SHG from bulk and surface of nanoparticle composites

Theory:

W. Luis Mochán,[1] Jesús Maytorena,[1,2] Bernardo S. Mendoza[3], Vera L. Brudny,[4]

Experiment:

M. Downer,[5] L. Sun, P. Figliozzi,[5] Y. Q. An,[5]

Y. Jiang,[5] P. T. Wilson,[5] N. Matlis,[5] B. Mattern[5],

C. W. White,[6] S. P. Withrow[6]

[1] Centro de Ciencias Físicas, UNAM

[2] Centro de Ciencias de la Materia Condensada, UNAM

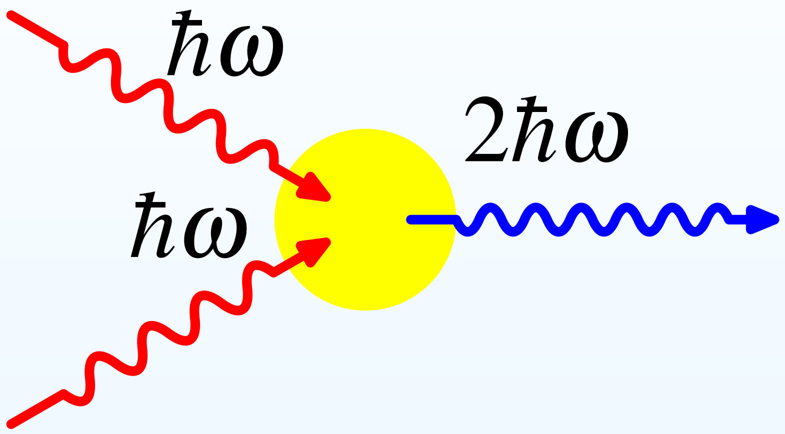
[3] Centro de Investigaciones en Optica

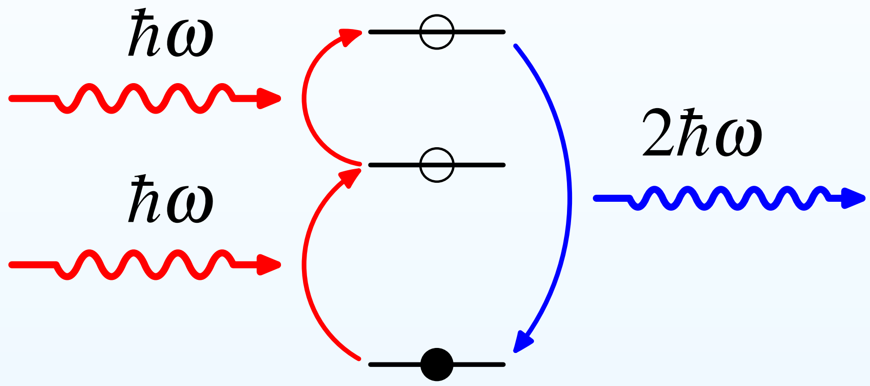
[4] Departamento de Fsica-UBA

[5] Department of Physics, Univ. of Texas at Austin

[6] ORNL

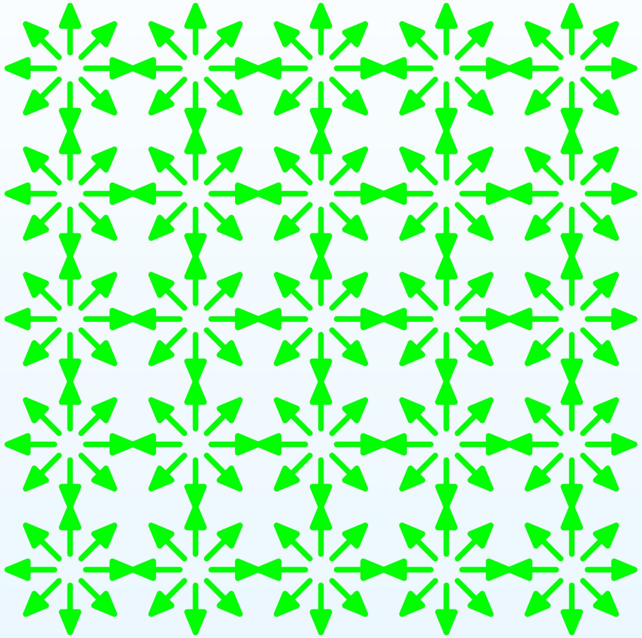
Second Harmonic Generation





$$\vec{P}(\vec{2}\omega) \propto \vec{E}(\omega)\vec{E}(\omega)$$

SHG and Symmetry



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

After an inversion

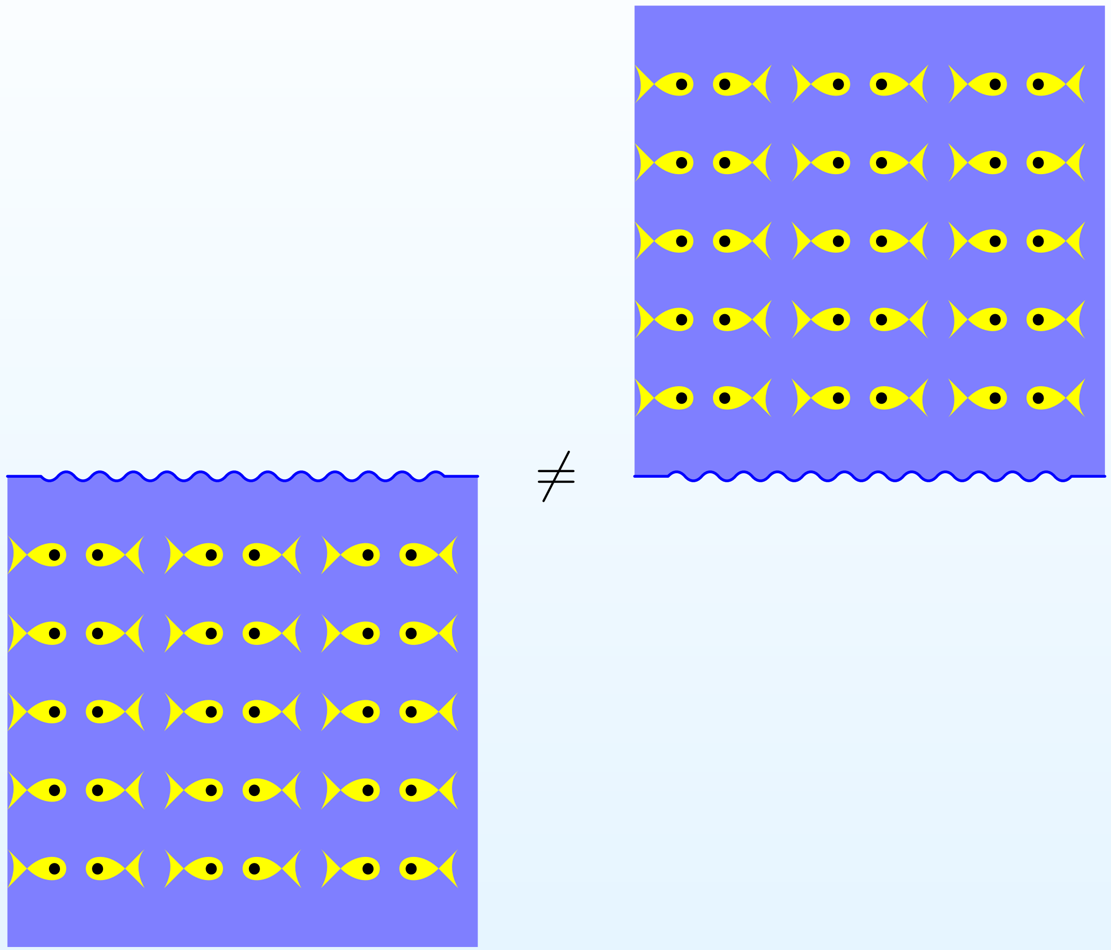
$$-\vec{P}^{(2)} = \chi_I^{(2)} (-\vec{E})(-\vec{E})$$

Centrosymmetry $\Rightarrow$

$$\chi_I^{(2)} = \chi^{(2)}$$

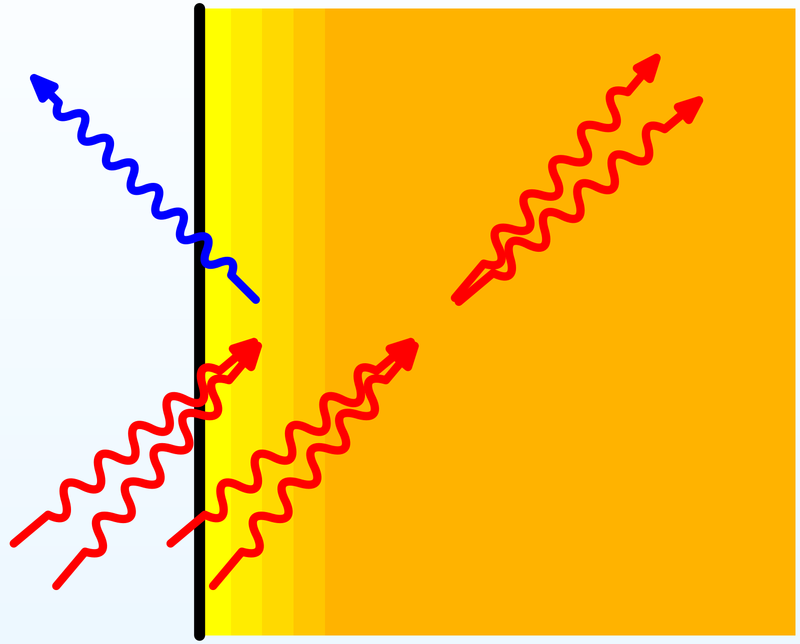
$$\Longrightarrow \vec{P}^{(2)} = 0, \quad \chi^{(2)} = 0$$

Centrosymmetry and Surfaces



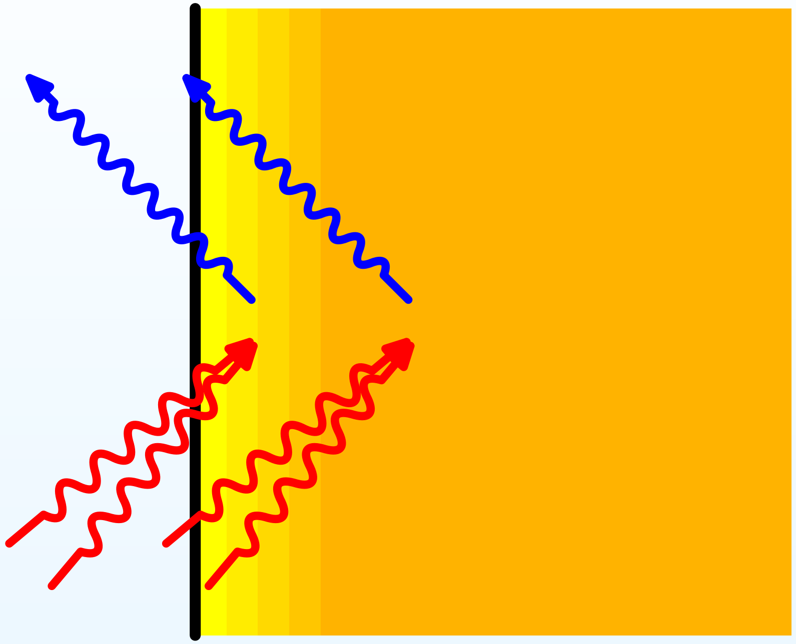
Surfaces are not centrosymmetric!

SHG and Surfaces



Dipolar SHG $P_i^{(2)} = \chi_{ijk} E_j E_k$ comes from the surface.

