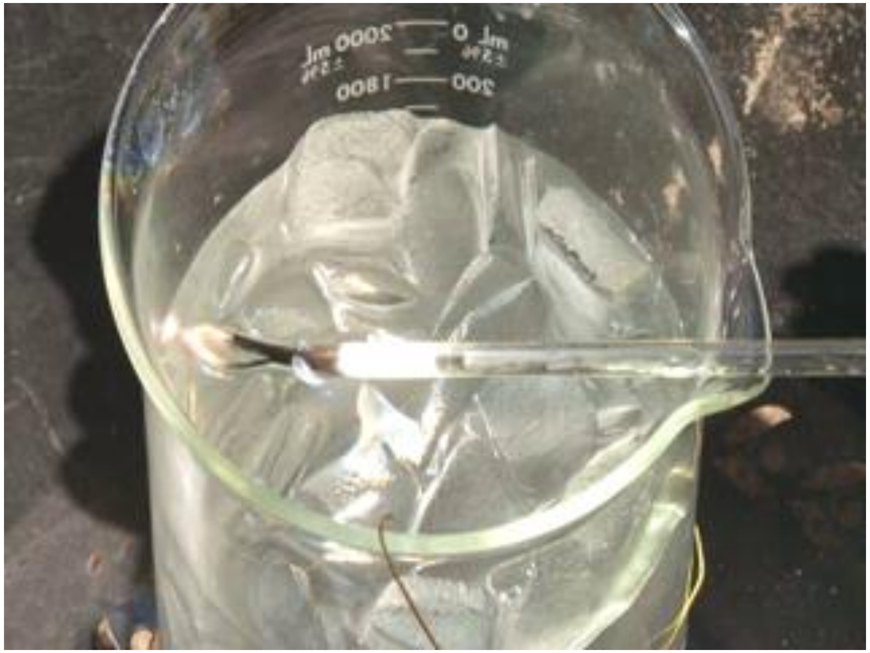
IPhO 44th Copenhagen Denmark 7-15 July 2013

Presentation of problem T2 (12 points): Plasmonic Steam Generator



Plasmonic Steam Generator

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Solar Vapor Generation Enabled by Nanoparticles

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Evolution of Light-Induced Vapor Generation at a Liquid-Immersed Metallic Nanoparticle

