united nations educational, scientific and cultural organization

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the **abdus salam** international centre for theoretical physics

SMR/1238-26

ADRIATICO RESEARCH CONFERENCE on

LASERS IN SURFACE SCIENCE

11-15 September 2000

Miramare - Trieste, Italy

Second harmonic generation from spherical particles

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Second harmonic generation from spherical particles

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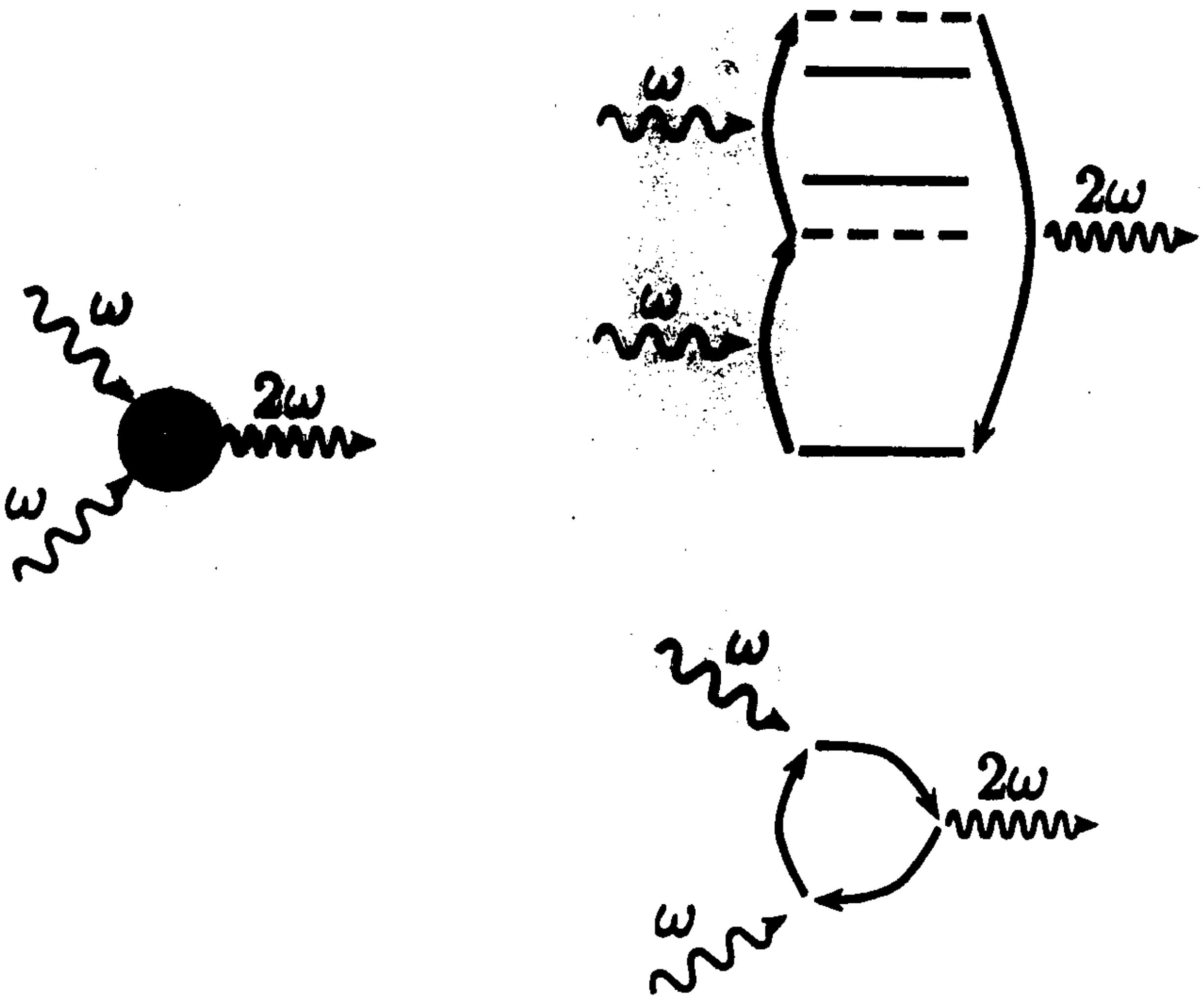
SHG

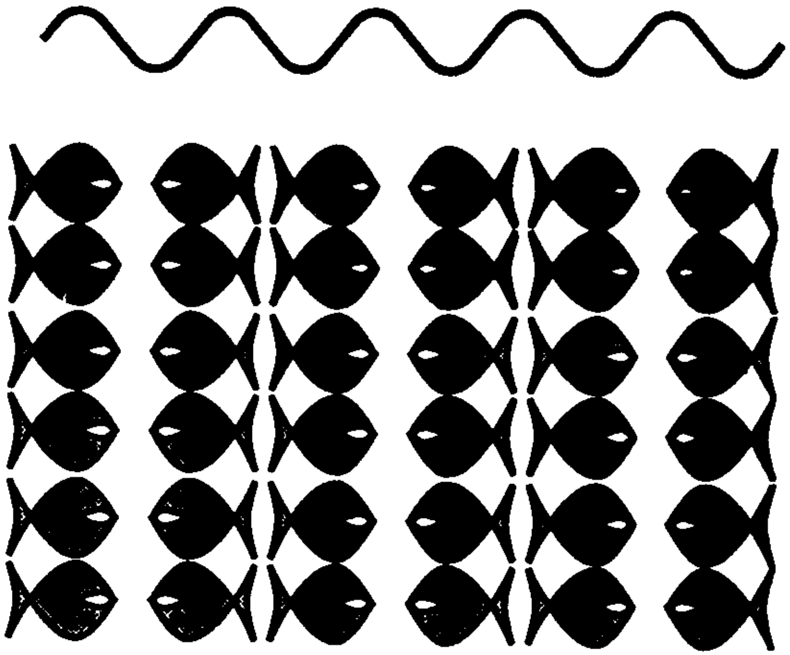


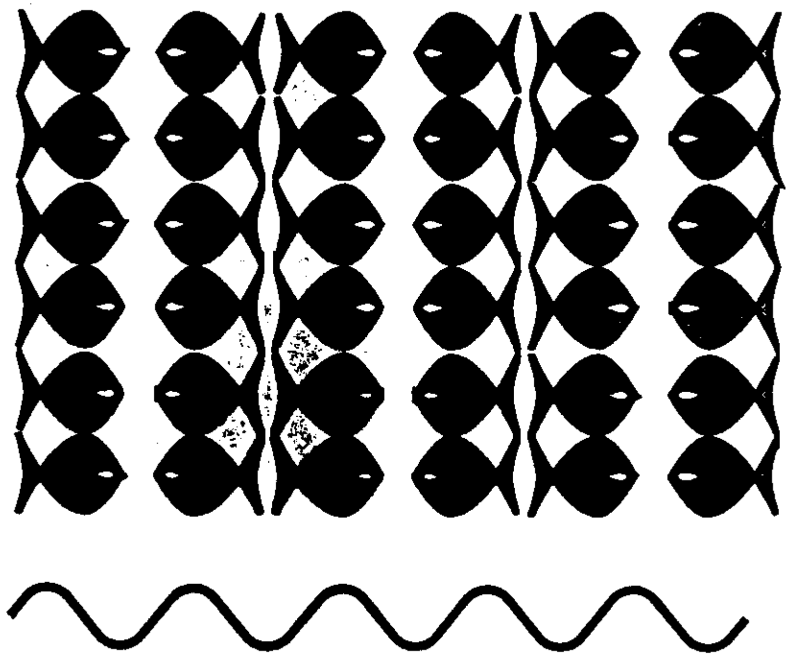
SHG and Symmetry

$$\vec{P}(2\omega) = \chi^{(2\omega)}\vec{E}\vec{E}$$
$$(-\vec{P}(2\omega)) = \chi^{(2\omega)}(-\vec{E})(-\vec{E})$$

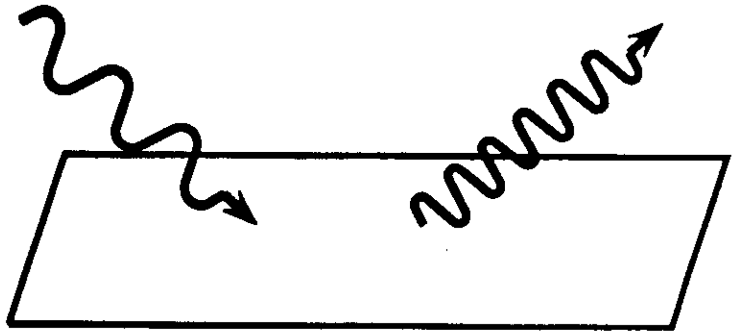
$$\text{Centrosymmetry} \longrightarrow \chi^{(2\omega)} \text{ is invariant}$$
$$\longrightarrow \chi^{(2\omega)} = 0$$

Surfaces are not



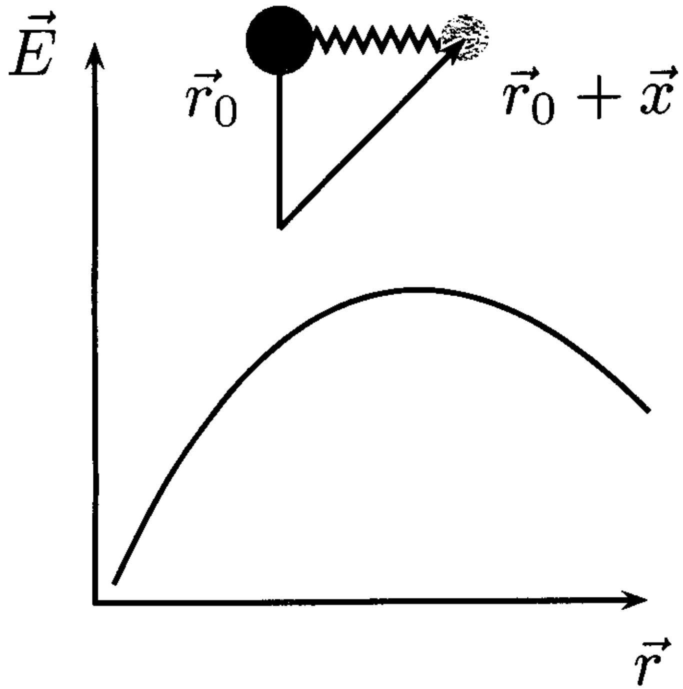


centrosymmetric!