SHG and Surfaces

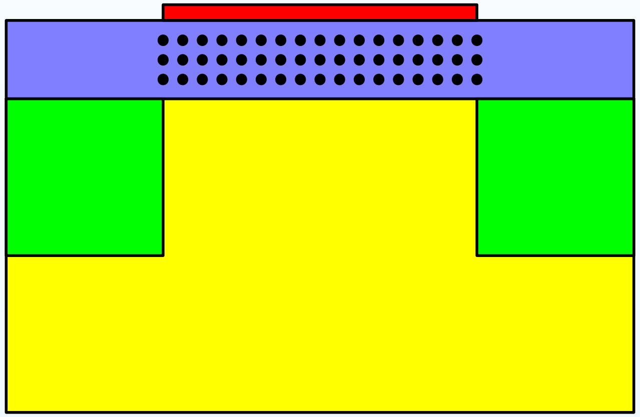


Dipolar SHG $P_i^{(2)} = \chi_{ijk} E_j E_k$ comes from the surface.
There might be SHG from bulk. . .
but it is *multipolar*

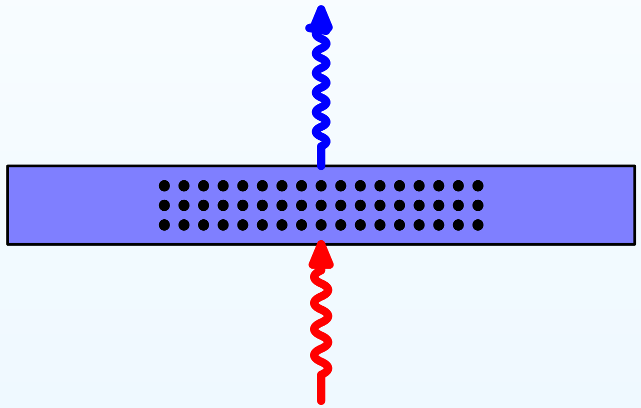
$$P_i^{(2)} = \chi_{ijkl} E_j \partial_k E_l.$$

Buried interfaces: nanoparticles

Flash memories



Observe interfaces with SHG



Experiment

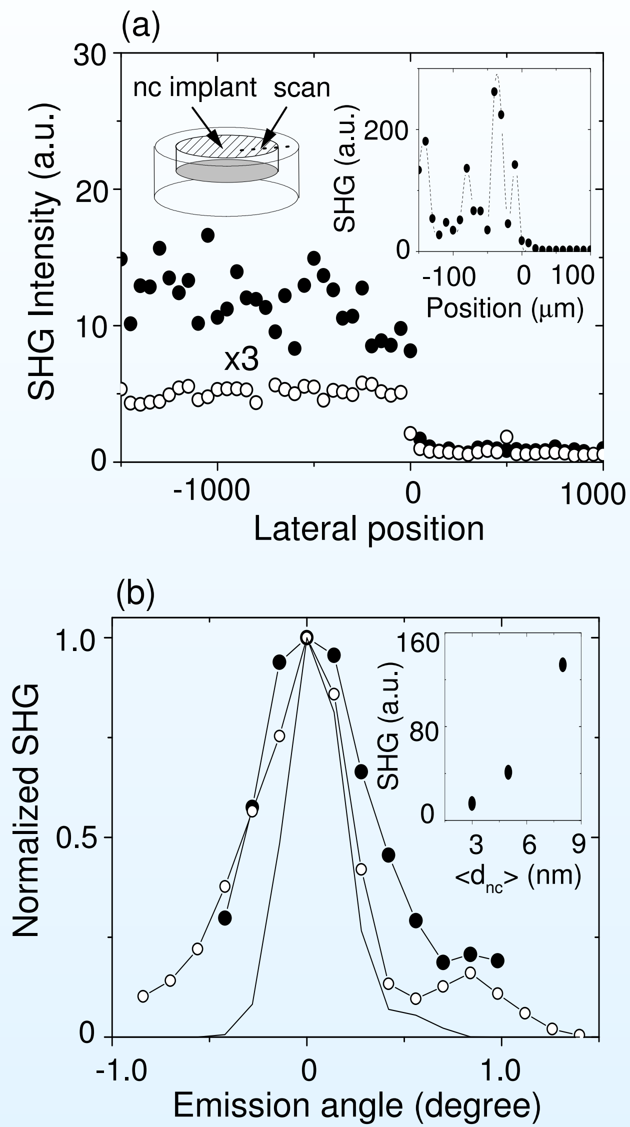
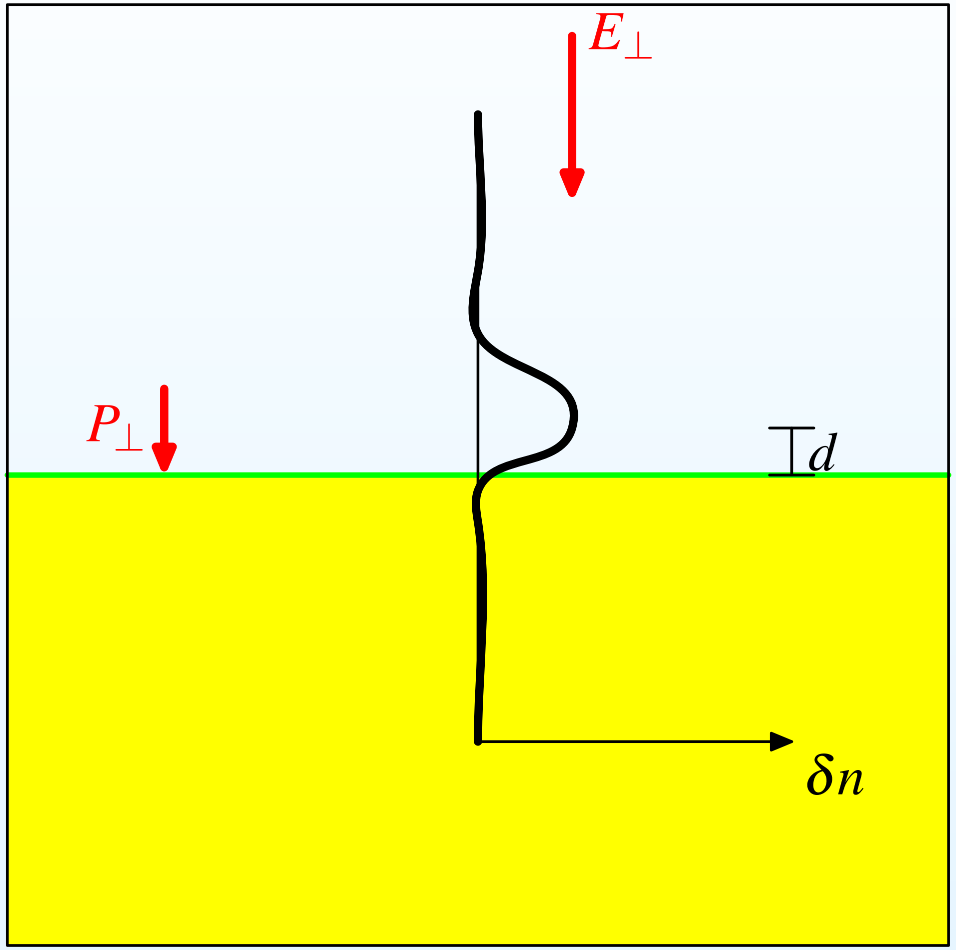


FIG. 3

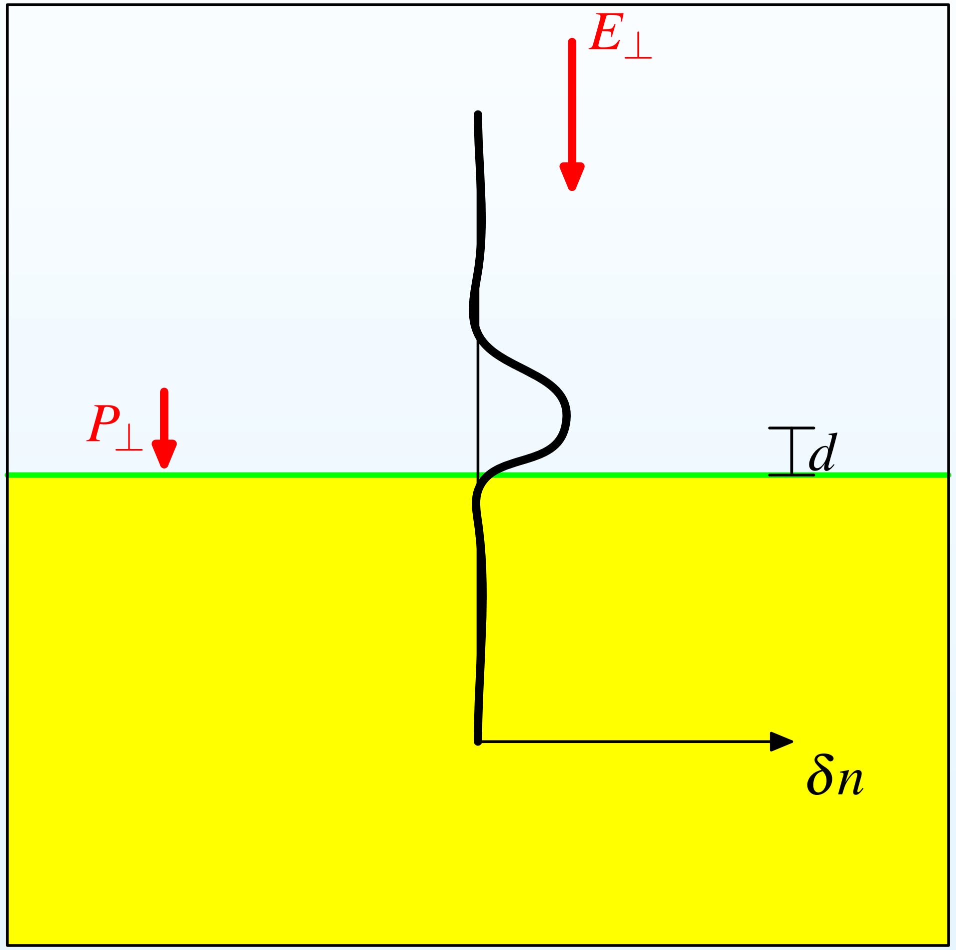
Y. Jiang, P. T. Wilson, M. C. Downer, C. W. White, and S. P. Withrow, Appl. Phys. Lett. **78**, 766 (2001).

- Signal comes from nanospheres.
- Interface sensitive (annealed in Ar vs. Ar/H_2).
- Forward SHG.