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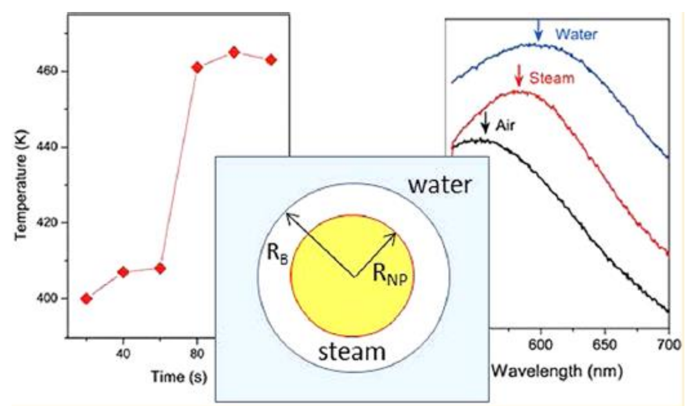
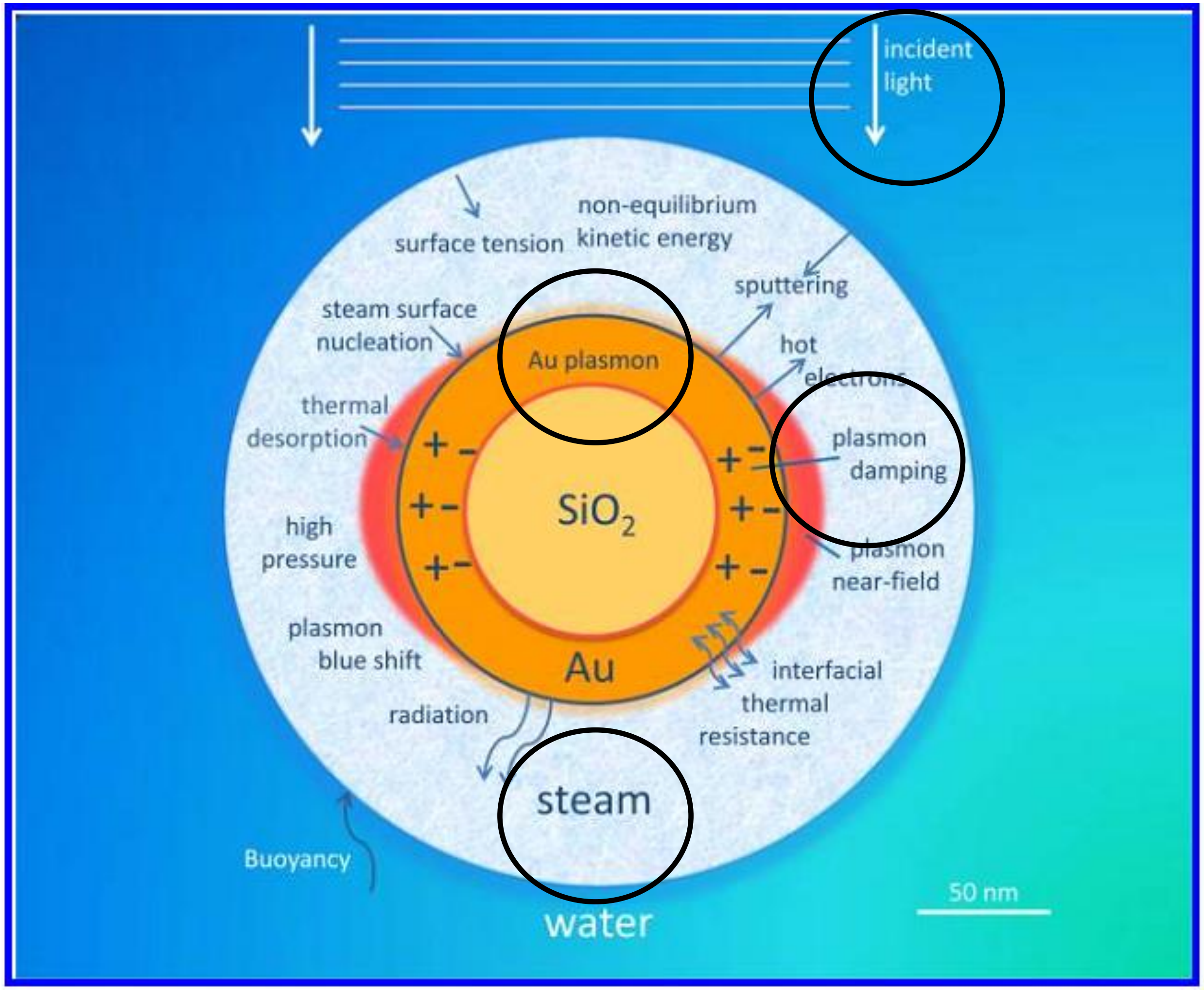
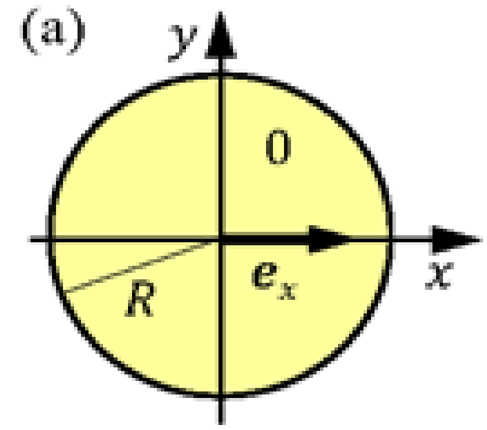



incident
light
non-equilibrium
kinetic energy
surface tension
sputtering
steam surface
nucleation
Au plasmon
hot
electrons
thermal
desorption
plasmon
damping
SiO_2
high
pressure
plasmon
near-field
plasmon
blue shift
Au
interfacial
thermal
resistance
radiation
steam
Buoyancy
50 nm
water