From linear to nonlinear response

Non linear response of harmonic oscillator



$$\vec{F} = -e\vec{E}(\vec{r}_0 + \vec{x})$$

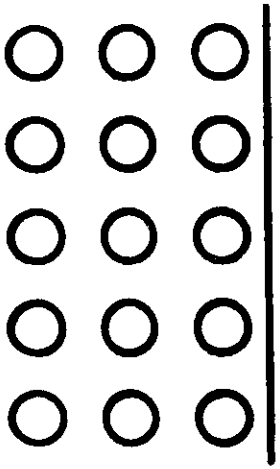
$$\begin{aligned} m\ddot{\vec{x}} &= -m\omega_0^2\vec{x} - e\vec{E}(\vec{r}_0) \\ &\quad -e\vec{x}\cdot\nabla\vec{E}(\vec{r}_0) - e\frac{\dot{\vec{x}}}{c}\times\vec{B}(\vec{r}_0) \end{aligned}$$

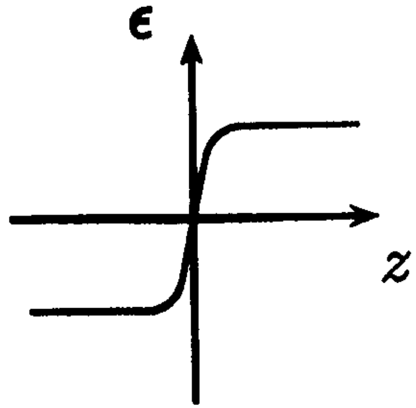
(parametric oscillator)

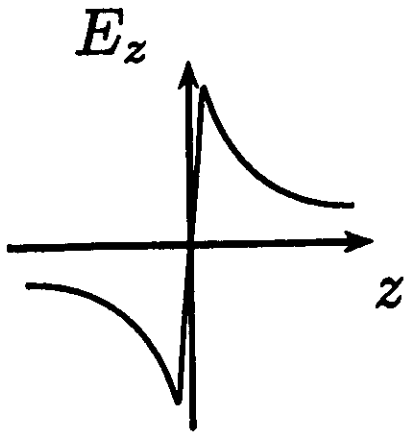
Dipolium

Single molecule $\vec{p}_{2\omega} = -\frac{1}{2e}\alpha(\omega)\alpha(2\omega)\nabla E_\omega^2$

Solid







B. Mendoza and W.L. Mochán PRB 53 4999 (96)

$$\vec{P}^i_{2\omega} = (\chi_s)^{ijk} E_j E_k$$

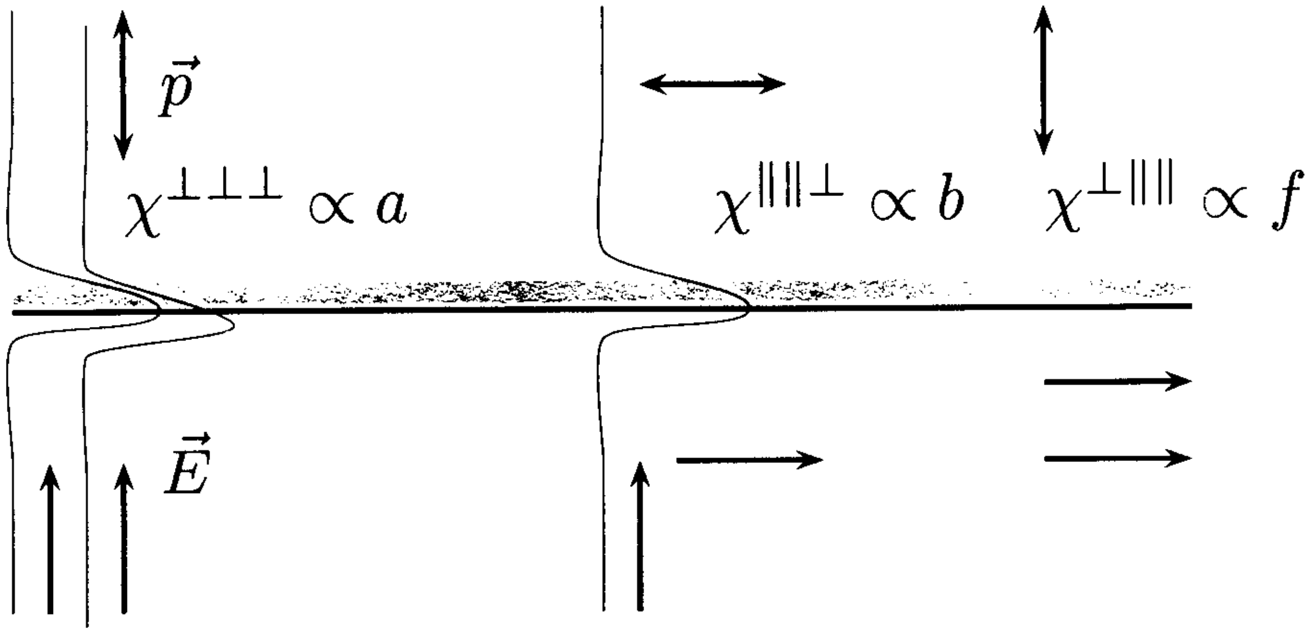
a: ⊥ ← ⊥⊥

b: ∥ ← ∥⊥

f: ⊥ ← ∥∥

$$(\chi_s)^{ijk} = (\chi_s)^{ijk}[a, b, f]$$

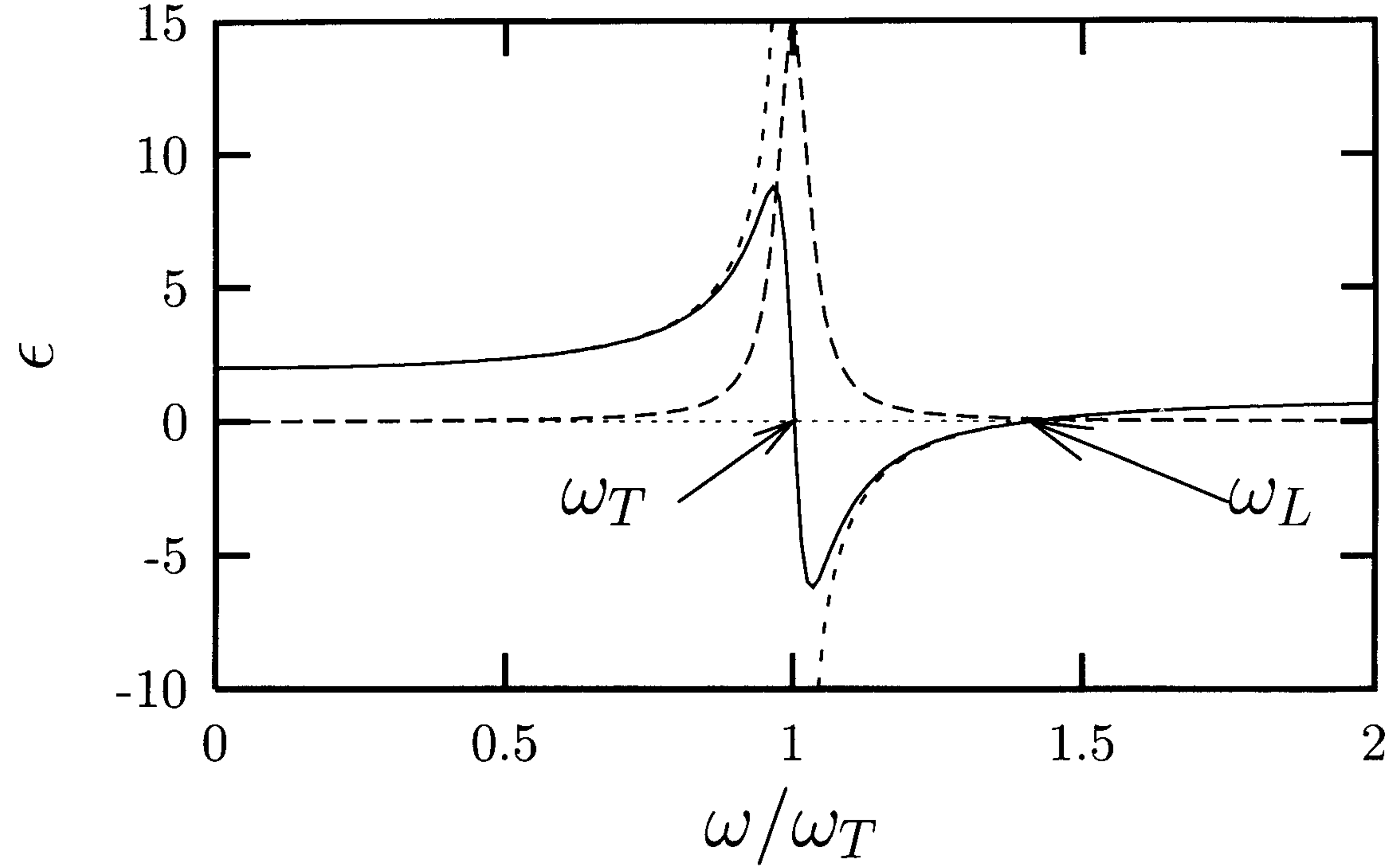
Flat surface



$$p_i = \chi^{ijk} E^i E^k$$

Bulk

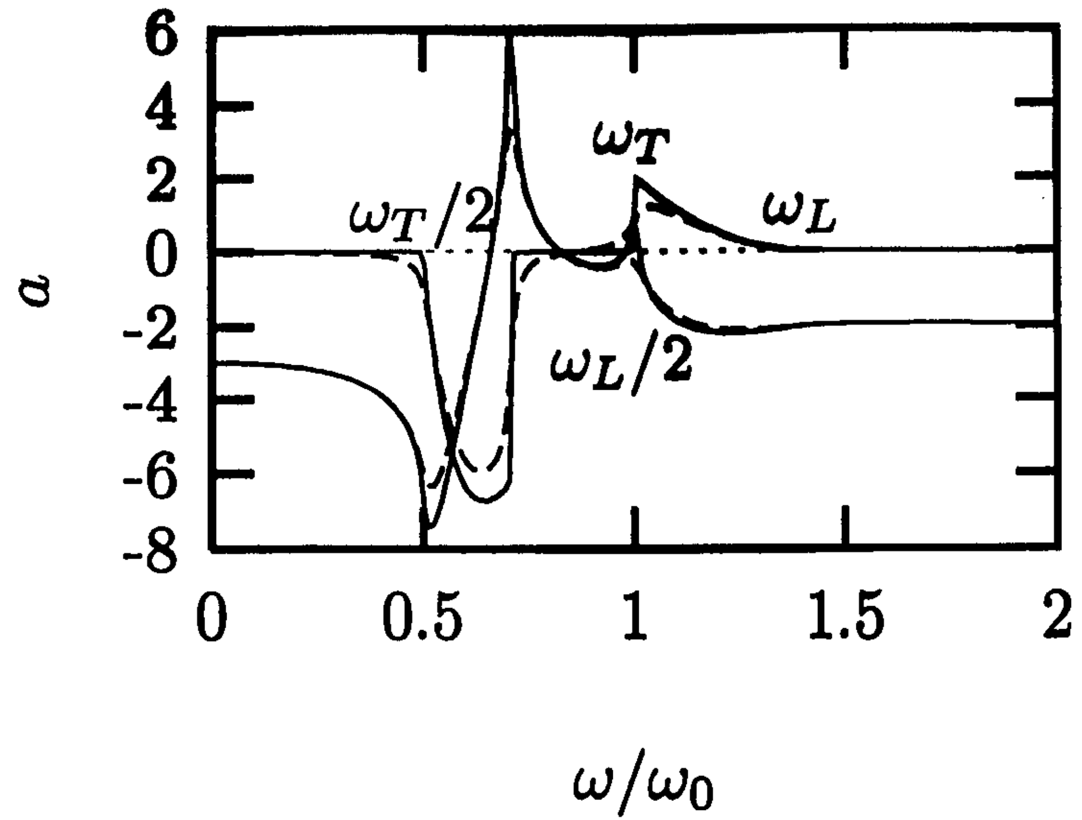
$$\vec{p} \propto \nabla E^2, \vec{E} \times \vec{B}$$