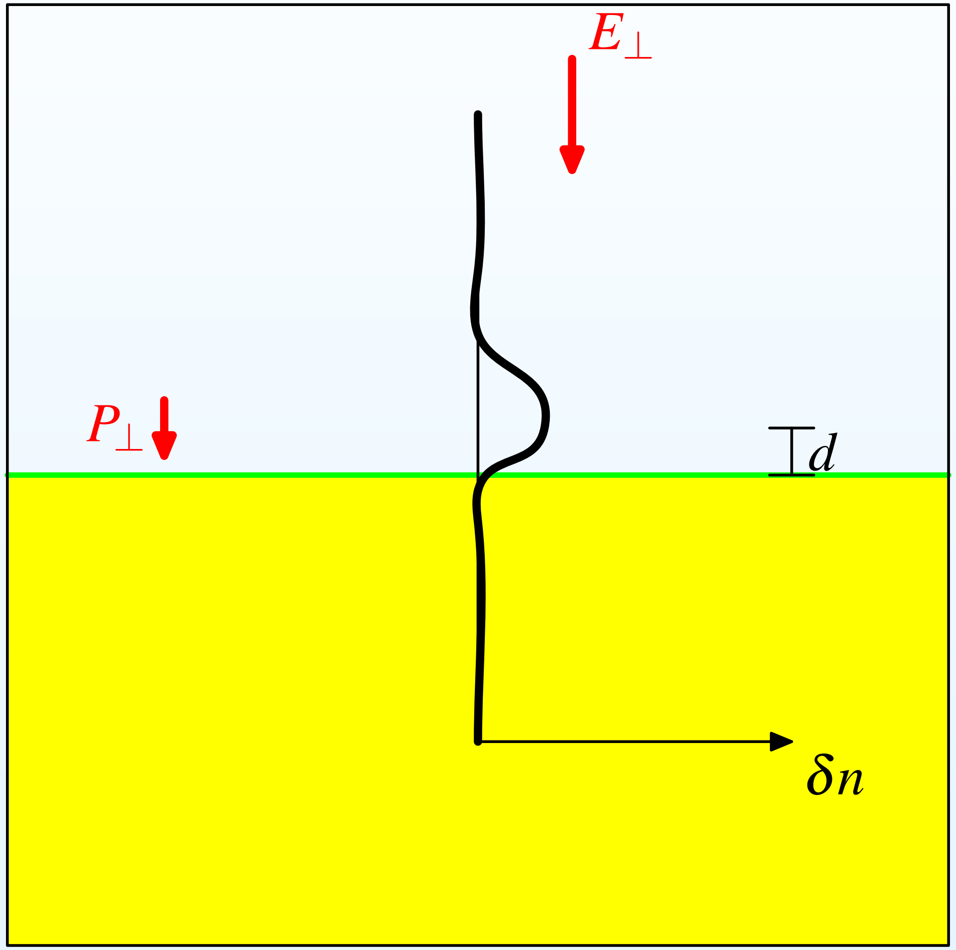
Nonlinear Surface Response: a



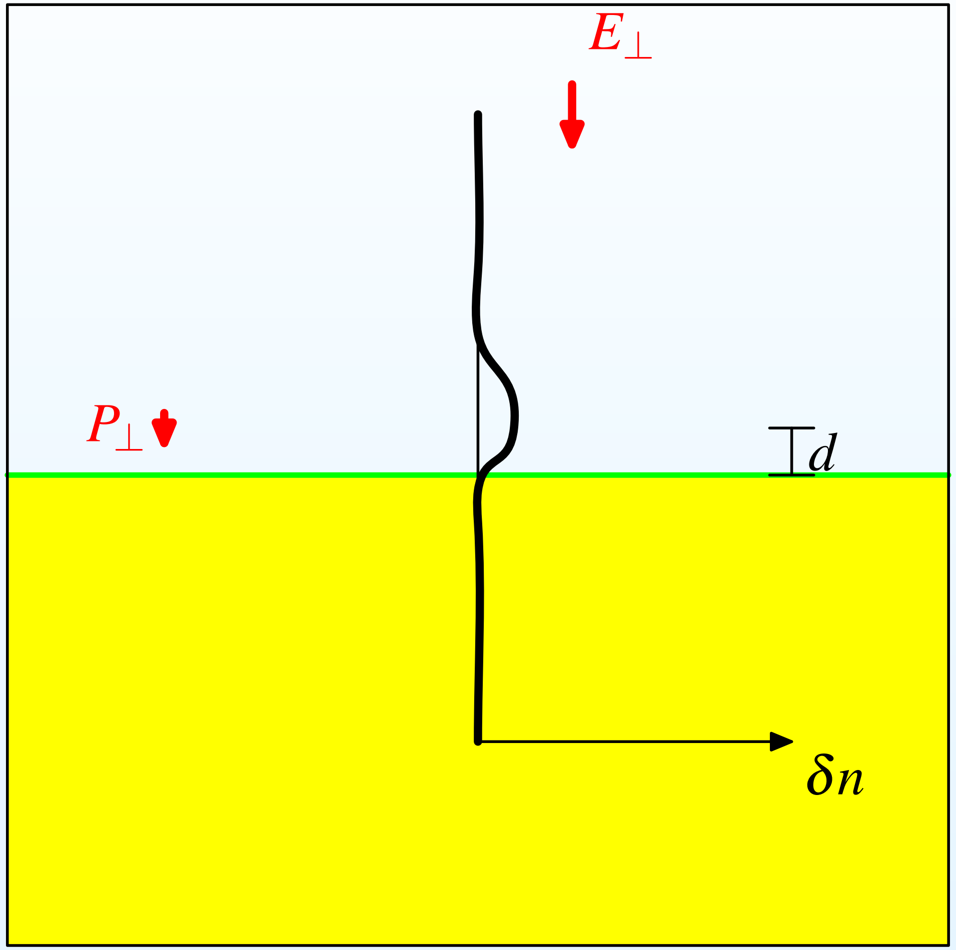
Nonlinear Surface Response: a



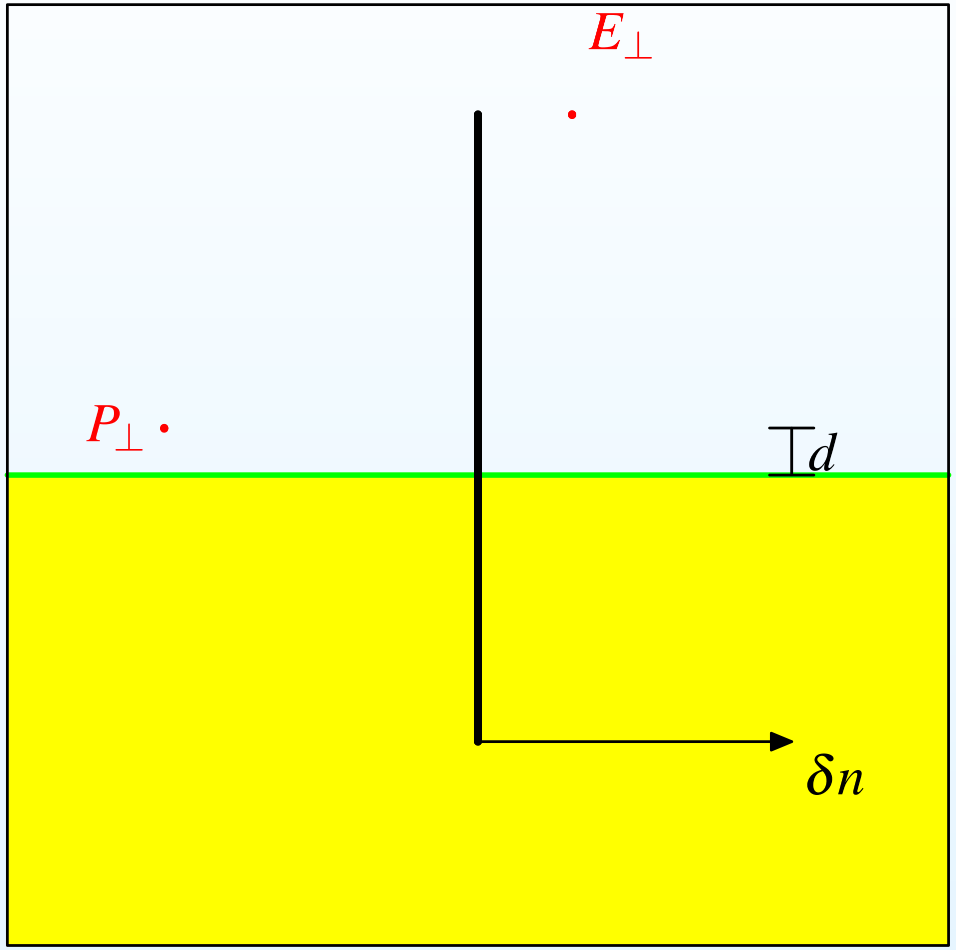
Nonlinear Surface Response: a



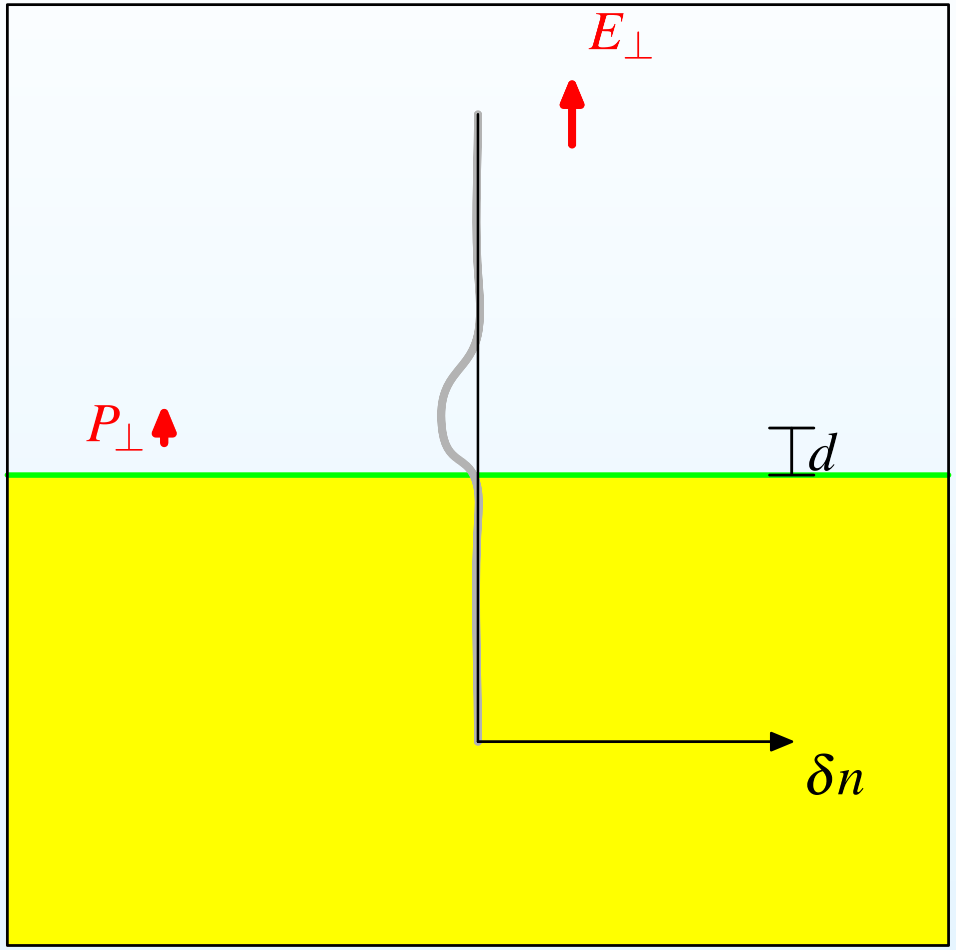
Nonlinear Surface Response: a



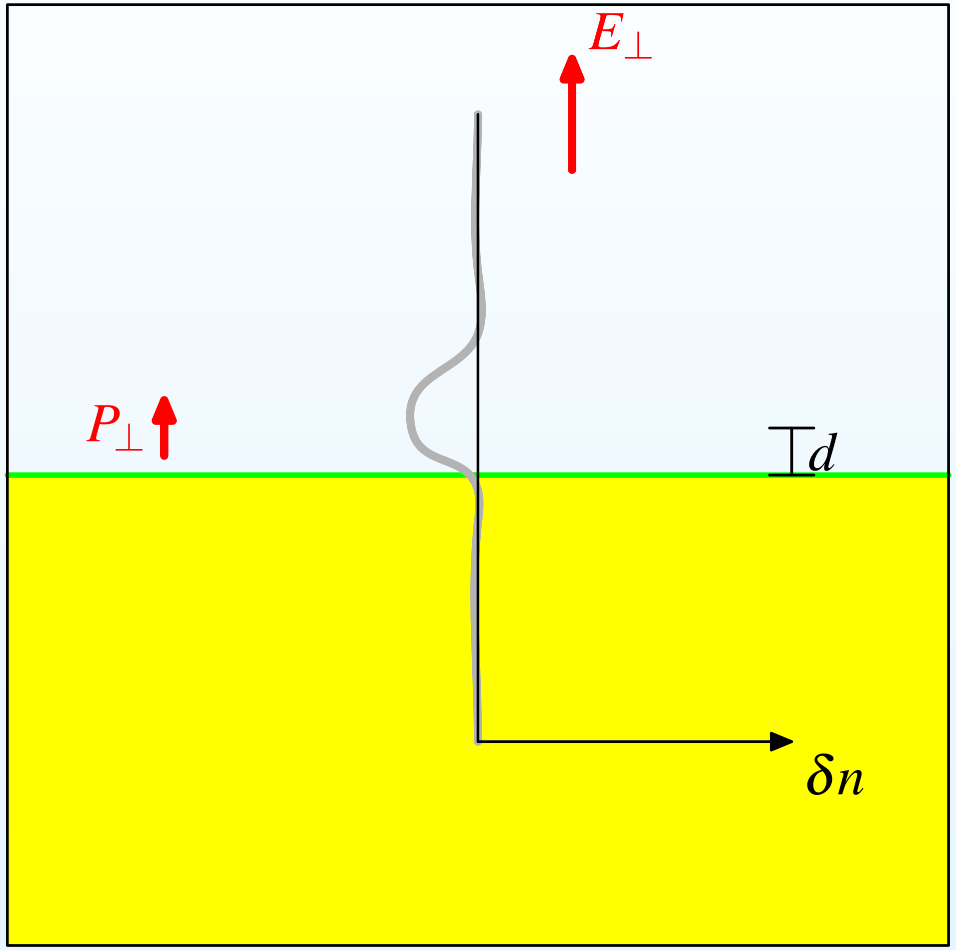
Nonlinear Surface Response: a



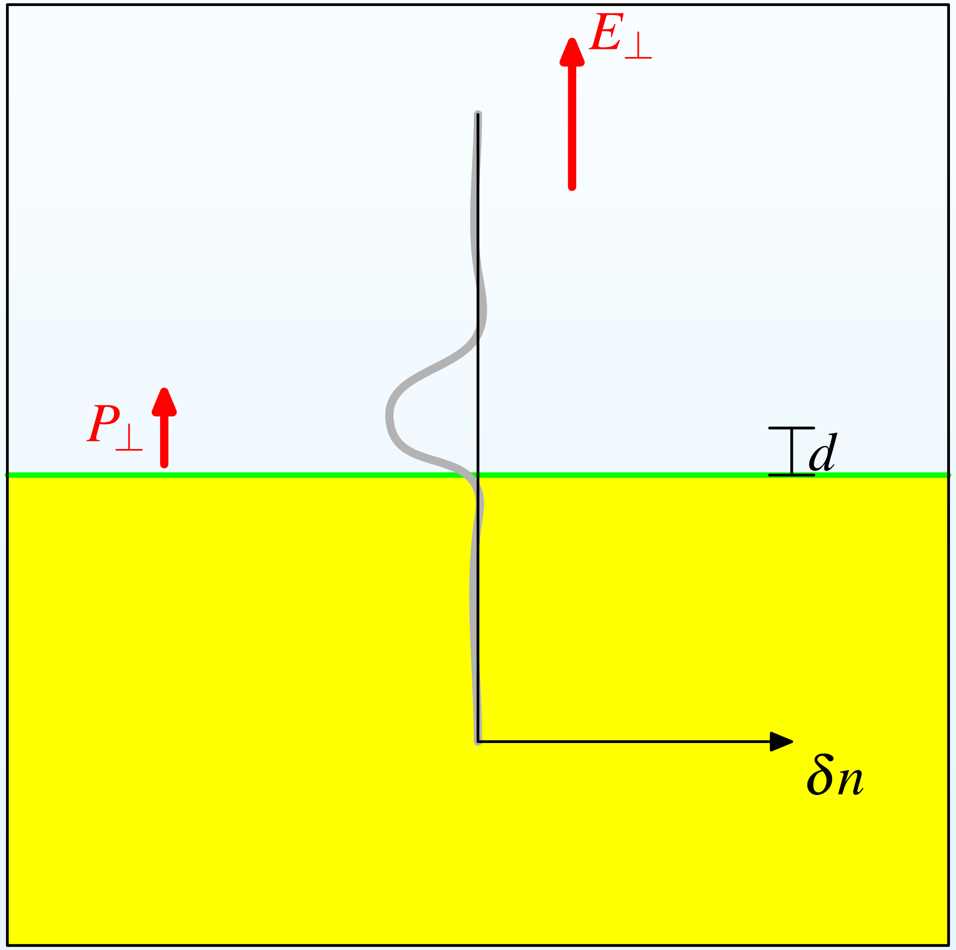
Nonlinear Surface Response: a



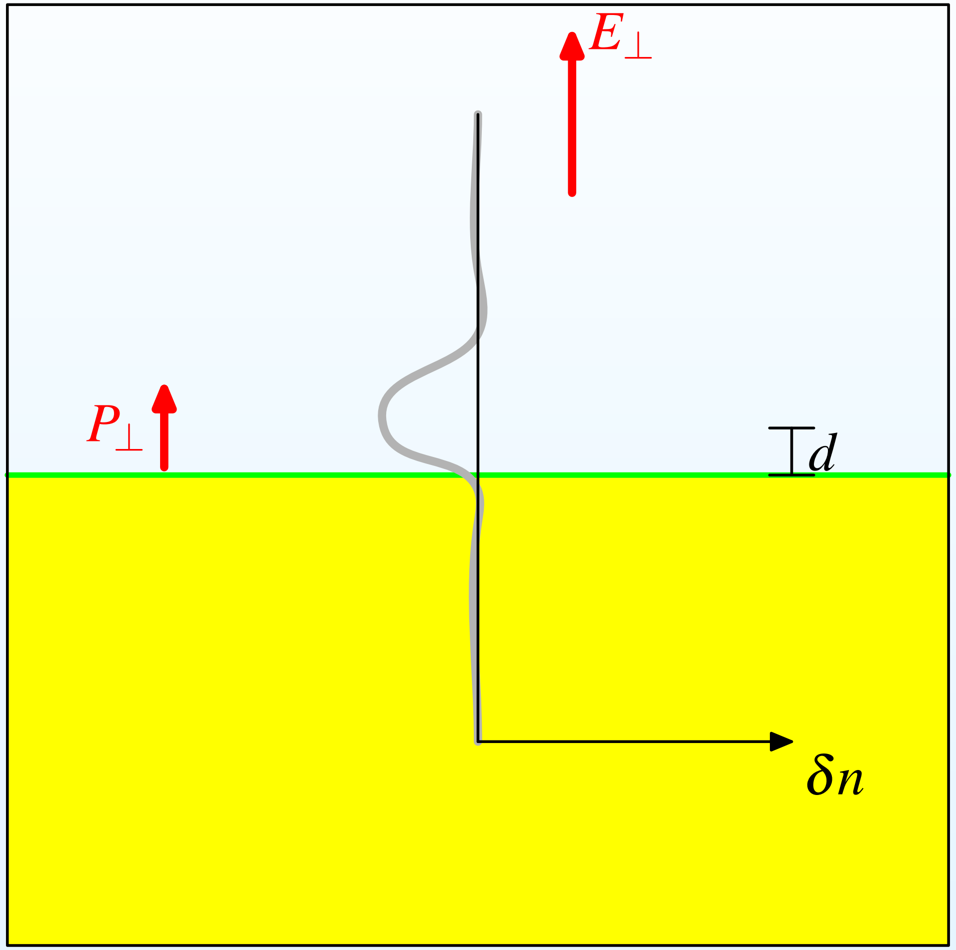