Step 1:
A single spherical silver nanoparticle

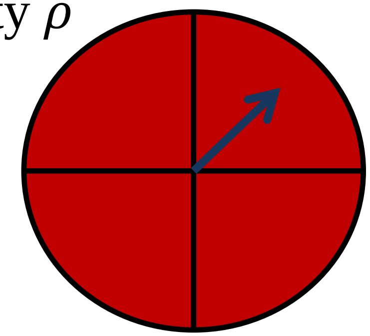
- Silver nanoparticle, R = 10 nm
- Fixed in the origin of the coordinate system
- Electrically neutral (yellowish)
- Simple model: one free (conducting) electron escapes from each atom
- Each atom becomes a positive ion



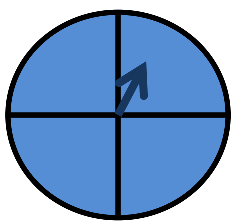
Find: The volume V and mass M of the nanoparticle, the number N and charge density ρ of silver ions in the particle, and for the free electrons their concentration n, their total charge Q, and their total mass m_0.

Step 2: Electric field in a charge-neutral region inside a charged sphere

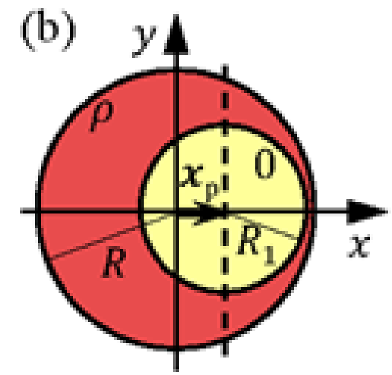
- There is a uniformly charged sphere (R) with charge density ρ
- Field **inside** such sphere (Gauss's theorem) $\boldsymbol{E}_+ = \frac{\rho}{3\varepsilon_0}\boldsymbol{r}$



- Field inside another sphere ($R_1<R$) (Gauss's theorem)



$$\boldsymbol{E}_- = \frac{-\rho}{3\varepsilon_0}\boldsymbol{r}'$$



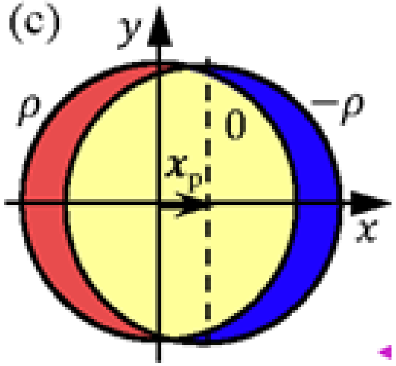
- Superimpose them displacing the blue one from the origin by $\boldsymbol{x}_\mathrm{p} = x_\mathrm{p}\,\boldsymbol{e}_x$

$$\boldsymbol{E}_- = \frac{-\rho}{3\varepsilon_0}(\boldsymbol{r} - \boldsymbol{x}_\mathrm{p})$$

$$\boldsymbol{E} = \boldsymbol{E}_+ + \boldsymbol{E}_- = \frac{\rho}{3\varepsilon_0}\boldsymbol{x}_\mathrm{p}$$

Step 3: The restoring force on the displaced electron cloud

- Electrons form an electron cloud (collective motion of all particles)
- Motionless sphere (R=10 nm) uniformly positively charged ρ (**red**)
- Electron cloud (R=10 nm) uniformly negatively charged - ρ (**blue**)
- **External force** $\boldsymbol{F}_{\text{ext}}$ moves the electron cloud in new equilibrium
- Consider charged regions infinitesimally small ($|x_{\text{p}}| \ll R$, $R_1 \to R$)



Field **inside** the particle $\boldsymbol{E}_{\text{ind}} = \frac{\rho}{3\varepsilon_0} x_{\text{p}}\, \boldsymbol{e}_x$

The number of electrons that produced $\boldsymbol{E}_{\text{ind}}$ is negligibly smaller than the number of electrons inside the particle $\boldsymbol{F} = Q\boldsymbol{E}_{\text{ind}} = (-eN)\frac{\rho}{3\varepsilon_0} x_{\text{p}}\, \boldsymbol{e}_x = -\frac{4\pi}{9\varepsilon_0} R^3 e^2 n^2 \boldsymbol{x}_{\text{p}}$

It is a restoration force similar to that appearing in any harmonic oscilator (mass on spring, LC-circuit, etc.)