15
10
5
0
-5
-10
ϵ
ω_T
ω_L
0
0.5
1
1.5
2
ω/ω_T

$$\epsilon = \frac{\omega_L^2 - \omega^2 - i\omega/\tau}{\omega_T^2 - \omega^2 - i\omega/\tau}$$

$$\omega_p = \omega_0,\ \omega_0\tau = 1000,\ 20,\ \omega_L = \sqrt{2}\omega_0$$



Applications:

SHG+SFG+DFG,

semiconductors and metals,

continuous + crystalline,

truncated bulk + surface relaxation,

clean + adsorbate covered,

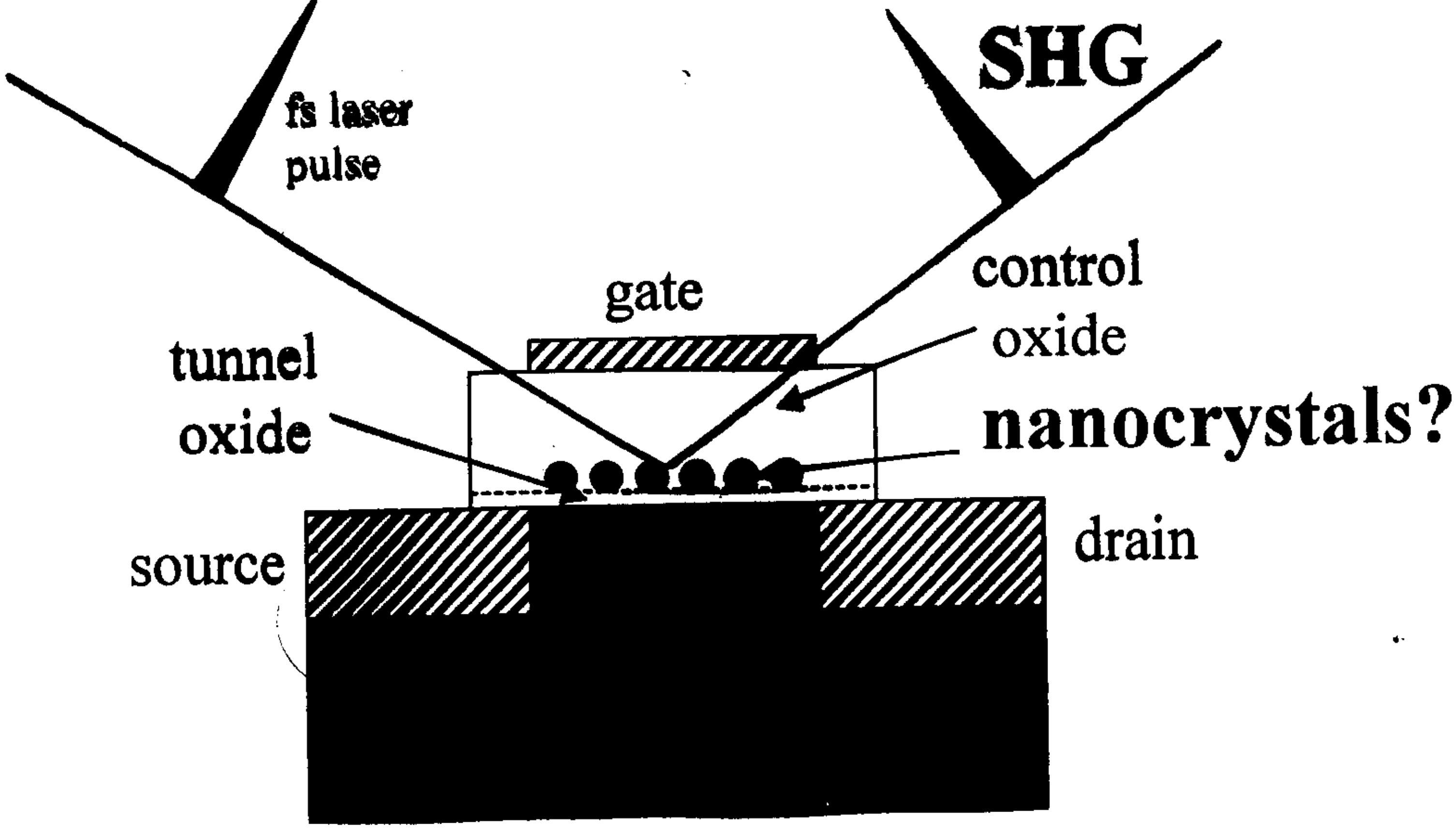
interband + intraband + collective excitations,

magnetism + chirality,

...

Next: 

Nanocrystal technology promises novel device that are challenging to fabricate and characterize



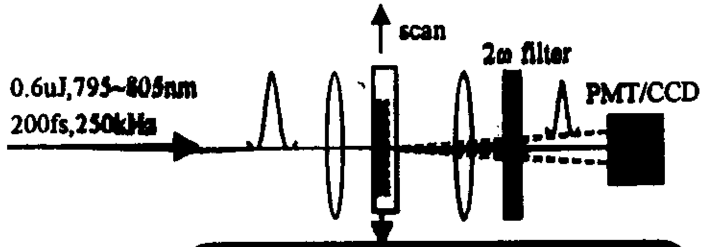
From Tiwari et al.,"A silicon nanocrystal based memory", APL 1996

stolen from M. Downer

30 – 80 um

Transmitted SHG from Si nanocrystals in glass

- experimental setup and scan signal



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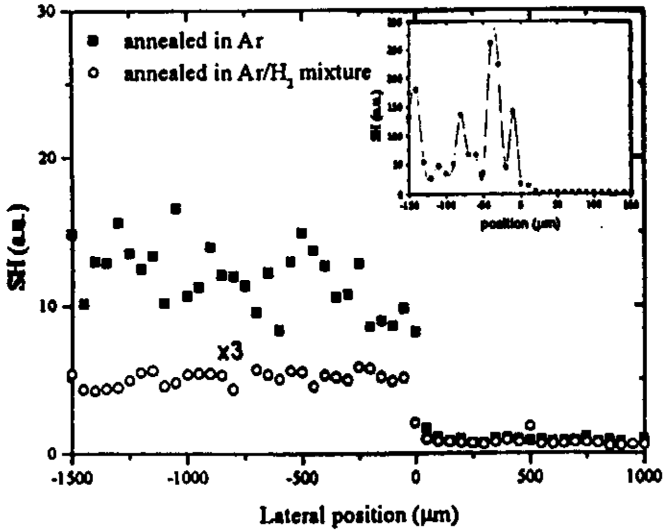

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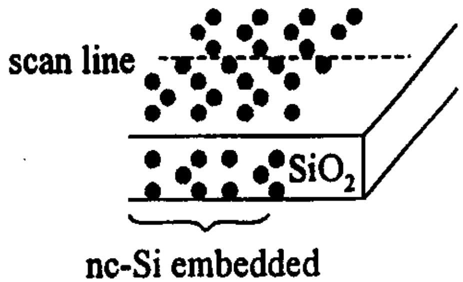
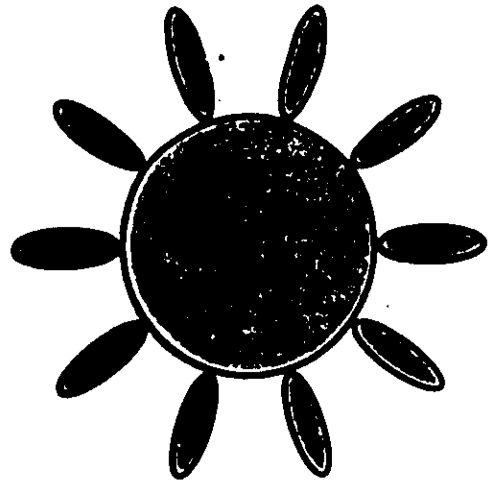


Sphere

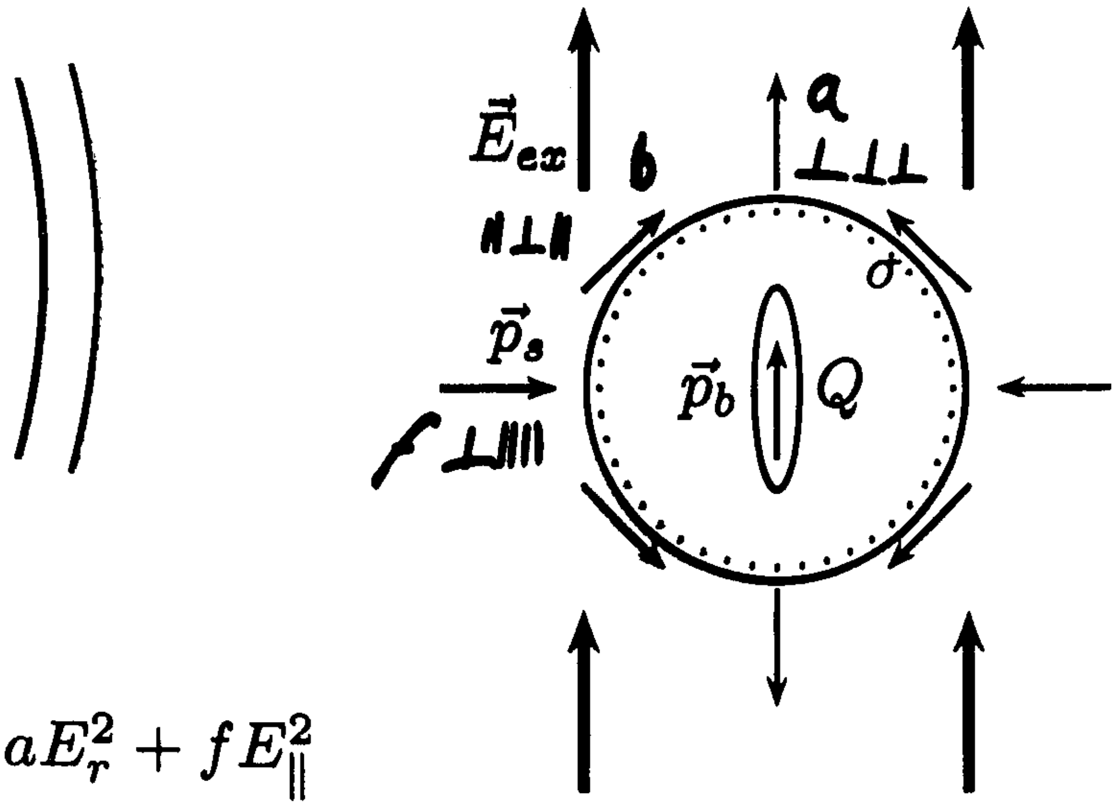


- Östling et al, Z. Phys., D **28**, 169 (93).
- Aktsipetrov et al, Surf. Sci. **325**, 343 (95).
- Wang et al, Chem. Phys. Lett. **259**, 15 (96).
- Antoine et al, J. Appl Phys. **84**, 4532 (98).
- Dadap et al, Phys. Rev. Lett. , (99).