Nonlinear Surface Response: a



Nonlinear Surface Response: a



Nonlinear Surface Response: a



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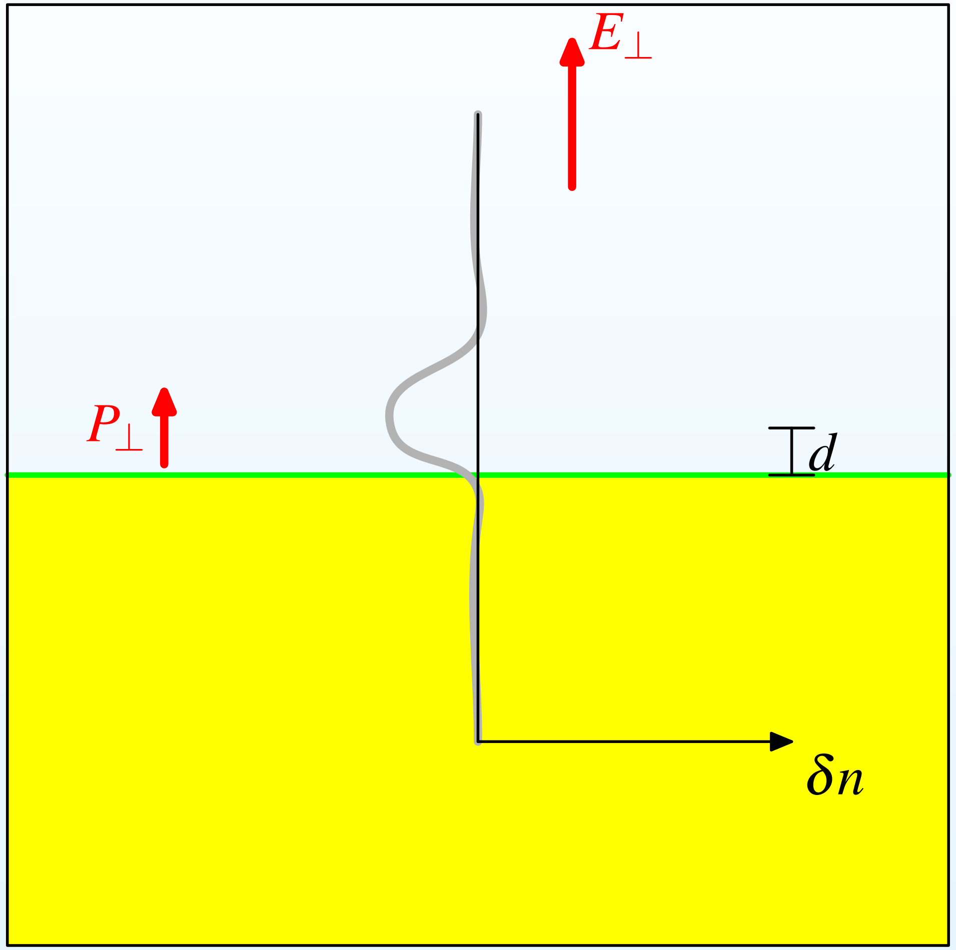

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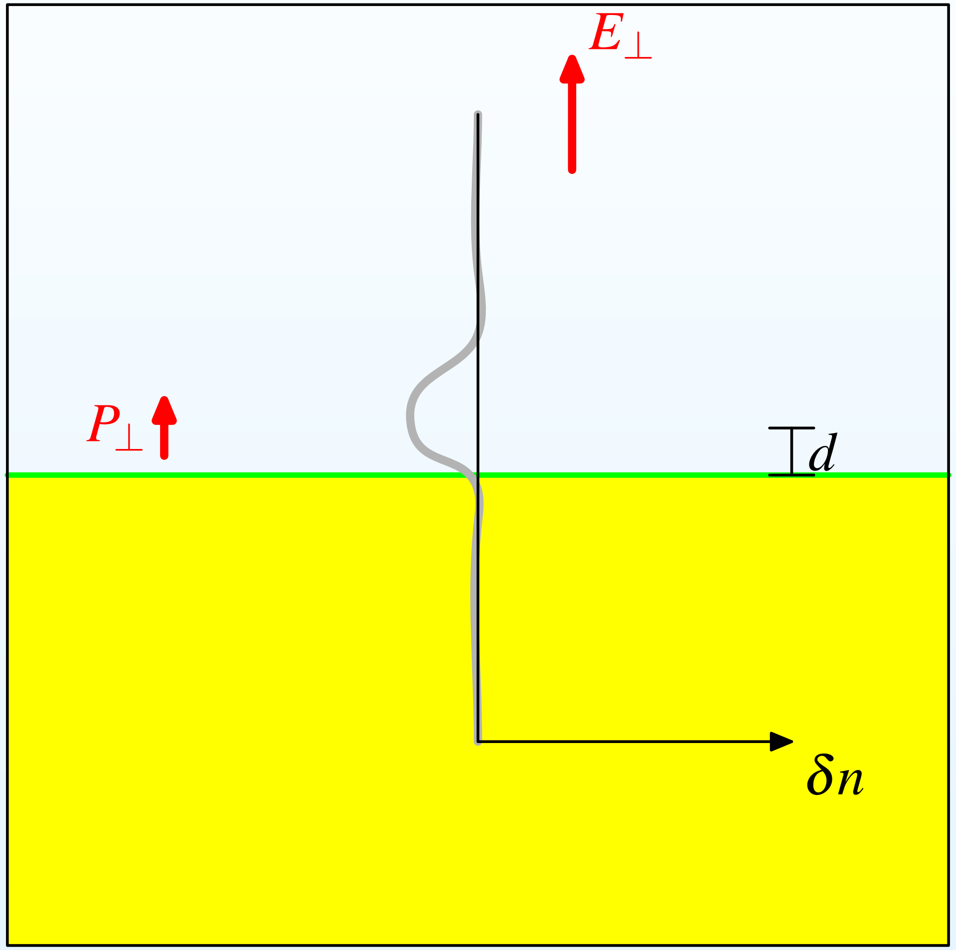

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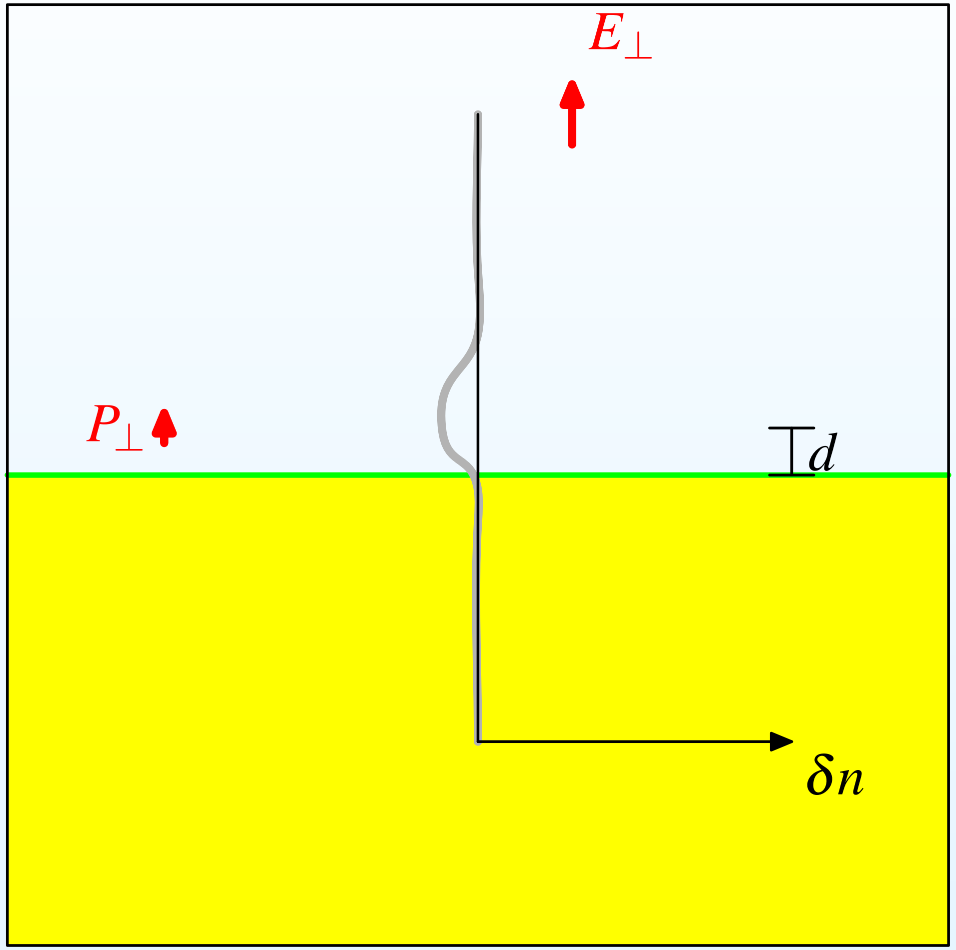

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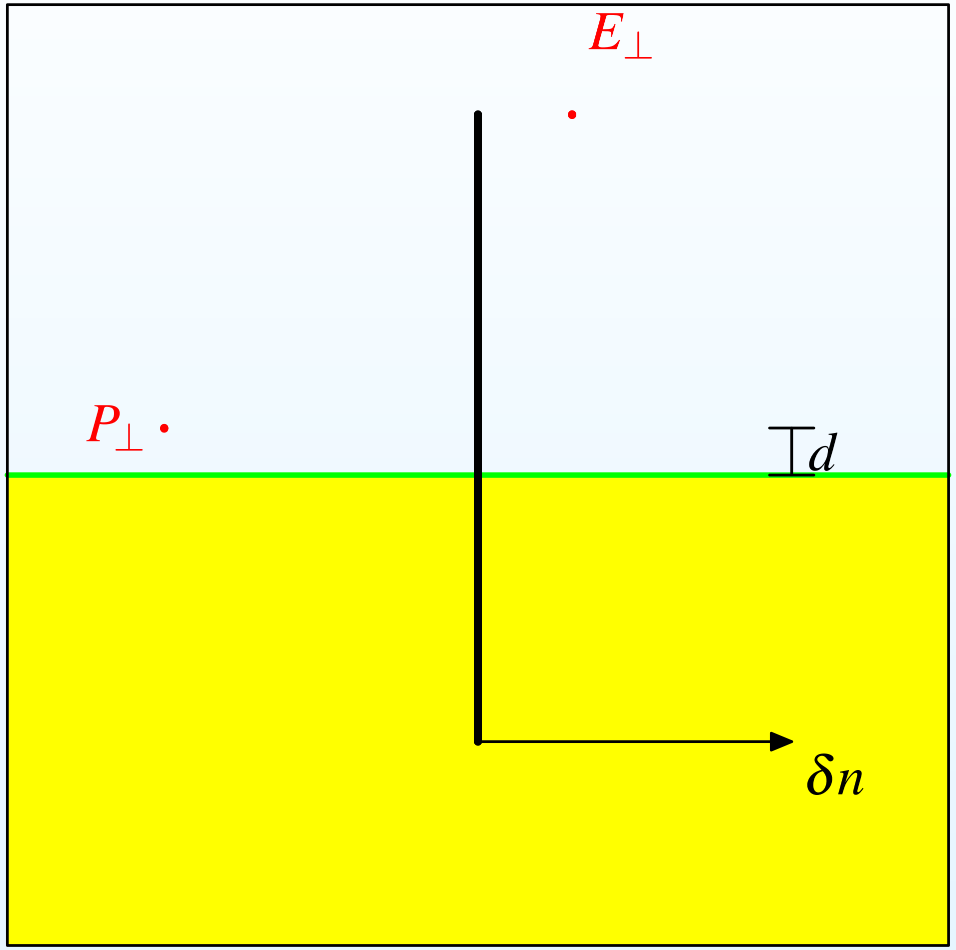