Work done by the force $\boldsymbol{F}_{\text{ext}} \sim x_{\text{p}}\, \boldsymbol{e}_x$ on distance x_{p}

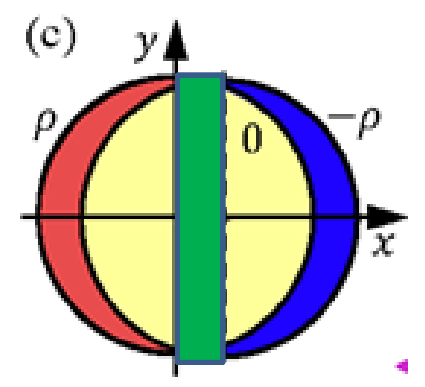
Step 4: The spherical silver nanoparticle in an external constant electric field

- Static homogeneous electric field is applied
- External force $\boldsymbol{F}_{\mathrm{ext}}$ displaces the electron cloud by small distance $|x_{\mathrm{p}}| \ll R$
- Displacement stops when $\boldsymbol{E}_0 + \boldsymbol{E}_{\mathrm{ind}} = 0$ inside the particle
- Find the displacement x_{p} of the electron cloud in terms of E_0

Determine the amount $-\Delta Q$ of electron charge displaced through the *yz*-plane at the center of the nanoparticle

It is the charge in the green box

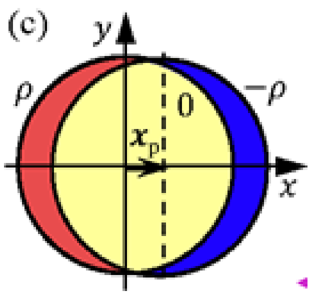
$$-\Delta Q = -\rho\, \pi R^2 x_{\mathrm{p}} = -\pi R^2\, ne\, x_{\mathrm{p}}$$

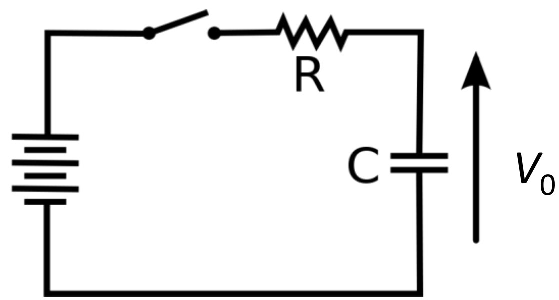


$$\boldsymbol{E}_0 = -E_0 \boldsymbol{e}_x$$

Step 5: The equivalent capacitance of the silver nanoparticle

- **The nanoparticle can be modeled as an equivalent electric circuit** !!!
- It includes an equivalent capacitor, equivalent inductor and equivalent resistors
- As a capacitor it has separated charges $\pm\Delta Q$
- It accumulates the energy due to the work done the external field $W_{\mathrm{el}} = \frac{\Delta Q^2}{2C}$



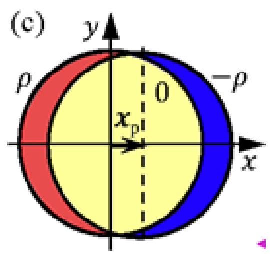


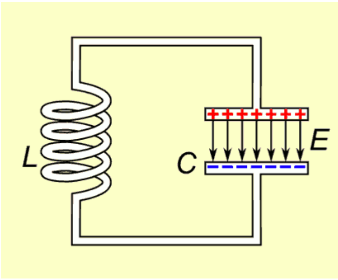
Equivalent capacitance of the nanoparticle $C = \frac{9}{4}\varepsilon_0 \pi R = 6.26 \times 10^{-19}$ F

The capacitor is under the voltage $V_0 = \frac{\Delta Q}{C} = \frac{4}{3} R E_0$

Step 6: The equivalent inductance of the silver nanoparticle

- In an alternative external field the **whole** electronic cloud moves with some velocity and therefore has a kinetic energy W_{kin}
- There is an electric current I in the central yz-plane of the particle





By combining $W_{\mathrm{kin}} = \frac{1}{2} m_e v^2 N$ and $I = -e\, nv\, \pi R^2$, the inductive properties of the nanoparticle can be modeled by an equivalent inductor with inductance $L = \frac{4\, m_e}{3\pi R n e^2} = 2.57 \times 10^{-14}$ H

Step 7: The plasmon resonance of the silver nanoparticle

The motion of the electron cloud displaced from the equilibrium and released can be modeled as oscillations of an ideal LC-circuit.

