resonance		
		frequency time-averaged voltage squared is $\langle V^2 \rangle = Z_R^2 \langle I^2 \rangle = (R_{\text{heat}} + R_{\text{scat}})^2 \langle I^2 \rangle$ .		
2.	.10a	And from (2.5b) $\langle V^2 \rangle = \frac{1}{2}V_0^2 = \frac{8}{9}R^2E_0^2$ , so Ohm's law results in $\langle I^2 \rangle = \frac{8R^2E_0^2}{9(R_{heat}+R_{scat})^2}$ .	1.2	
		The time-averaged power losses are $P_{\text{heat}} = R_{\text{heat}} \langle I^2 \rangle = \frac{8R_{\text{heat}}R^2}{9(R_{\text{heat}} + R_{\text{scat}})^2} E_0^2$ and		
		$P_{\text{scat}} = \frac{8R_{\text{scat}}R^2}{9(R_{\text{heat}} + R_{\text{scat}})^2} E_0^2 = \frac{R_{\text{scat}}}{R_{\text{heat}}} \langle P_{\text{heat}} \rangle.$		
2.	.10b	Starting with the electric field amplitude $E_0 = \sqrt{2S/(\varepsilon_0 c)} = 27.4 \text{ kV/m}$ , we calculate $P_{\text{heat}} = 6.82 \text{ nW}$ and $P_{\text{scat}} = 6.81 \text{ nW}$ .	0.3	

#### Steam generation by light

2.11a	Total number of nanoparticles in the vessel: $N_{\rm np} = h^2 a n_{\rm np} = 7.3 \times 10^{11}$ . Then the total time-averaged Joule heating power: $P_{\rm st} = N_{\rm np}P_{\rm heat} = 4.98$ kW. This power goes into the steam generation: $P_{\rm st} = \mu_{\rm st}L_{\rm tot}$ , with $L_{\rm tot} = c_{\rm wa}(T_{100} - T_{\rm wa}) + L_{\rm wa} + c_{\rm st}(T_{\rm st} - T_{100}) = 2.62 \times 10^6$ J kg <sup>-1</sup> . Thus the mass of steam produced in one second is: $\mu_{\rm st} = \frac{P_{\rm st}}{L_{\rm tot}} = 1.90 \times 10^{-3}$ kg s <sup>-1</sup> .	0.6
2.11h	The power of light incident on the vessel $P_{tot} = h^2 S = 0.01 \text{m}^2 \times 1 \text{ MW m}^{-2} = 10.0 \text{ kW}$ , and the power directed for steam production by nanoparticles is given in 2.11a. Efficiency of the process is $\eta = \frac{P_{st}}{P_{tot}} = \frac{4.98 \text{ kW}}{10.0 \text{ kW}} = 0.498$ .	0.2

Total