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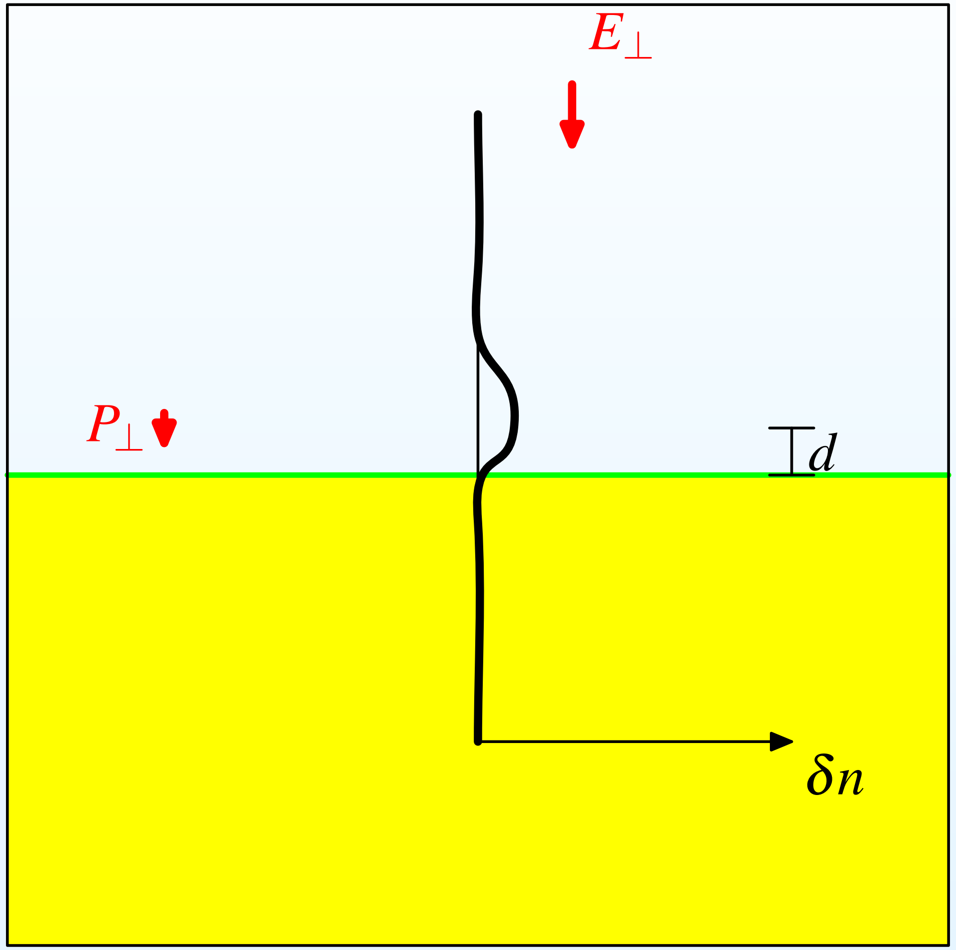

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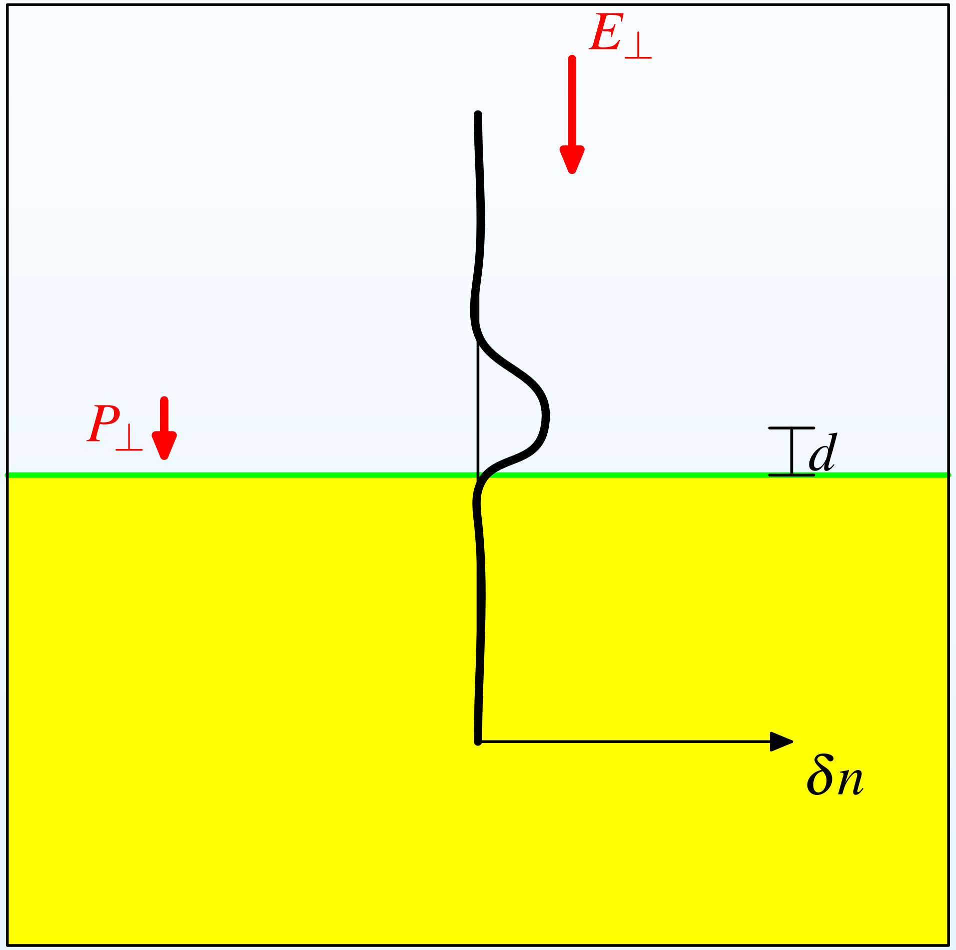

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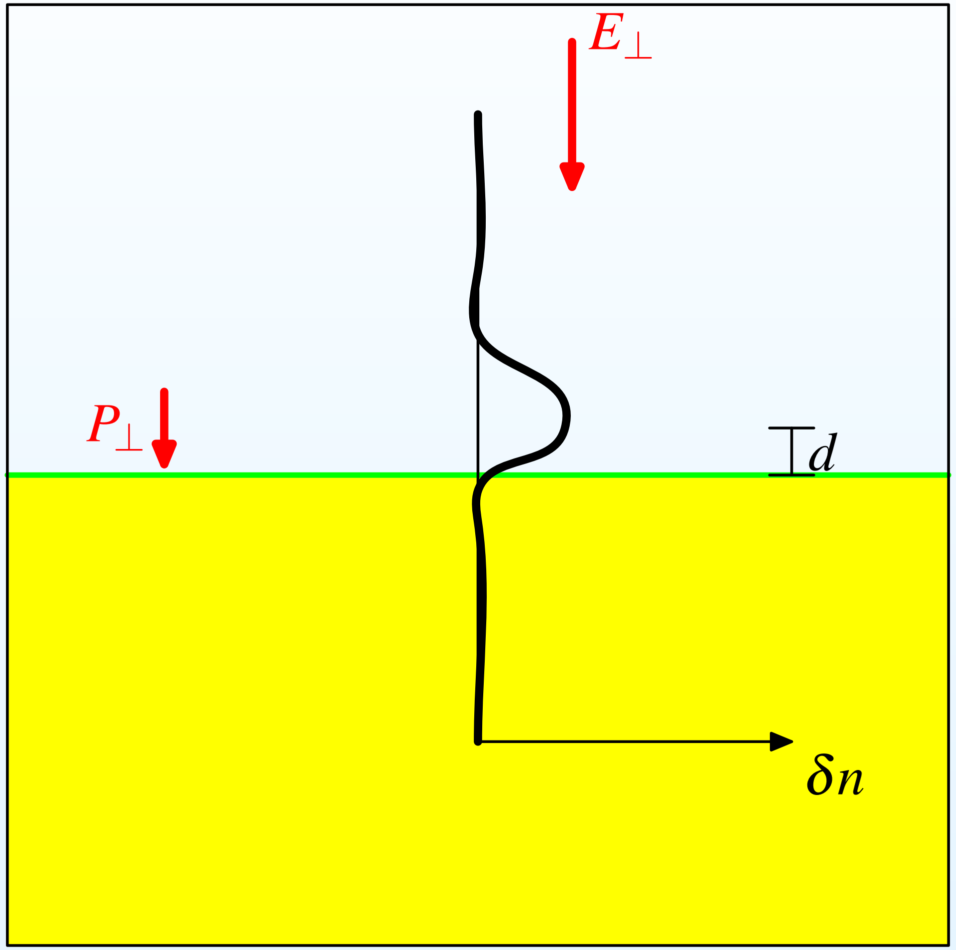

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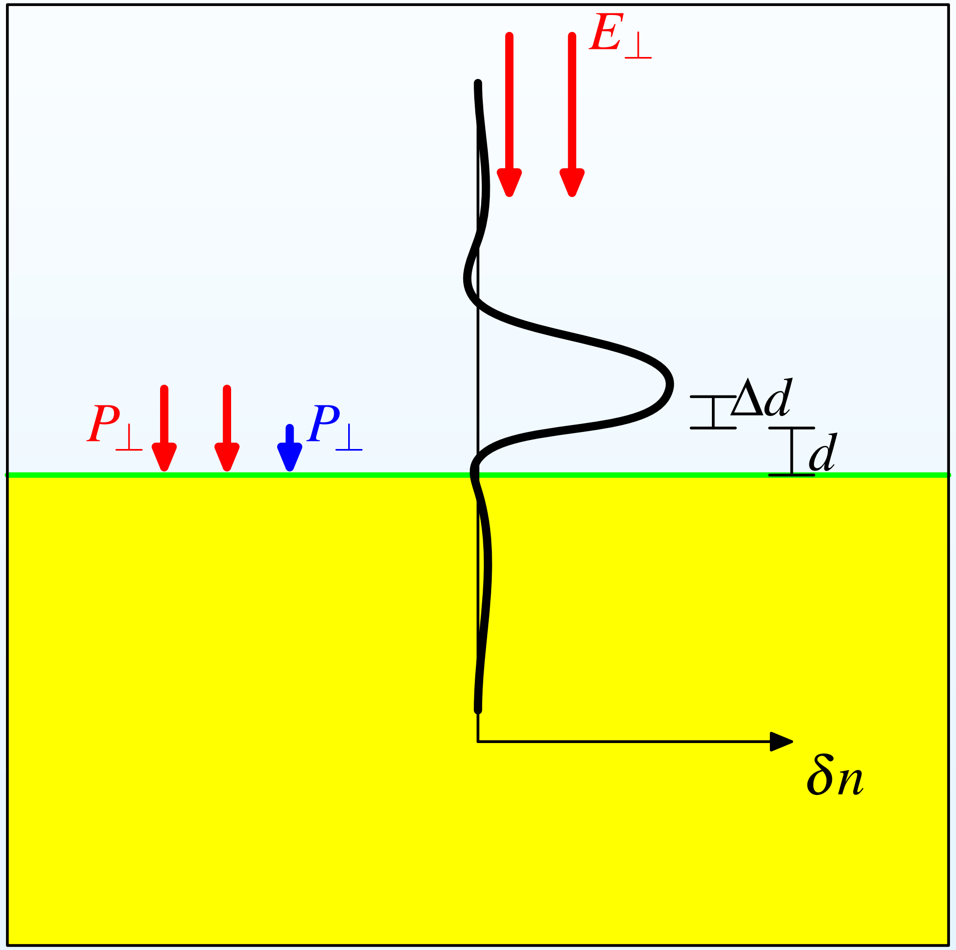
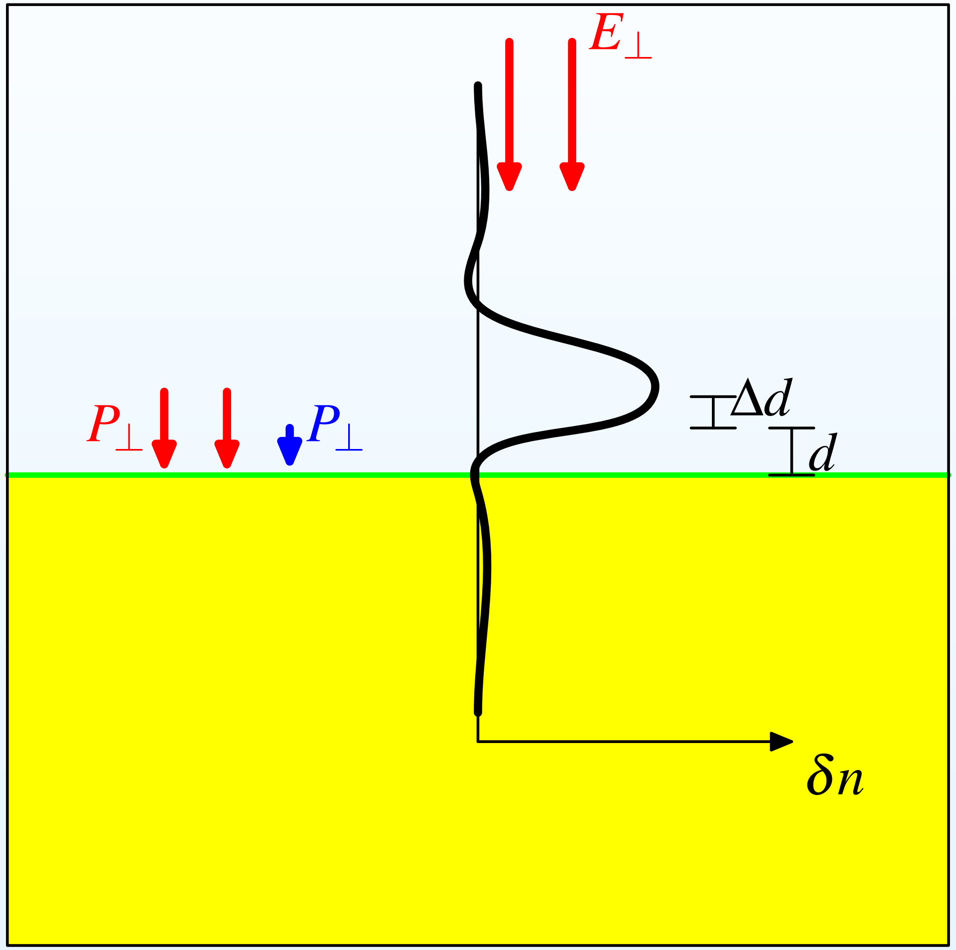