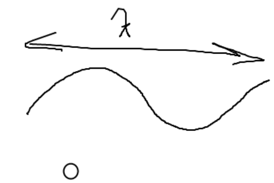
The resonance frequency of a LC-circuit is $\omega_{\mathrm{p}} = \frac{1}{\sqrt{LC}} = \sqrt{\frac{ne^2}{3\varepsilon_0 m_e}}$

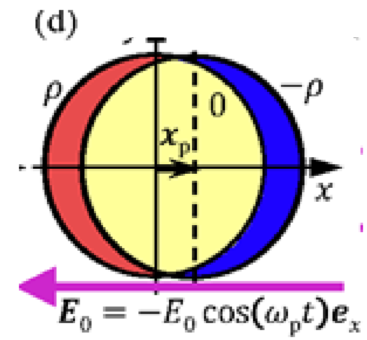
It is exactly $\omega_{pl}/\sqrt{3}$ - the resonance frequency of the **plasmon resonance** in a spherical nanoparticle known in plasmonics!!!!

$\omega_{\mathrm{p}} = 7.88 \times 10^{15}$ rad/s, $\lambda_{\mathrm{p}} = 2\pi c/\omega_{\mathrm{p}} = 239$ nm

Step 8: The nanoparticle illuminated with light at the plasmon frequency

- The nanoparticle is illuminated by monochromatic light with plasmon resonance frequency ω_p
- As the wavelength $\lambda_\mathrm{p} \gg R$, the nanoparticle is effectively placed in a homogeneous oscillating field $\boldsymbol{E}_0 = -E_0 \cos(\omega_\mathrm{p} t)\, \boldsymbol{e}_x$.
- the electron cloud oscillates at frequency ω_p with velocity $\boldsymbol{v} = \mathrm{d}\boldsymbol{x}_\mathrm{p}/\mathrm{d}t$ and constant amplitude x_0.





Plasmon oscillations lead to absorption of light. The energy captured by the particle

↓ Joule heating

↓ re-emitted by the particle as scattered light

Step 8: Joule losses in the nanoparticle

- **Joule heating** is caused by random **inelastic** collisions, where any free electron once in a while hits a silver ion and loses **all** its kinetic energy, which is converted into vibrations of the silver ions (heat).

The average time between collisions $\tau = 5.24 \times 10^{-15}$ s $\gg 1/\omega_\mathrm{p}$ in a silver nanoparticle is much higher than for bulk silver

The time-averaged kinetic energy of electrons can be introduced

$$\langle P_\mathrm{heat} \rangle = \frac{1}{\tau} W_\mathrm{kin} = \frac{1}{2\tau} m_e \langle v^2 \rangle \left(\frac{4}{3} \pi R^3 \, n \right)$$

Such power of the energy dissipation is equavalent to

$$R_\mathrm{heat} = \frac{W_\mathrm{kin}}{\tau I^2} = \frac{2 m_e}{3 \pi n e^2 R \tau} = 2.46\ \Omega$$

Step 9: Scattering losses of the nanoparticle

- A nanoparticle is a **nanoantenna**, which scatters light (by re-emission).
- It is difficult to derive the formula for **the scattering power** P_{scat} of the nanoparticle.
- But it is an important part of losses and must be taken into account!
- We ask for the dimension analysis to find the exact expression

$$P_{\text{scat}} = \frac{Q^2 x_0^2 \omega_{\text{p}}^4}{12\pi\varepsilon_0 c^3}$$

Equivalent resistor for scattering losses

$$R_{\text{scat}} = \frac{\langle P_{\text{scat}} \rangle}{\langle I^2 \rangle} = \frac{Q^2 x_0^2 \omega_{\text{p}}^4}{12\pi\varepsilon_0 c^3} \frac{16R^2}{9Q^2 \langle v^2 \rangle} = \frac{8\omega_0^2 R^2}{27\pi\varepsilon_0 c^3} = 2.45\ \Omega$$