– M. Downer

– T. Heinz

Locally flat sphere



$\vec{E}$ homogeneous $\Longrightarrow \vec{p} = 0$

$$P_r \propto aE_r^2 + fE_\|^2$$

$$P_\| \propto bE_rE_\|$$

Phenomenology

$\vec{E}$ homogeneous $\Rightarrow \vec{p} = 0$.

Then, $\vec{p} \approx \vec{E}, \vec{E}, \nabla, \nabla^2, \ldots$

ρ^{ex}

$\vec{E} \times \vec{B}$

Isotropy

$$\vec{p} = \gamma^d \vec{E} \cdot \nabla \vec{E} + \ldots \vec{E} \nabla \cdot \vec{E} + \ldots \nabla \vec{E} \cdot \vec{E}$$

$$Q^{ij} = \gamma^Q \left(E^i E^j - \frac{1}{3} E^2 \delta^{ij} \right)$$

$\gamma^d(\omega) =?$ $\gamma^Q(\omega) =?$

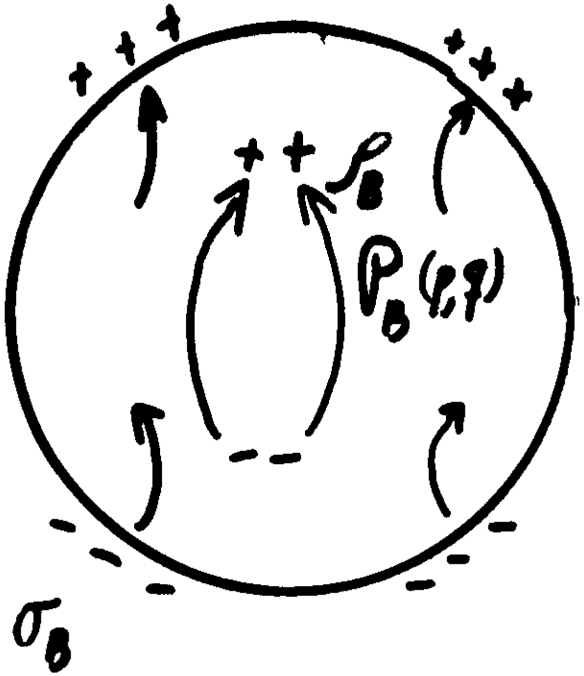
Inhomogeneous field

$$\phi^{\text{ex}} = A_{10} r Y_{10} + A_{20} r^2 Y_{20}.$$

Linear screening

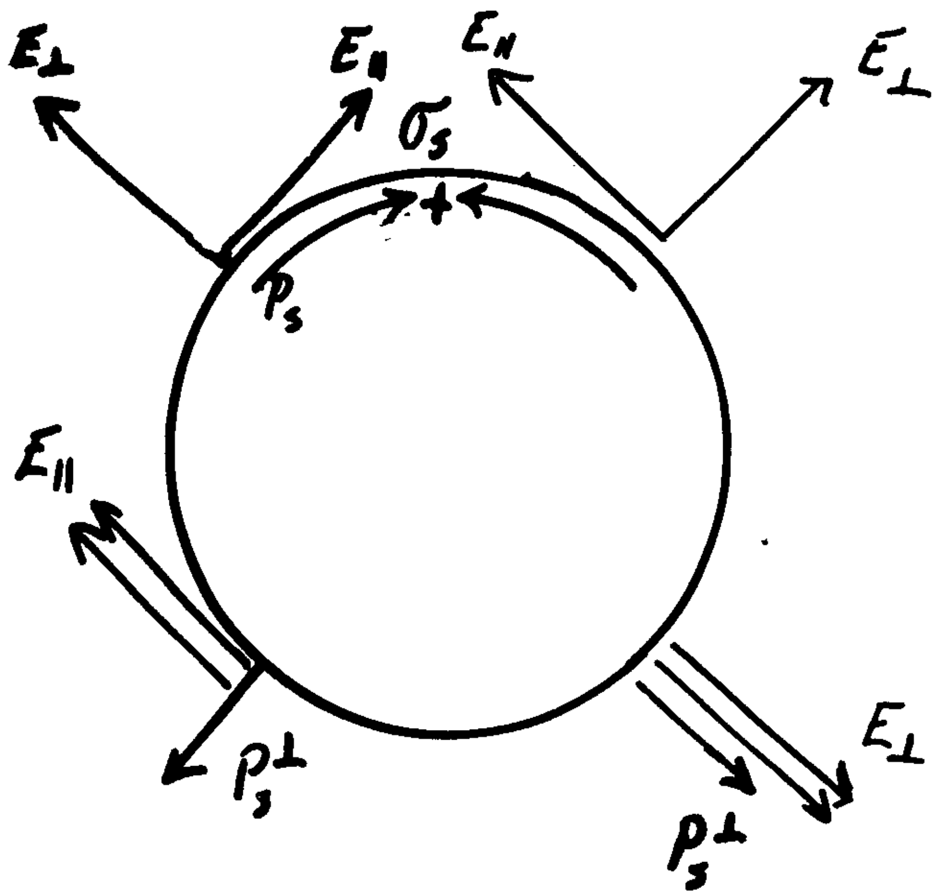
$$\phi_1 = \begin{cases} A_{10}\left(1 - \frac{\epsilon_1 - 1}{\epsilon_1 + 2}\left(\frac{R}{r}\right)^3\right) r Y_{10} \\ \quad + A_{20}\left(1 - 2\frac{\epsilon_1 - 1}{2\epsilon_1 + 3}\left(\frac{R}{r}\right)^5\right) r^2 Y_{20}, & r > R, \\ A_{10}\frac{3}{\epsilon_1 + 2} r Y_{10} + A_{20}\frac{5}{2\epsilon_1 + 3} r^2 Y_{20}, & r < R, \end{cases}$$

Sources



Bulk induced

Surface induced



$$\vec{P}^{\mathrm{nl}} = n\vec{p}^{\,\mathrm{nl}} - \frac{1}{2} n \nabla \cdot q^{\mathrm{nl}}$$

$$\vec{p}^{\,\mathrm{nl}} = -\frac{1}{2e} \alpha_1 \alpha_2 \nabla E_1^2$$

$$q^{\mathrm{nl}} = -\frac{1}{e} \alpha_1^2 \vec{E}_1 \vec{E}_1$$

$$\rho^{\mathrm{nl}} = -\nabla \cdot \vec{P}^{\mathrm{nl}} = -\frac{375n}{4\pi e} \frac{\alpha_1(\alpha_1 - 2\alpha_2)}{(3+2\epsilon_1)^2} A_{20}^2 \propto |\nabla \vec{E}^{\mathrm{ex}}|^2$$

$$\begin{aligned} \sigma^{\mathrm{nl}\,b} &= \vec{P}^{\mathrm{nl}}(R^-) \cdot \hat{r} \\ &= \frac{5n}{16\pi e} \alpha_1(\alpha_1 - 2\alpha_2) \left(\frac{12\sqrt{15}\cos\theta}{(\epsilon+2)(2\epsilon+3)} A_{10} A_{20} \right) + \ldots \end{aligned}$$

$$\begin{aligned}
\sigma^s &= -\nabla_{\|} \cdot \vec{P}^s_{\|} \\
&= \frac{3(\epsilon_1 - 1)^2 b}{256 n e \pi^3 R} \left(9 \frac{(1 + 3\cos 2\theta)}{(\epsilon_1 + 2)^2} A_{10}^2 \right. \\
&\quad \left. + 20\sqrt{15} R \frac{2\cos\theta + 3\cos 3\theta}{(\epsilon_1 + 2)(2\epsilon_1 + 3)} A_{10} A_{20} + \ldots \right)
\end{aligned}$$

$$\begin{aligned}
P^s_{\perp} &= \frac{(\epsilon_1 - 1)^2}{256 n e \pi^3} \left(27 \frac{a\cos^2\theta + f\sin^2\theta}{(\epsilon_1 + 2)^2} A_{10}^2 \right. \\
&\quad \left. + 15\sqrt{15} R \cos\theta \frac{4a + 6(f - a)\sin^2\theta}{(\epsilon_1 + 2)(2\epsilon_1 + 3)} A_{10} A_{20} + \ldots \right).
\end{aligned}$$

Non linear field eqs.

$$\phi_2 = \phi^b + \phi^s,$$

ϕ^b has bulk sources, not yet screened, while ϕ^s has surface sources, already screened.

$$\nabla^2 \phi^b = -4\pi\rho^{\mathrm{nl}}/\epsilon_2 \,(\text{inside}),\ \ 0\,(\text{outside})$$

$$\nabla^2 \phi^s = 0 \ \ (\text{inside and outside})$$

Boundary conditions

$$\phi^b(R^+) - \phi^b(R^-) = 0,$$

$$\phi^s(R^+) - \phi^s(R^-) = 4\pi P_\perp^s,$$

$$\frac{\partial}{\partial R}\phi^b(R^+) - \epsilon_2 \frac{\partial}{\partial R}\phi^b(R^-) = -4\pi\sigma^b,$$

$$\frac{\partial}{\partial R}\phi^s(R^+) - \frac{\partial}{\partial R}\phi^s(R^-) = -4\pi\sigma^s.$$

Solution

$$\phi_{l0}^{\lambda} = \begin{cases} F_{l0}^{\lambda} r^{l}, & \text{(inside)} \\ \dfrac{4\pi}{2l+1} \dfrac{q_{l0}^{\lambda}}{r^{l+1}}, & \text{(outside)} \end{cases}$$