$$\chi_{\perp\perp\perp} \propto a \propto \Delta d$$

Nonlinear Surface Response: a



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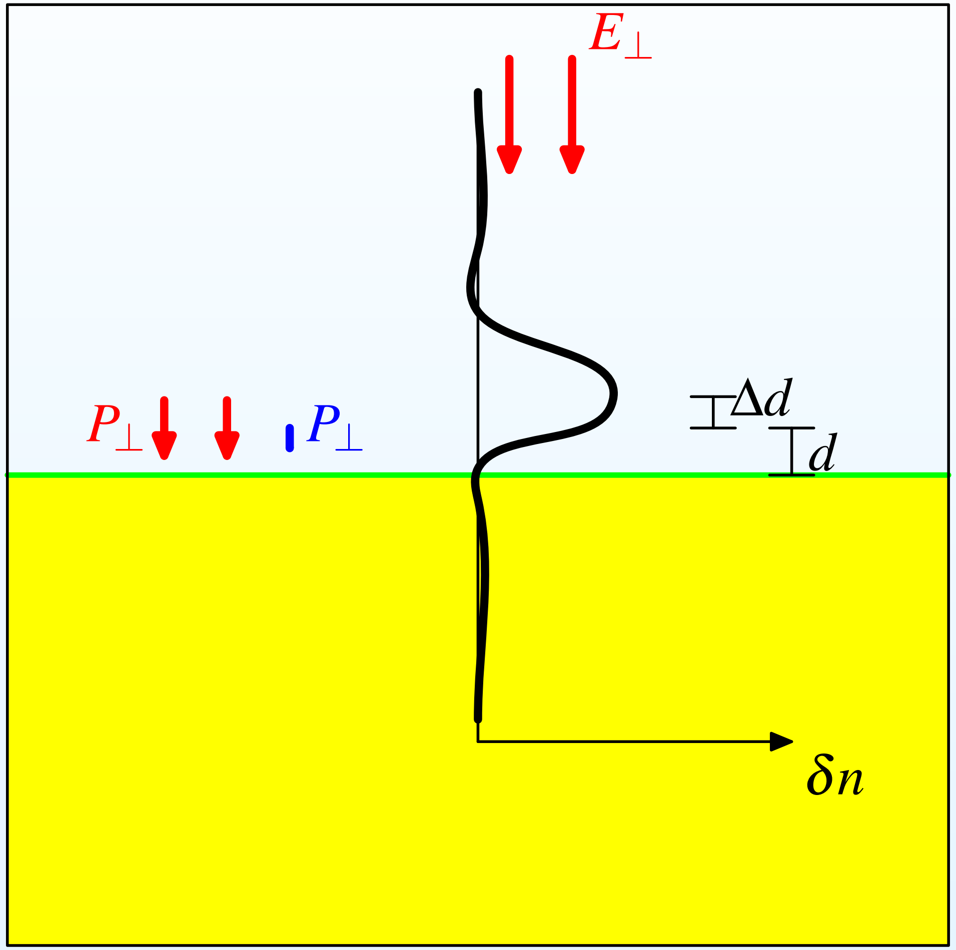

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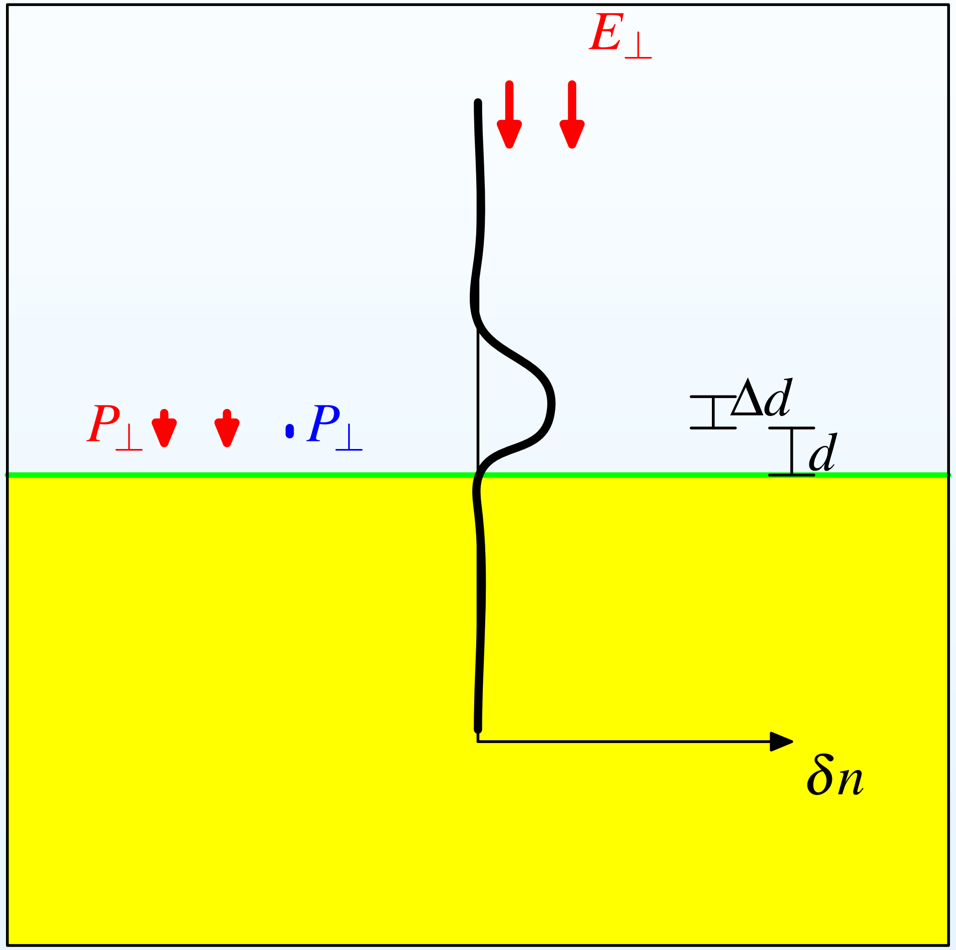

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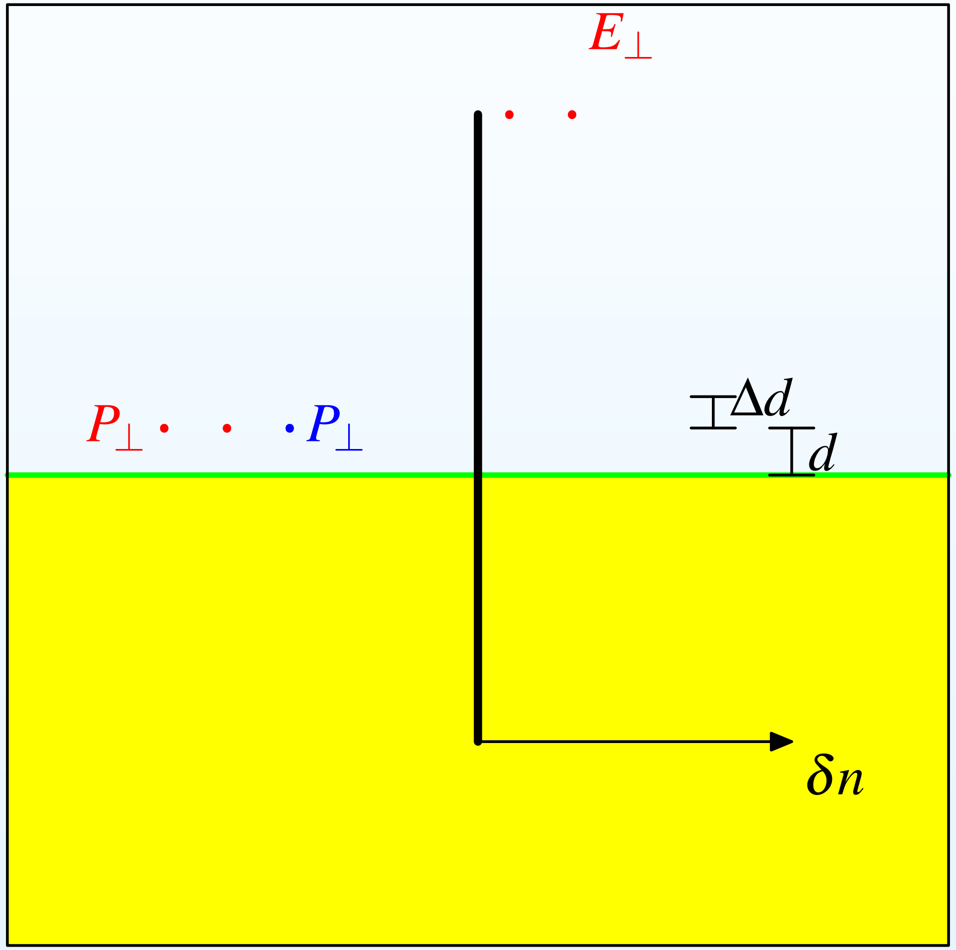

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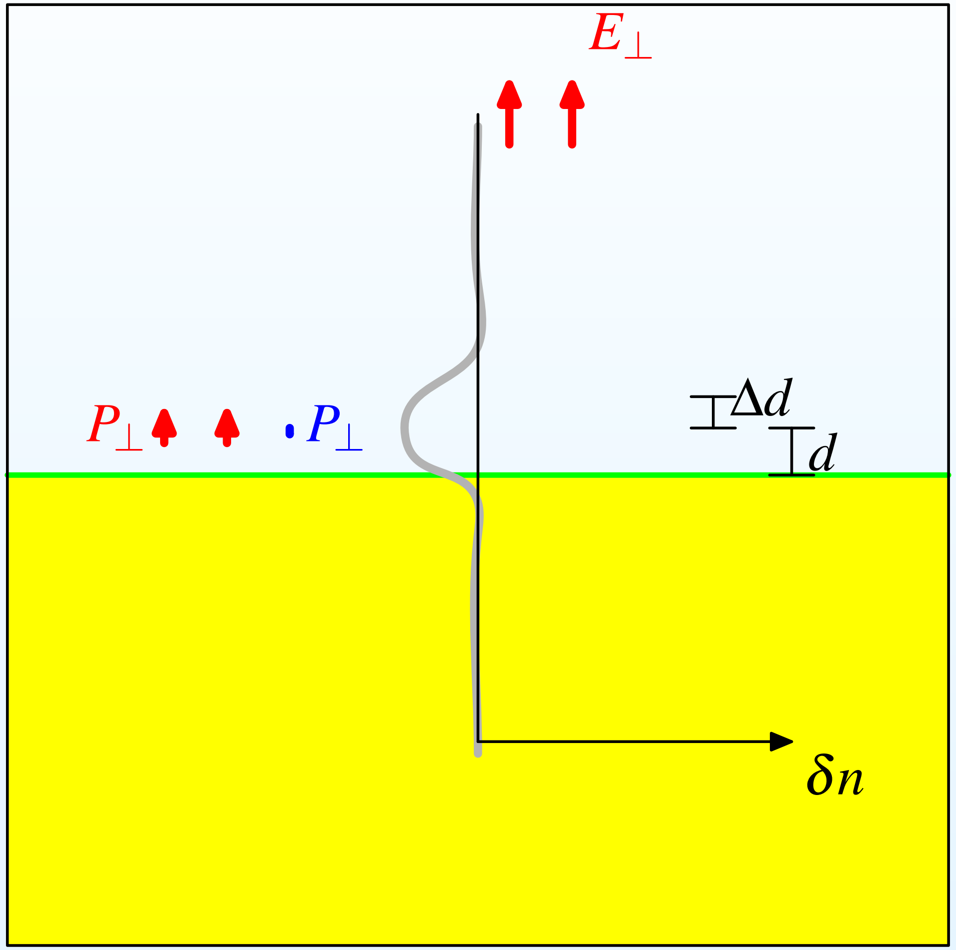