Step 10: Equivalent LCR-model

- The LCR equivalent scheme with L, C, R_{heat} and R_{scat}
- Ohm's law $I_0 = \frac{V_0}{\sqrt{(R_{heat}+R_{scat})^2+\left(\omega L-\frac{1}{\omega C}\right)^2}}$

In the resonance $\langle V^2\rangle = (R_{heat} + R_{scat})^2\langle I^2\rangle$

But $\langle V^2\rangle = \frac{1}{2}V_0^2 = \frac{8}{9}R^2E_0^2$, where V_0 comes from the equivalent capacitor model

$$\langle I^2\rangle = \frac{8R^2E_0^2}{9(R_{heat} + R_{scat})^2}$$

$$\langle P_{heat}\rangle = R_{heat}\langle I^2\rangle = \frac{8R_{heat}R^2}{9(R_{heat} + R_{scat})^2}E_0^2 \quad \langle P_{scat}\rangle = R_{scat}\langle I^2\rangle = \frac{8R_{scat}R^2}{9(R_{heat} + R_{scat})^2}E_0^2$$

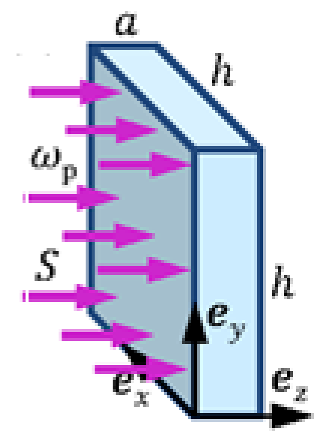
$E_0 = \sqrt{2S/(\varepsilon_0 c)} = 27.4\ \mathrm{kV/m}$ $\quad\langle P_{heat}\rangle = 6.82\ \mathrm{nW}$ $\quad\langle P_{scat}\rangle = 6.81\ \mathrm{nW}$

Step 11: Plasmons versus photons

- Plasmon oscillations are fast ($\omega_p = 7.88 \times 10^{15}$ rad/s is equivalent to UV light)
- Period of one plasmon oscillation $t_p = 2\pi/\omega_p$= 0.8 fs
- Energy of one photon in UV is high $E_p = \hbar\omega_p$= 8.3 10^{-19} J
- Time interval to emit one photon with source of $\langle P_{scat} \rangle = 6.81$ nW is 0.12 ns
- Number of plasmon oscillations is $N_{osc} \approx 1.5 \times 10^5$

Step 12: **Steam generation by light**

- A nanoparticle is heated by light with P_{heat} power. Its temperature grows and heat transfer to surrounding water begins
- When the nanoparticle is illuminated with resonant light of sufficient intensity, a "nanobubble" of vapor, surrounding the particle, is formed. This is the nanoscale liquid boiling, occurring at a single nanoparticle nucleation site
- In steady state all Joule heating of the nanoparticle goes to the production of steam
- The temperature of water is $T_{\text{wa}} = 20\ ^\circ\text{C}$ (constant) and temperature of released steam $T_{\text{st}} = 110\ ^\circ\text{C}$ (constant)
- Concentration of particles is too low, so reabsorption of scatterred light and screening effect is neglected



Step 12: Steam generation by light

- Total number of nanoparticles: $N_{\text{np}} = h^2 a\, n_{\text{np}} = 7.3 \times 10^{11}$. Total power of Joule heating: $P_{\text{st}} = N_{\text{np}} P_{\text{heat}} = 4.98$ kW!!!

- This power every second heats up mass of steam μ_{st}: $P_{\text{st}} = \mu_{\text{st}} L_{\text{tot}}$, where
$$L_{\text{tot}} = c_{\text{wa}}(T_{100} - T_{\text{wa}}) + L_{\text{wa}} + c_{\text{st}}(T_{\text{st}} - T_{100}) = 2.62 \times 10^6 \text{ J kg}^{-1}.$$

- Thus $\mu_{\text{st}} = \frac{P_{\text{st}}}{L_{\text{tot}}} = 1.90 \times 10^{-3} \text{ kg s}^{-1}$.