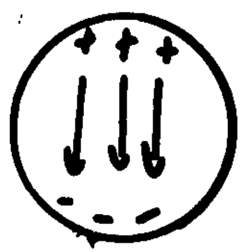
$q_{l0}^{\lambda} = q_{l0}^{\lambda}(\rho^{\mathrm{nl}}, \sigma^{\mathrm{nl}\,b}, \sigma^{s}, P_{\perp}^{s})$ =(spherical) multipoles

$\Longrightarrow \gamma^{d}, \gamma^{Q}$

Hyperpolarizabilities

$$\gamma^d = \frac{1}{8\pi ne} \frac{\epsilon_1 - 1}{(\epsilon_1 + 2)(2\epsilon_1 + 3)} \left(15 \frac{\epsilon_1 - 2\epsilon_2 + 1}{\epsilon_2 + 2} + (\epsilon_1 - 1)(2a + b + 3f) \right) R^3,$$

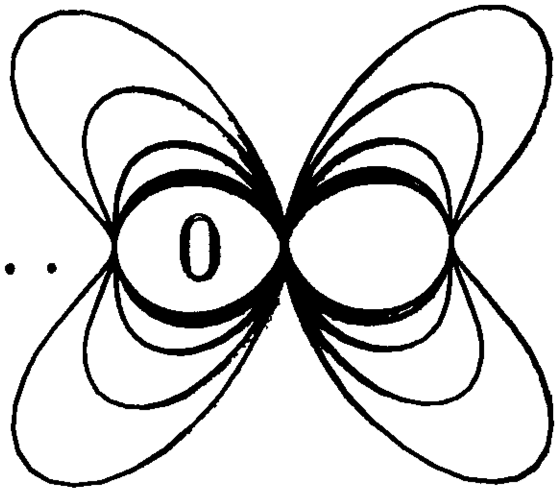
$$\gamma^Q = \frac{9}{20\pi ne} \frac{(\epsilon_1 - 1)^2}{(\epsilon_1 + 2)^2} (a + 3b - f) R^3.$$



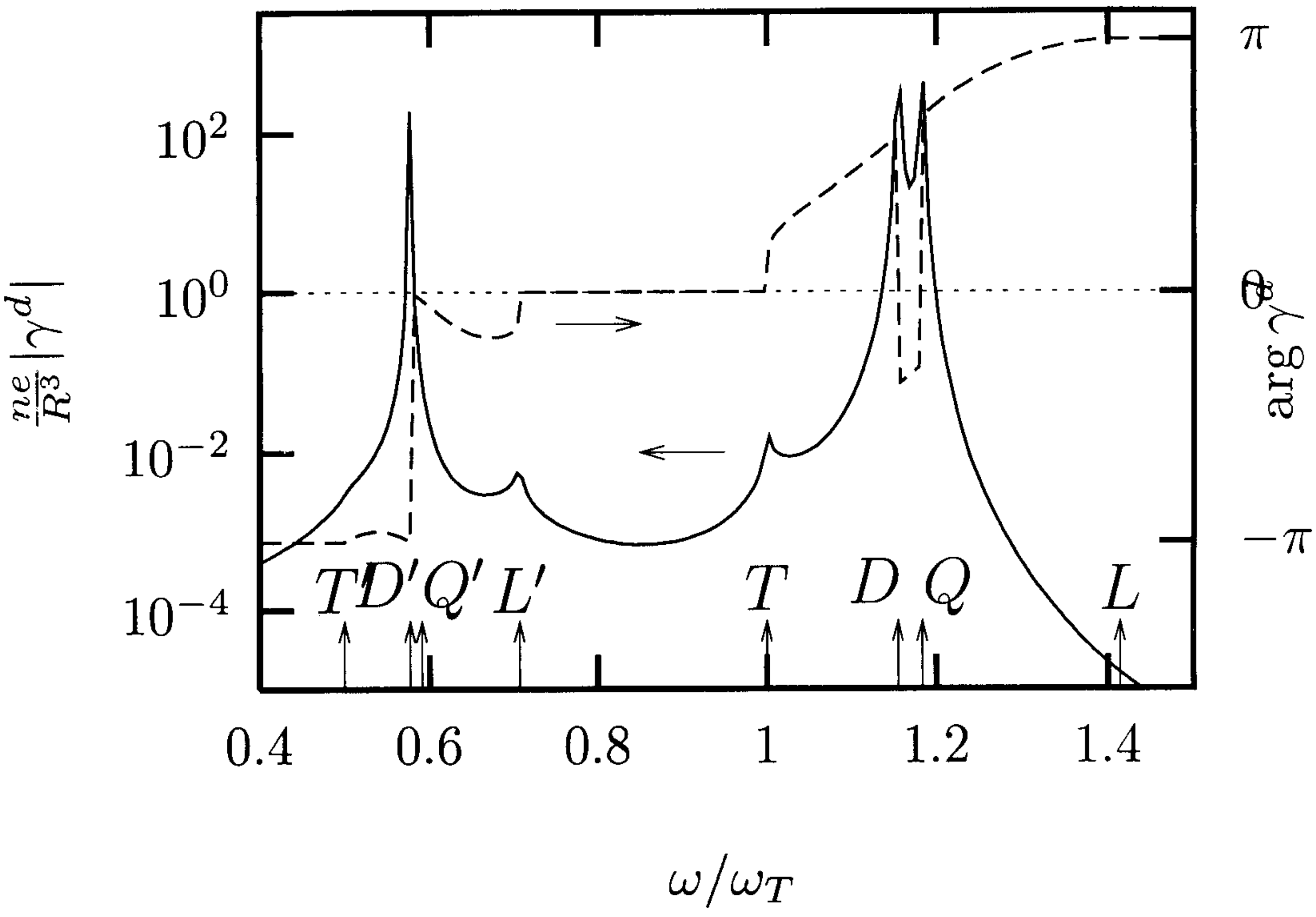
$\epsilon_1 = \epsilon_2 = 2,\ a = -2,\ b = -1,\ f = 0$