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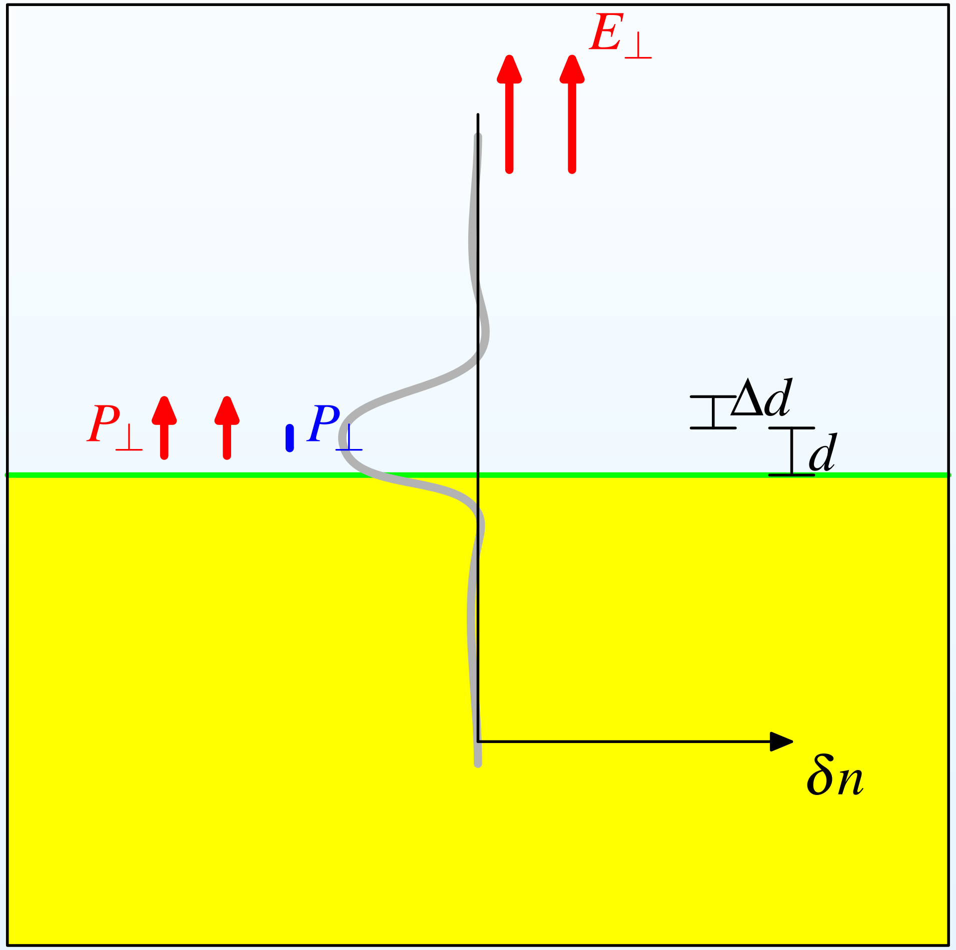

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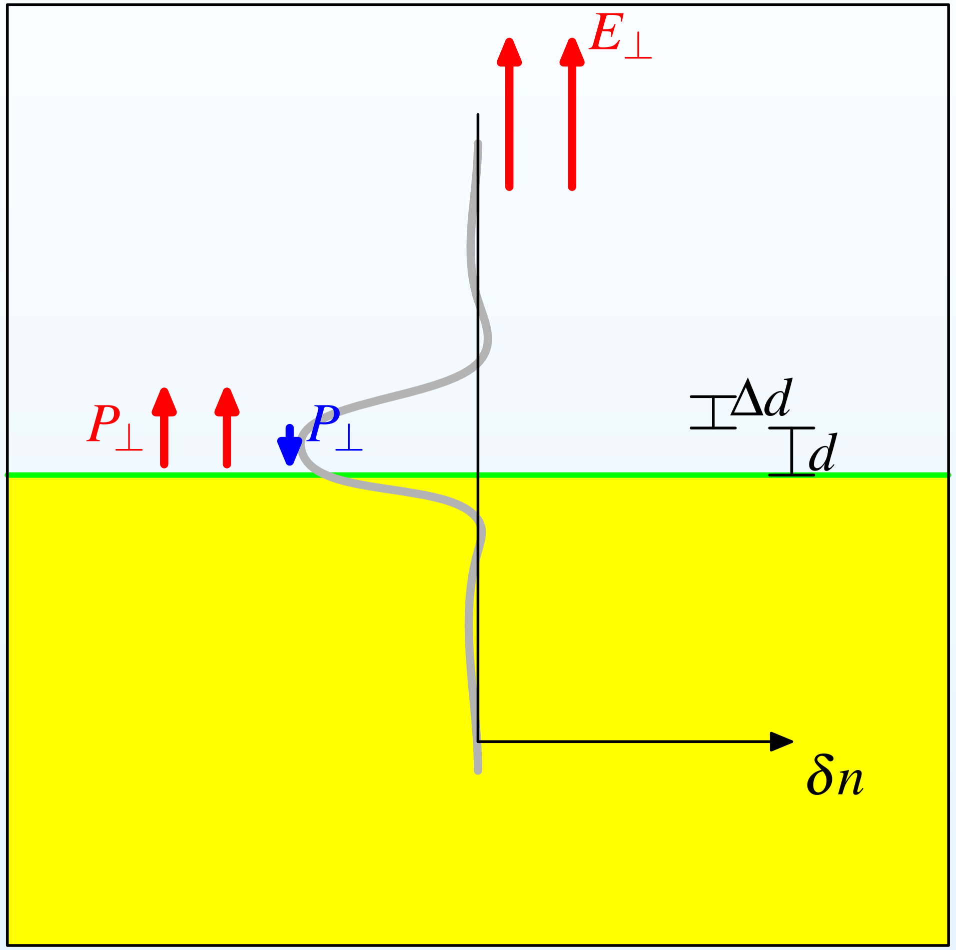

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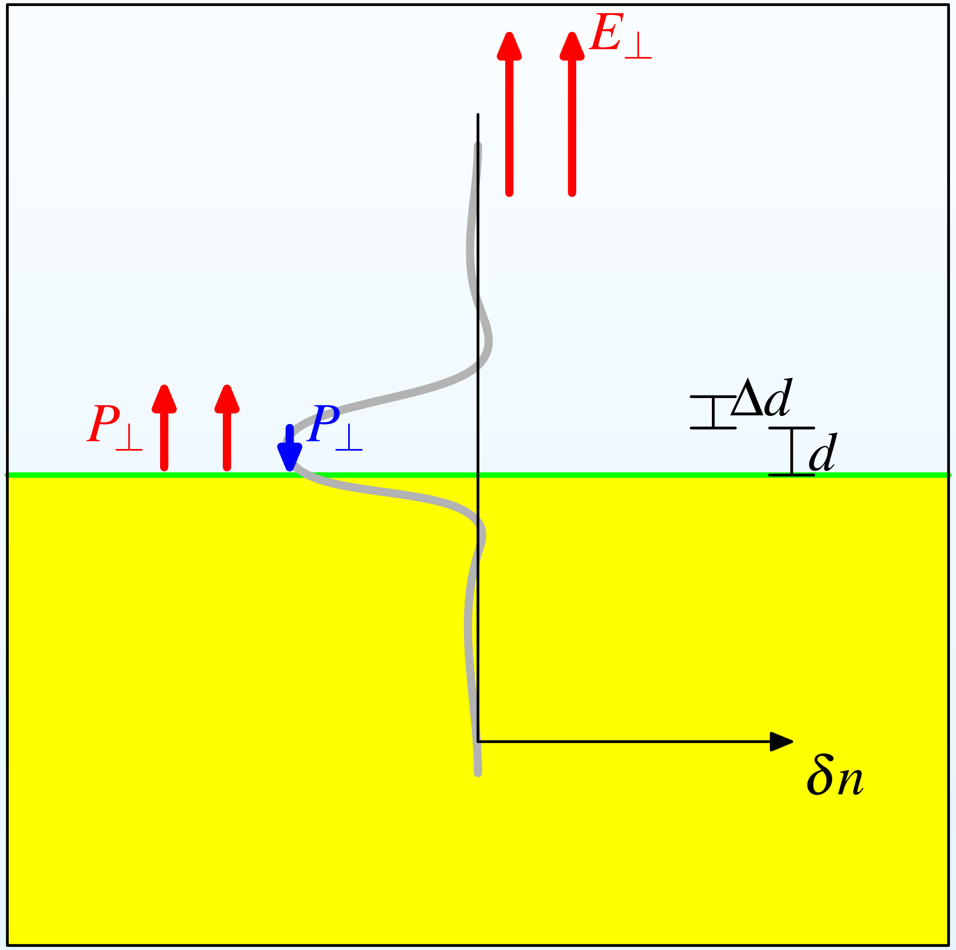

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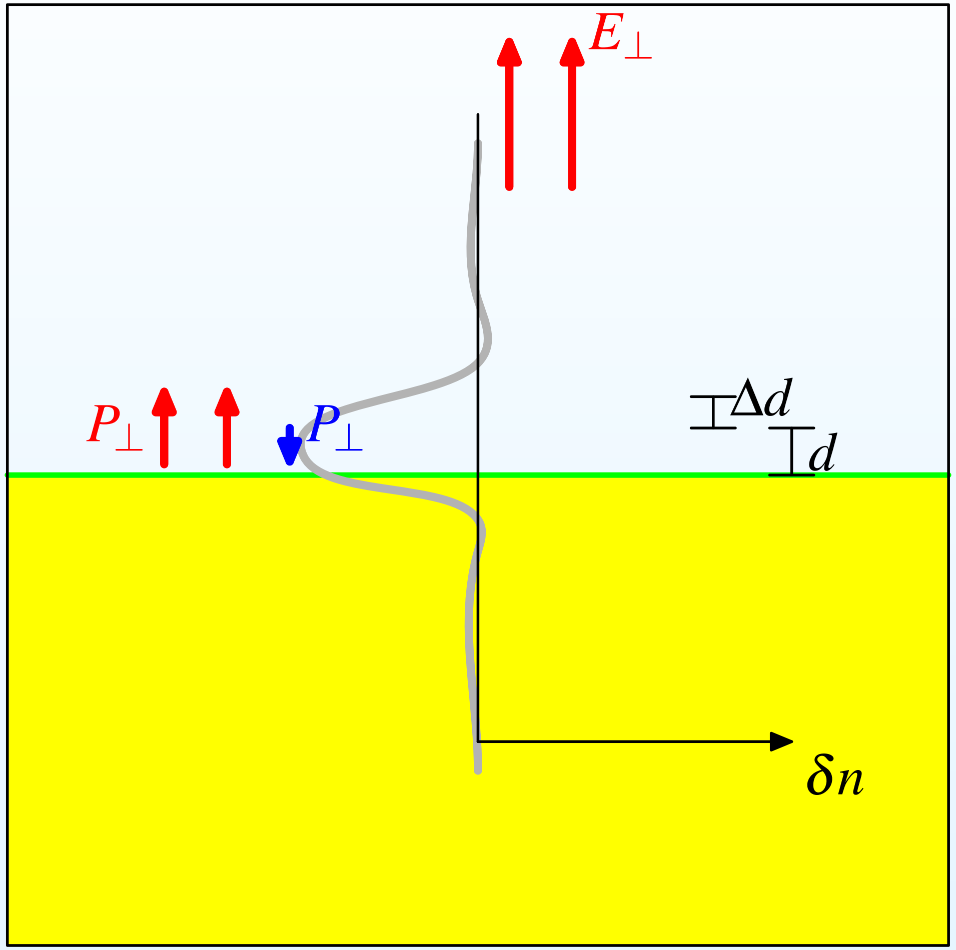