$$P_{\text{tot}} = h^2 S = 0.01\text{m}^2 \times 1 \text{ MW m}^{-2} = 10.0 \text{ kW},$$

$$\text{So } \eta = \frac{P_{\text{st}}}{P_{\text{tot}}} = \frac{4.98 \text{ kW}}{10.0 \text{ kW}} = 0.498$$

The IPhO syllabus in relation to the problem

Problem	Syllabus
2.1 A single spherical silver nanoparticle	2. b) Avogadro's number
2.2 The electric field in a charge-neutral region inside a charged sphere	6. b) Electric field, potential, Gauss' law , Gauss' law confined to simple symmetric systems like sphere, cylinder, plate etc
2.3 The restoring force on the displaced electron cloud	6. b) Electric field; 1. c) Closed and open systems, momentum and energy, work, power; 5. a) Harmonic oscillations
2.4 The spherical silver nanoparticle in an external constant electric field	6. a) Conservation of charge
2.5a The equivalent capacitance	6. c) Capacitors, capacitance
2.5b The equivalent voltage	6. c) Capacitors, capacitance
2.6a Express both W_{kin} and I in terms of the velocity v.	2.
2.6b The equivalent inductance	7. d) Law of electromagnetic induction, inductance

The IPhO syllabus in relation to the problem

Problem	Syllabus
2.7a, 2.7b Find an expression for the angular plasmon frequency; Calculate the frequency	8. a) Oscillatory circuit, frequency of oscillations; 8. d) Electromagnetic waves
2.8a Time-averaged Joule heating power	6. b)
2.8b Equivalent ohmic resistance	6. b)
2.9a Time-averaged scattering power. Dimension analysis	General d) (SI units)
2.9b Equivalent ohmic resistance	6.
2.10a, 2.10b Time-averaged power losses	7. e) Alternating current, resistors, inductors and capacitors in AC-circuits, voltage and current (parallel and series) resonances
2.11 Plasmon oscillations and photon emission.	9. a) energy and impulse of the photon
2.12a, 2.12b Steam production and generator efficiency	2. a) Internal energy, work and heat, first and second laws of thermodynamics. Thermal equilibrium, quantities depending on state and quantities depending on process

Syllabus check

1. Mechanics

- a) Vector description of the position of the point mass, velocity and acceleration as vectors
- c) Closed and open systems, momentum and energy, work, power

2. Thermodynamics and Molecular Physics

- a) Internal energy, work and heat, first and second laws of thermodynamics. Thermal equilibrium, quantities depending on state and quantities depending on process
- b) Avogadro's number. Also molecular approach to such simple phenomena in liquids and solids as boiling, melting etc.

5. Oscillations and waves

- a) Harmonic oscillations, equation of harmonic oscillation. Solution of the equation for harmonic motion, attenuation and resonance -qualitatively
- b) Harmonic waves, propagation of waves, transverse and longitudinal waves, linear polarization. Displacement in a progressive wave and understanding of graphical representation of the wave, propagation of waves in homogeneous and isotropic media
- c) Realization that intensity of wave is proportional to the square of its amplitude.

6. Electric Charge and Electric Field

- a) Conservation of charge, Coulomb's law
- b) Electric field, potential, Gauss' law Gauss' law confined to simple symmetric systems like sphere, cylinder, plate etc., electric dipole moment
- c) Capacitors, capacitance, dielectric constant, energy density of electric field

Syllabus check

7. Current and Magnetic Field

- a) Current, resistance, internal resistance of source, Ohm's law, Kirchhoff's laws, work and power of direct and alternating currents, Joule's law . Simple cases of circuits containing non-ohmic devices with known V-I characteristics
- d) Law of electromagnetic induction, magnetic flux, Lenz's law, self-induction, inductance, permeability, energy density of magnetic field
- e) Alternating current, resistors, inductors and capacitors in AC-circuits, voltage and current (parallel and series) resonances Simple AC-circuits, time constants, final formulae for parameters of concrete resonance circuits are not required

8. Electromagnetic waves

- a) Oscillatory circuit, frequency of oscillations, generation by feedback and resonance
- d) Electromagnetic waves as transverse waves, polarization by reflection, polarizers

9. Quantum Physics

- a) Photoelectric effect, energy and impulse of the photon. Einstein's formula is required