$\frac{d\sigma}{d\Omega}$ vs. ϑ

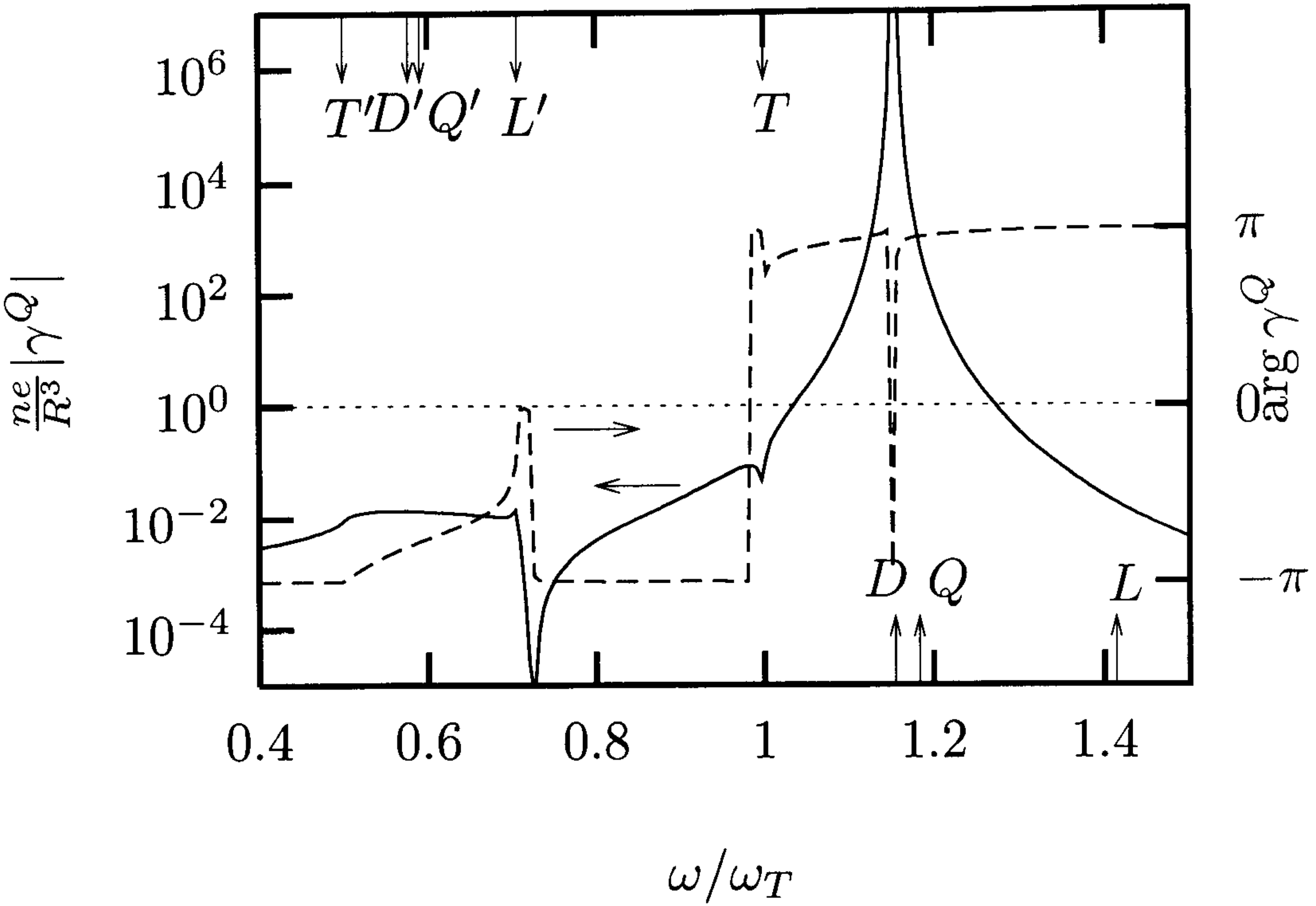
$k_1 l = 2 \ldots$



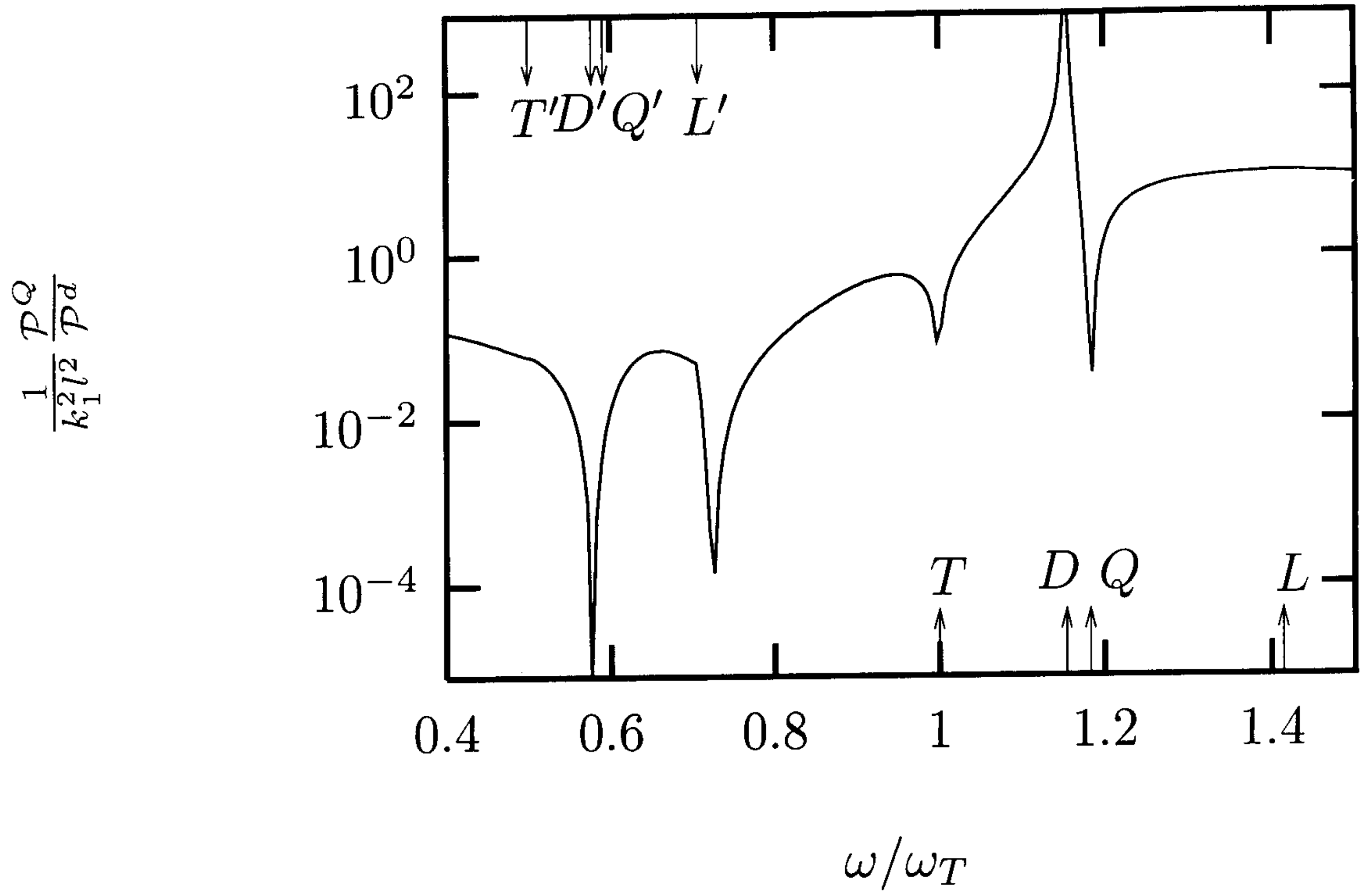
$l = |E / \nabla E|$



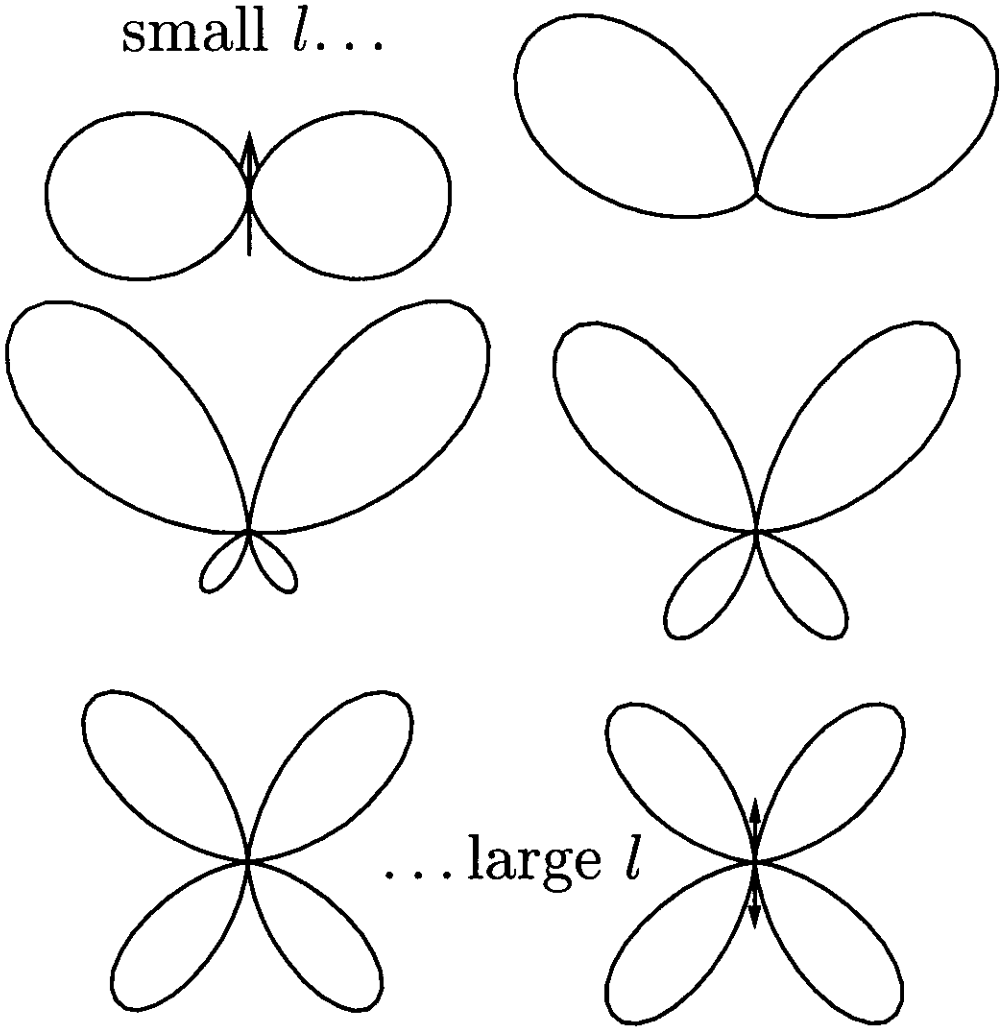
10^2
10^0
10^{-2}
10^{-4}
$\frac{ne}{R^3}|\gamma^d|$
π
0
$-\pi$
$\arg \gamma$
T' D' Q' L'
T D Q L
0.4
0.6
0.8
1
1.2
1.4
ω/ω_T

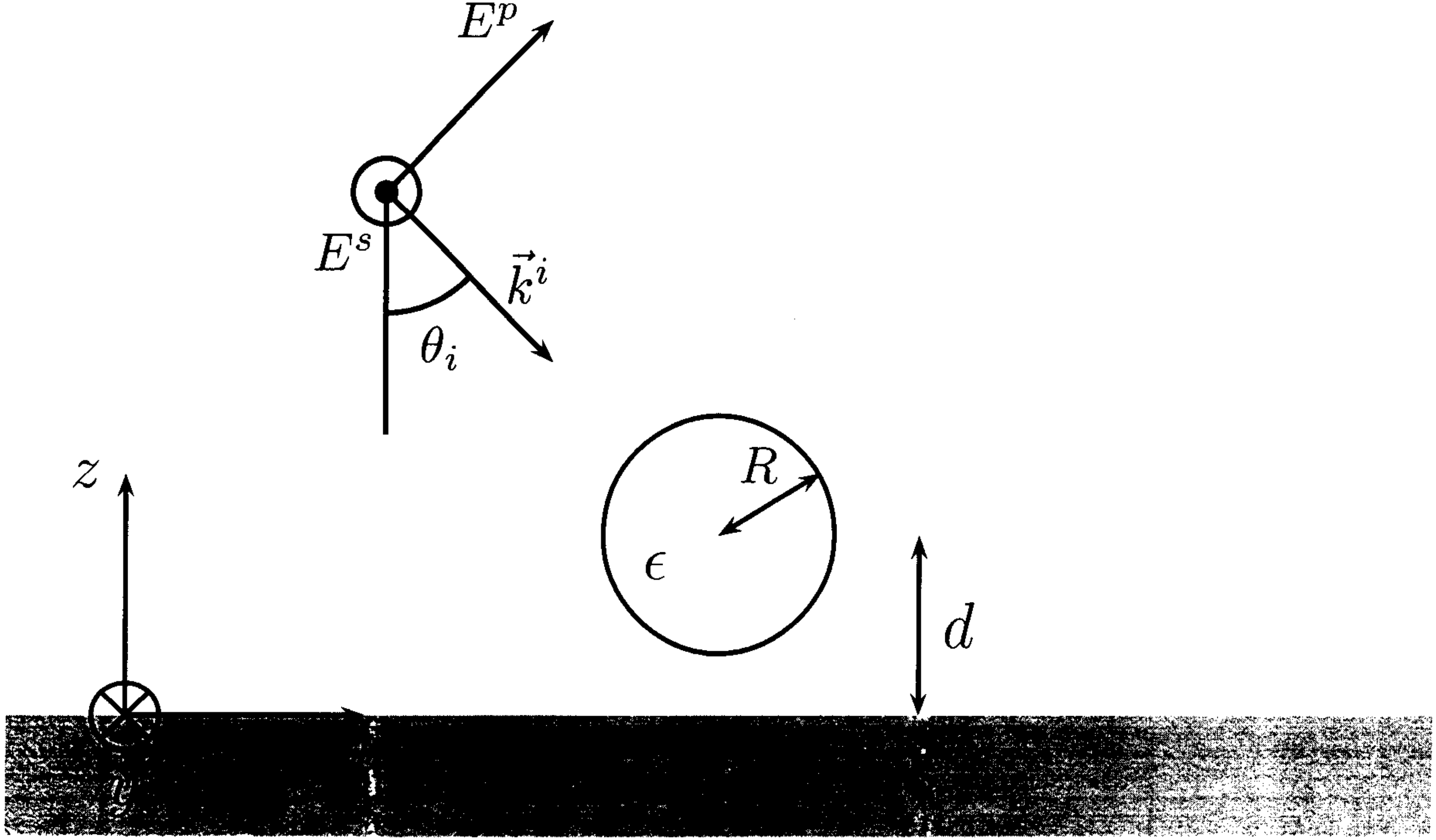


10^6
10^4
10^2
10^0
10^{-2}
10^{-4}
$T'D'Q'$ L'
T
D Q
L
π
0
$-\pi$
$\frac{ne}{R^3}|\gamma^Q|$
$\arg\gamma^Q$
0.4
0.6
0.8
1
1.2
1.4
ω/ω_T

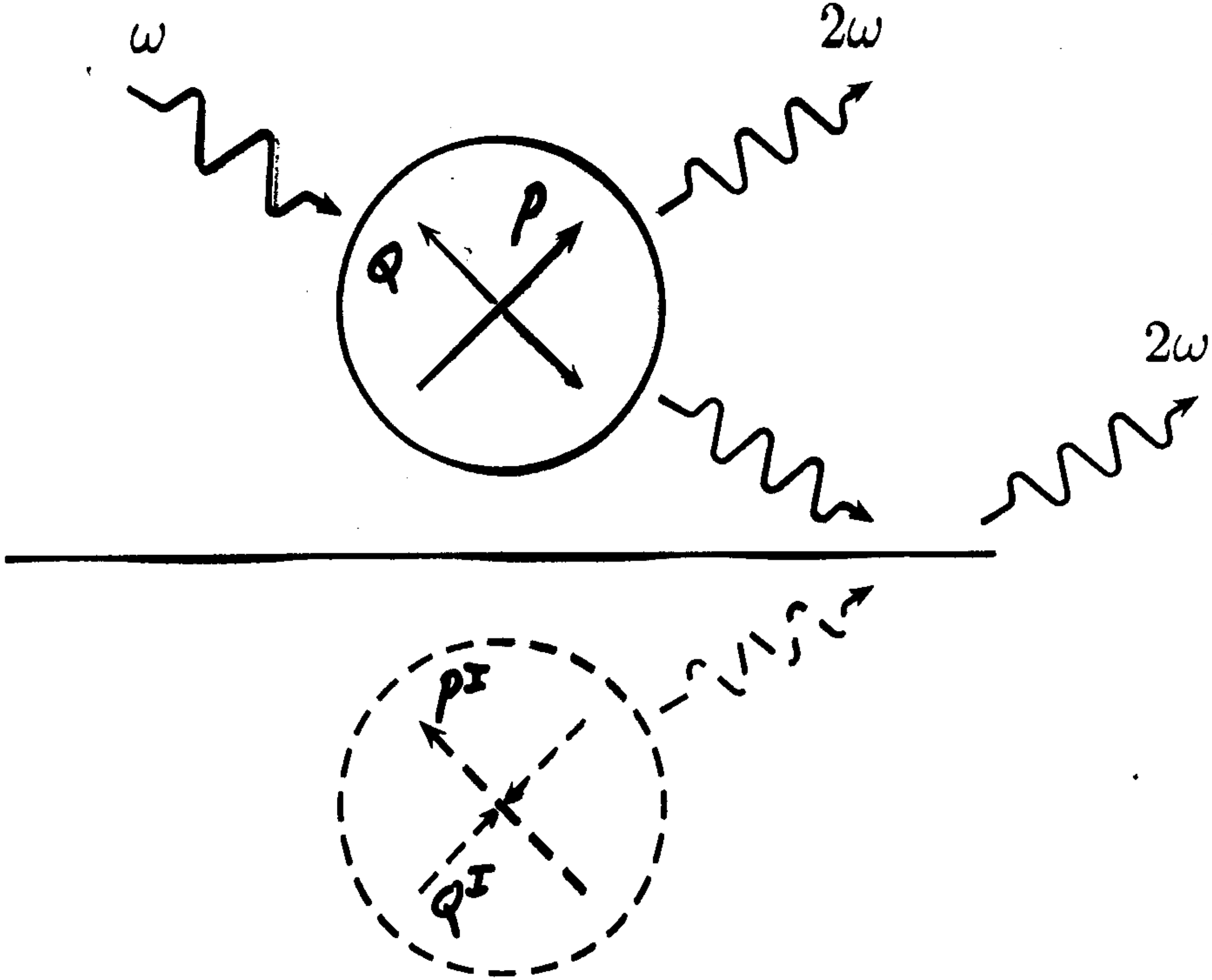


10^2
10^0
10^{-2}
10^{-4}
$T'D'Q'\ L'$
T
$D\ Q$
L
0.4
0.6
0.8
1
1.2
1.4
$\frac{1}{k_1^2 l^2} \frac{\mathcal{P}^Q}{\mathcal{P}^d}$
ω/ω_T


small l...
...large l

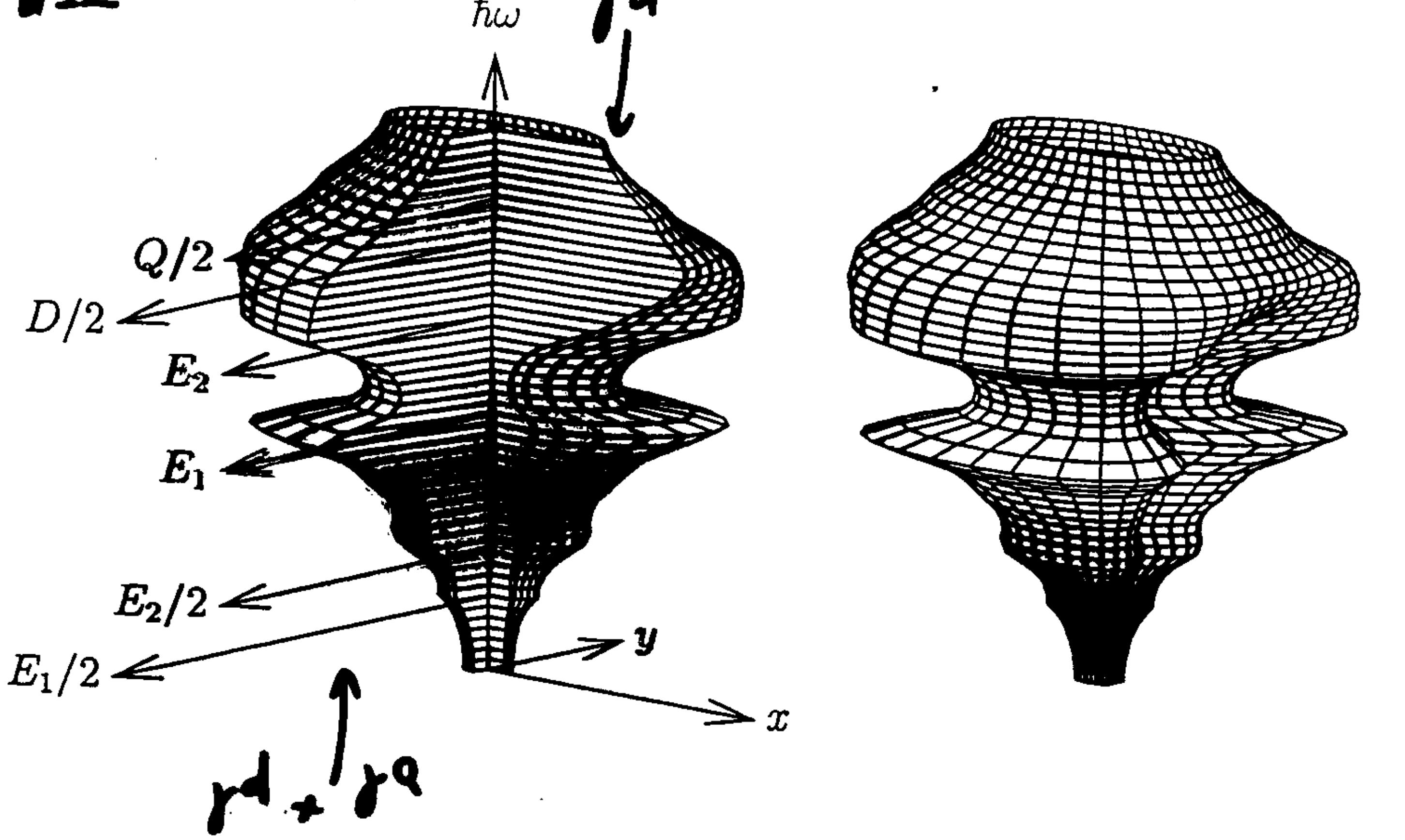


E^p
E^s
$\vec{k}^i$
θ_i
z
R
ϵ
d

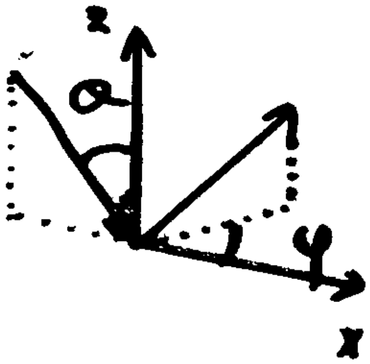


ω
2ω
2ω
q
p
pI
qI

$\frac{1}{\omega^5}\frac{d\sigma}{d\Omega}$ vs. ω, φ



•) Normalized SH efficiency $(d\sigma/d\Omega)/\omega^5$ scattered by a Si sphere of radius R = 4
e an inert substrate with $\epsilon^s = 2.34$, illuminated with s polarized light at an angle of inci
polar angle $\theta = 45°$ as a function of the azimuthal angle φ and of the incident photon e
nce is $x - z$. We indicate the cartesian axis, the E_1 and E_2 resonances of bulk Si, their
he dipolar D and quadrupolar Q resonances of the sphere.



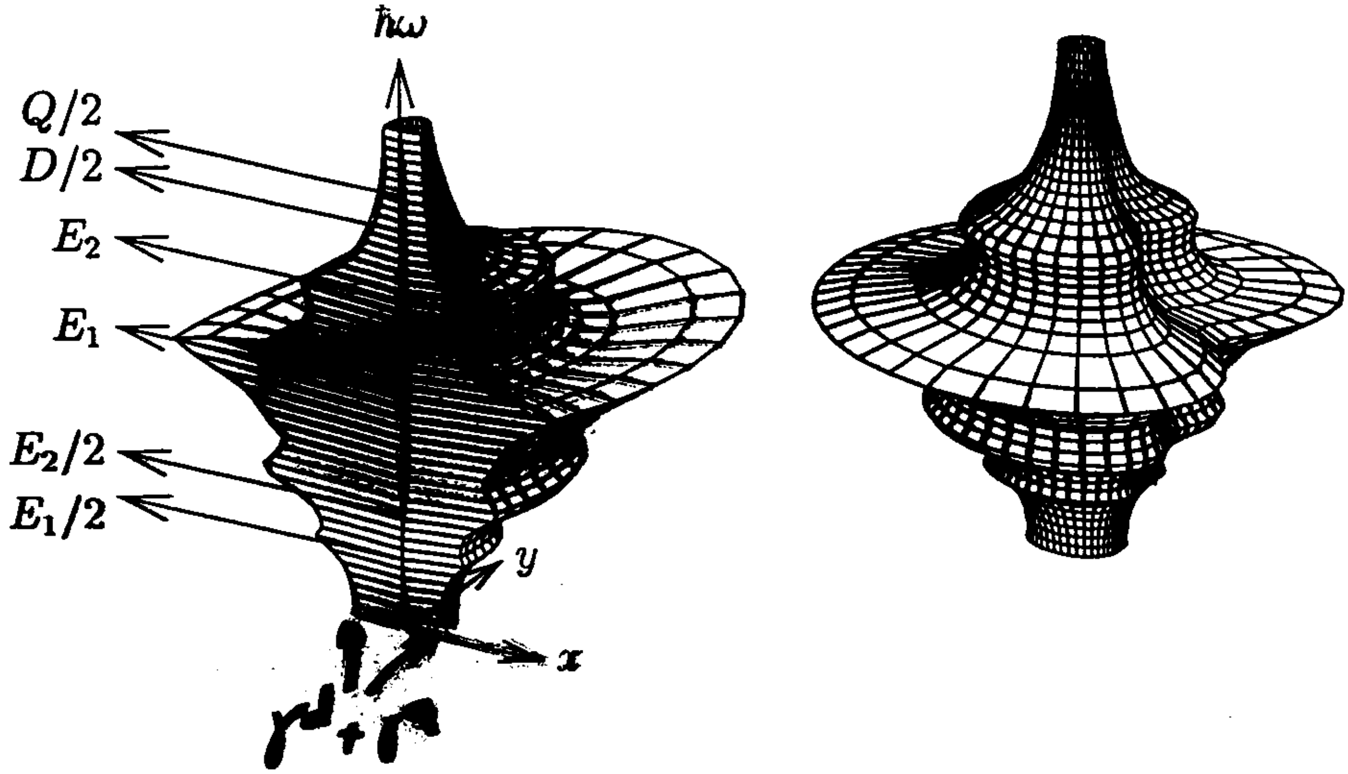
s pol.

R=4nm Si

Z=1.2R

ϵ_s=2.34

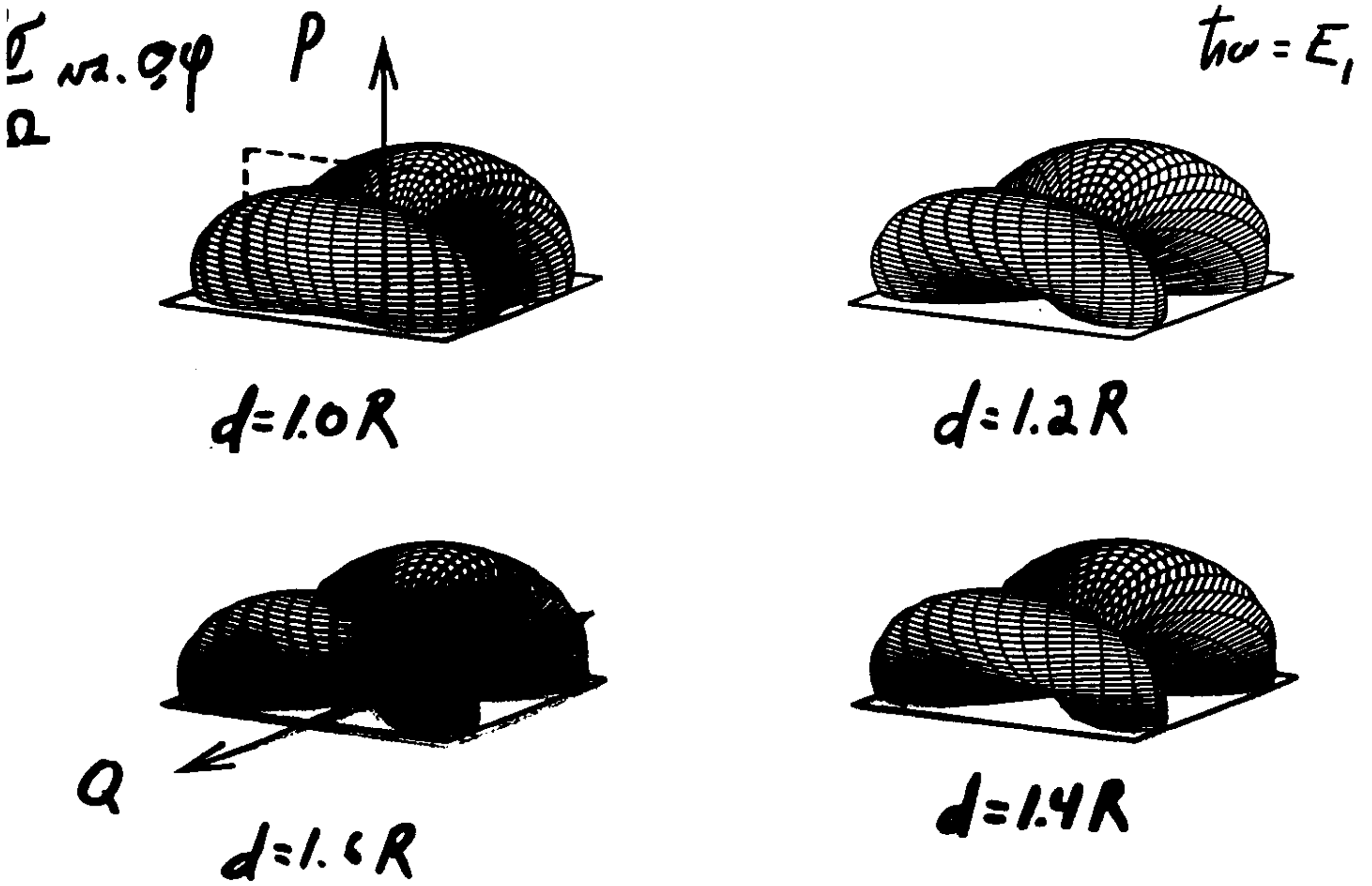
θ=45°



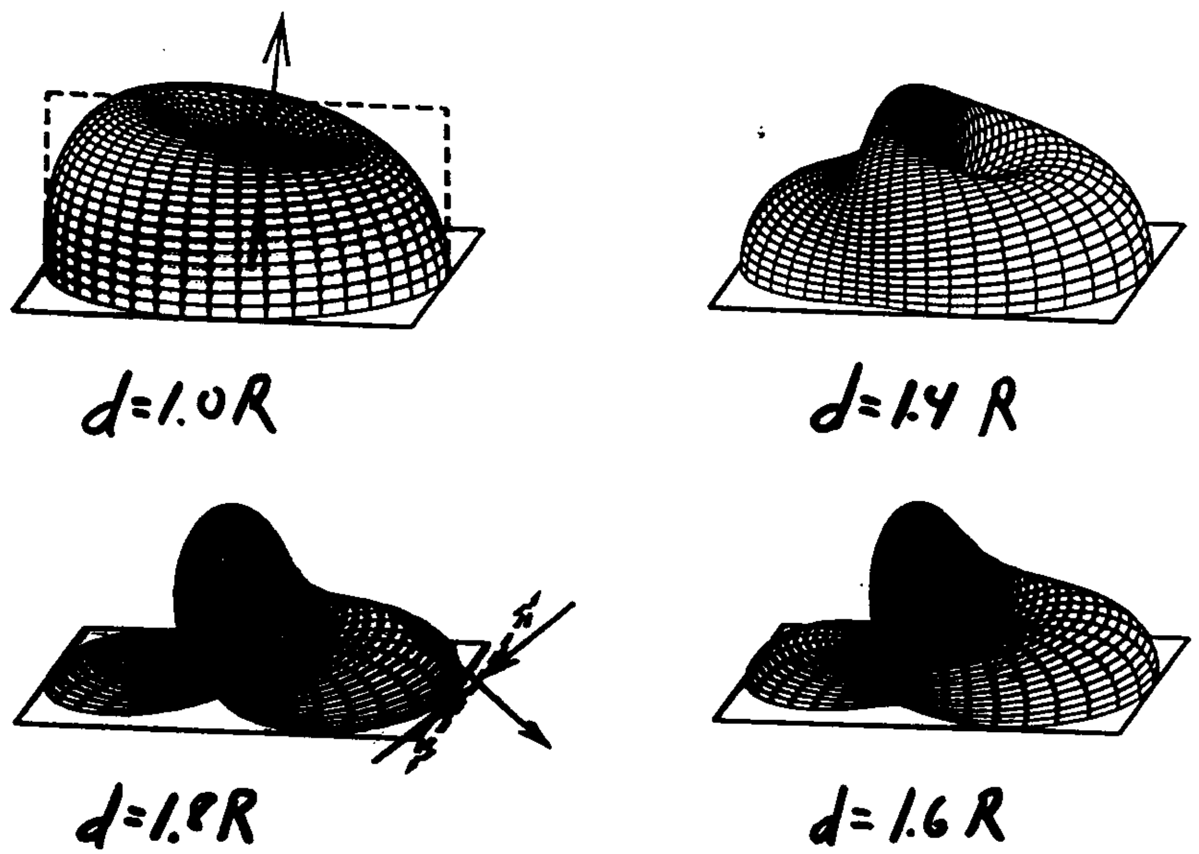
rsonicos) Normalized SH efficiency $(d\sigma/d\Omega)/\omega^5$ as in Fig. 8 (helado), but for p polarize
s at a distance $z = 1.4R$ over the substrate.

P. pol.

$z = 1.4R$



) Efficiency $d\sigma/d\Omega$ of the SH radiation patterns produced by a 4nm Si nanosphere at se
;, $1.4R$, and $1.6R$ (clockwise from upper left) over a dielectric substrate ($\epsilon^s = 2.34$) illu
of energy $\hbar\omega = E_1$, as a function of the outgoing direction θ and φ. We indicate the
plane of incidence (dashed rectangle), the direction of the induced dipole moment (single
the induced quadrupolar moment (double headed arrow).



…P) **Efficiency $d\sigma/d\Omega$ of the SH radiation patterns produced by a 4nm** Si nanosphere at s… **4R, 1.6R, and 1.8R (clockwise from upper left) over a dielectric substrate** ($\epsilon^s = 2.34$)… light of **energy $\hbar\omega = E_1$**, as a function of the outgoing direction θ and φ. We indic… gle) and the **plane of incidence** (dashed rectangle). For $d = R$ we show the direction… nt (**single headed arrow**). For $d = 1.8R$ **we show with double headed arrows the** approx… ong (solid) and normal to (dashed) the incidence plane. Their size indicates that of th… of $\overleftrightarrow{Q}$; converging arrows correspond to nearly opposite phases than diverging arrows.

Conclusions

- Dipolium model for SHG of particles in inhomogeneous field.
- Analytical expressions for γ^d and γ^Q.
- $\gamma^\lambda \propto R^3/ne$ (bulk and surface).
- Comparable bulk and surface, dipole and quadrupole signals.
- Surface ($a(\omega)$) resonances and sphere resonances: dipolar_ω, $\text{dipolar}_{2\omega}$, and $\text{quadrupolar}_\omega$.
- $\sigma \approx (R/\lambda)^{6-\zeta}(R/\ell)^\zeta/(cn^2e^2)$, $\zeta = 0\ldots 2$.
- p or Q (or none) dominate, depending on ℓ.

- Si spheres over a substrate, E_1 and E_2, dipolar and quadrupolar resonances.
- Radiation pattern changes from dipolar to quadrupolar for $z \approx R \to 2R$. Asymmetric for p-polarization.