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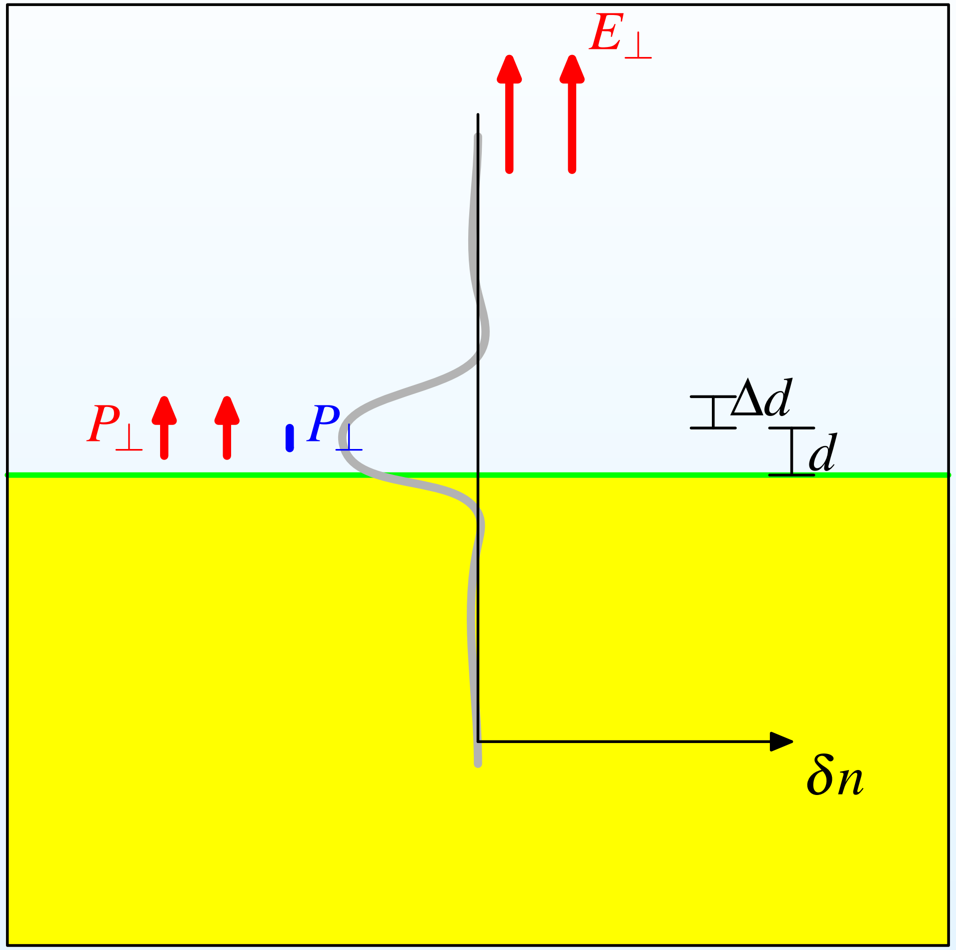

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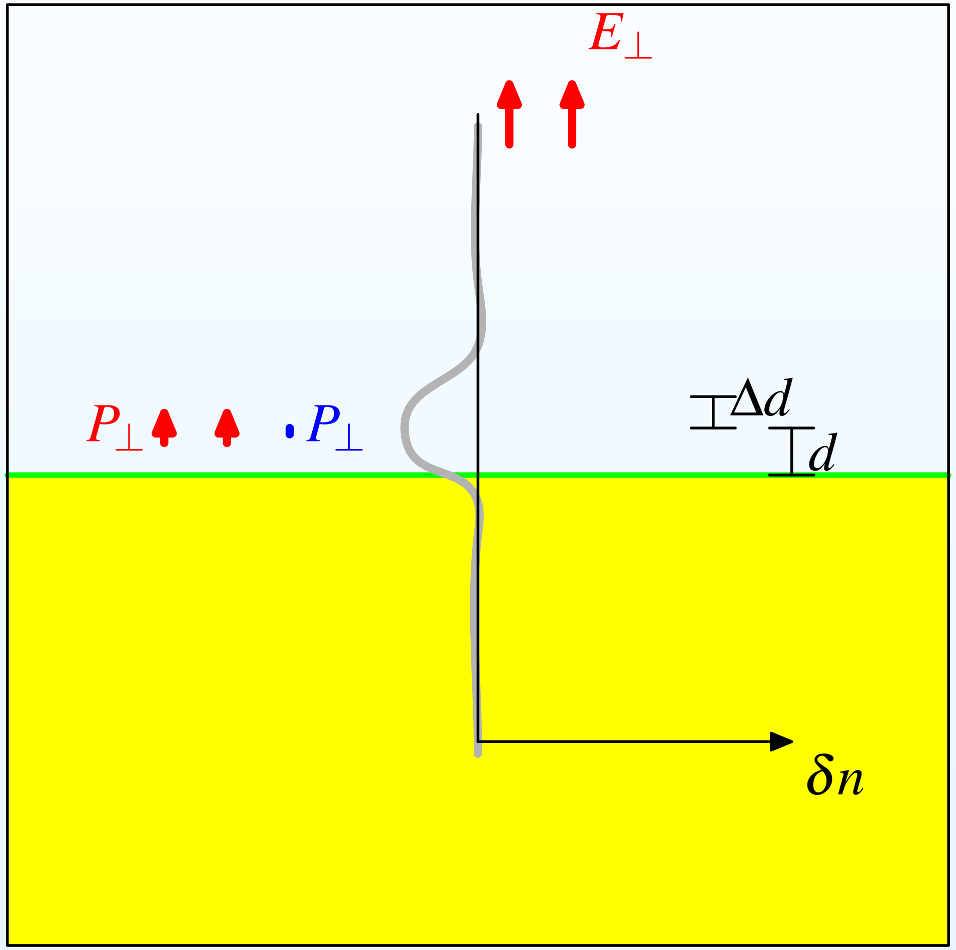

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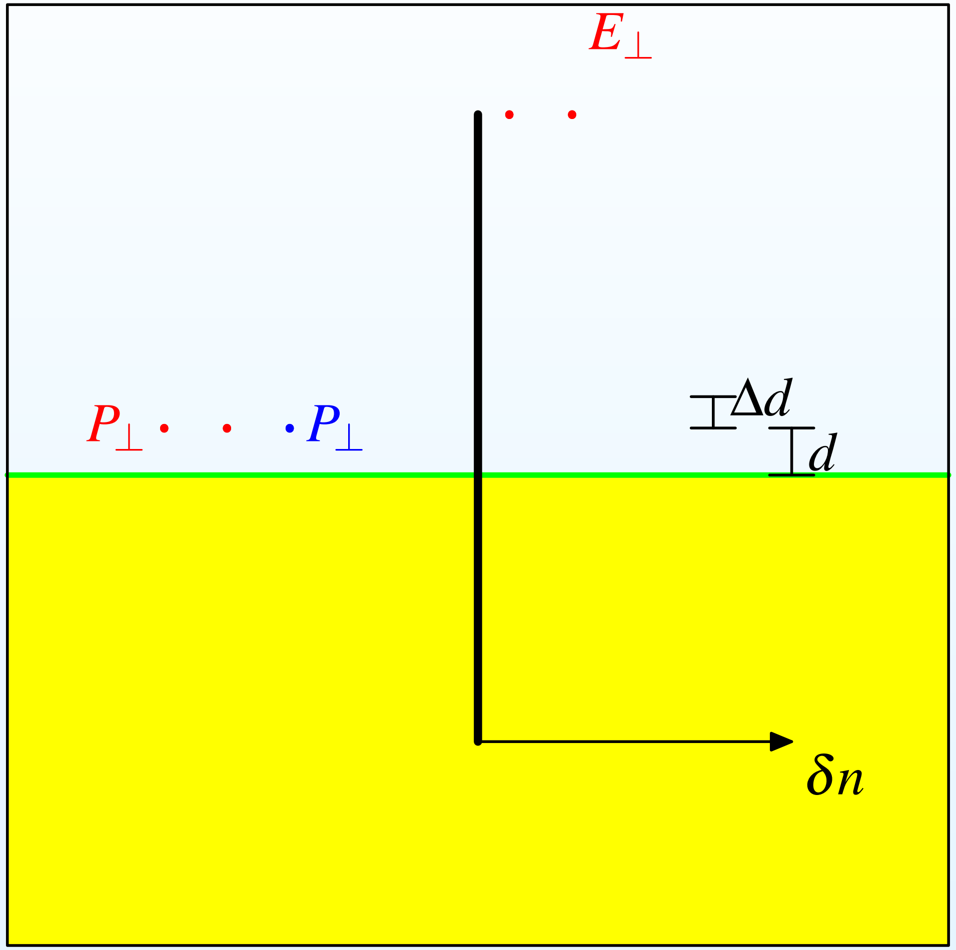

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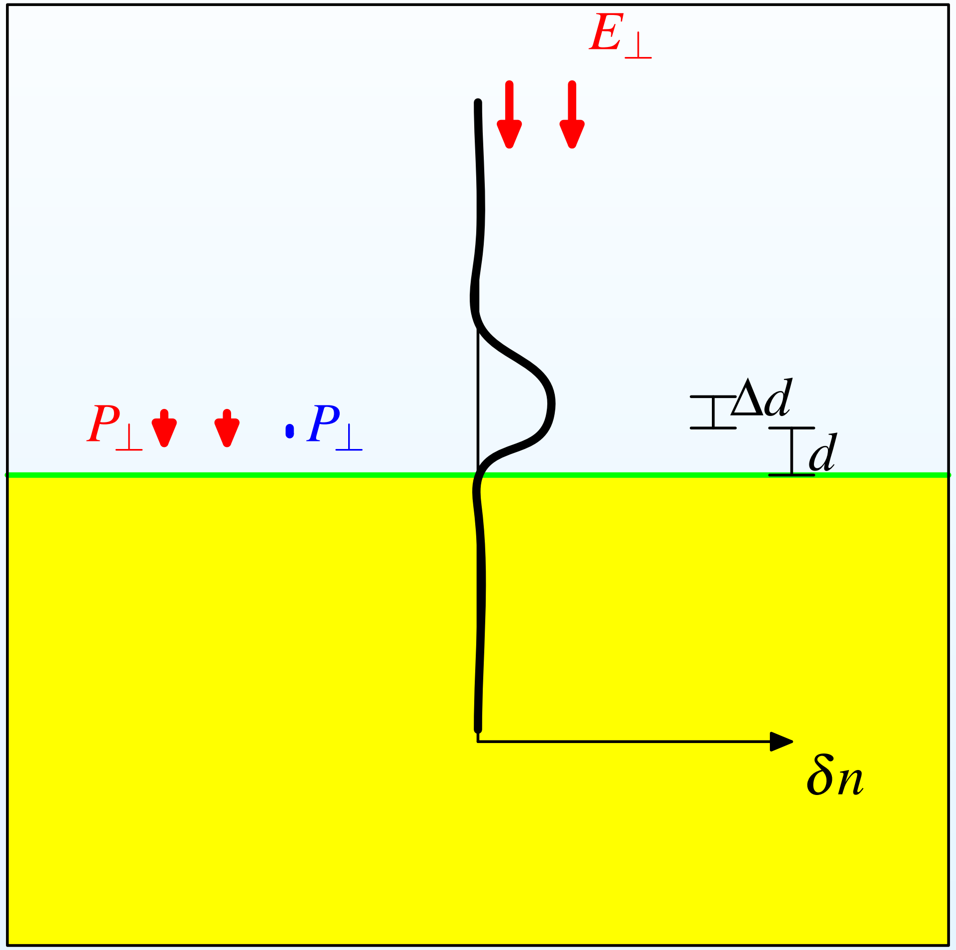

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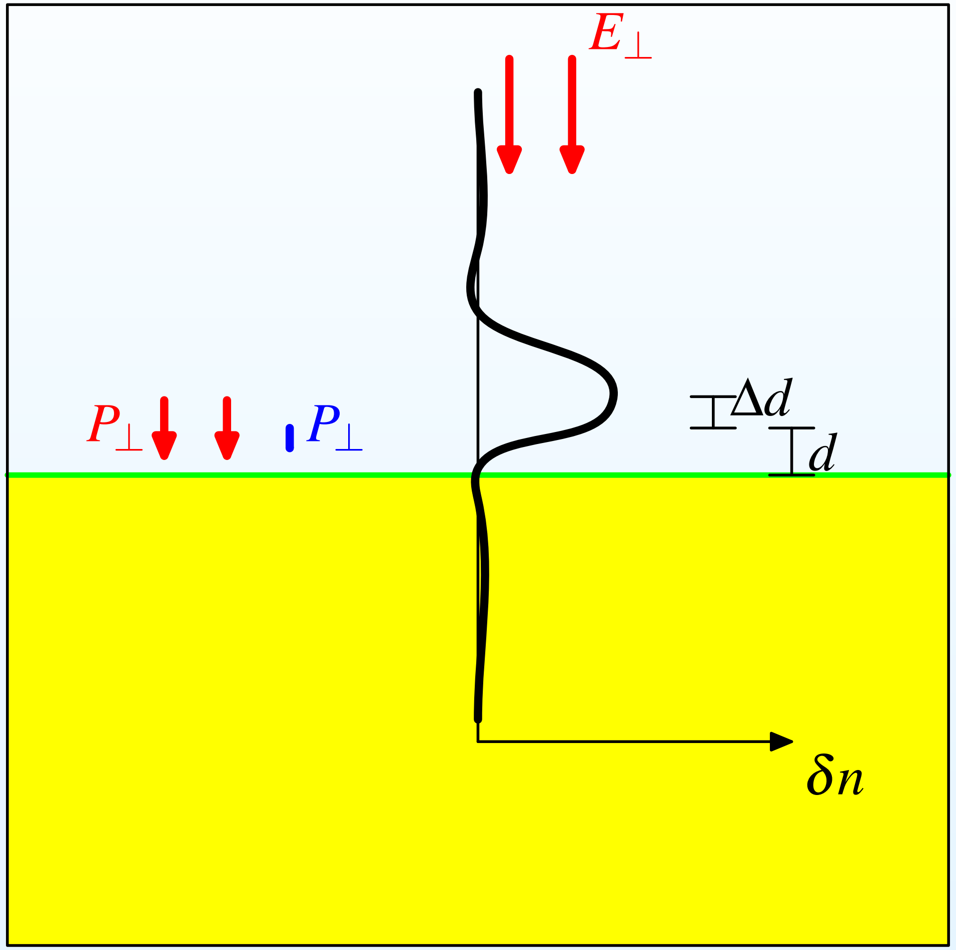

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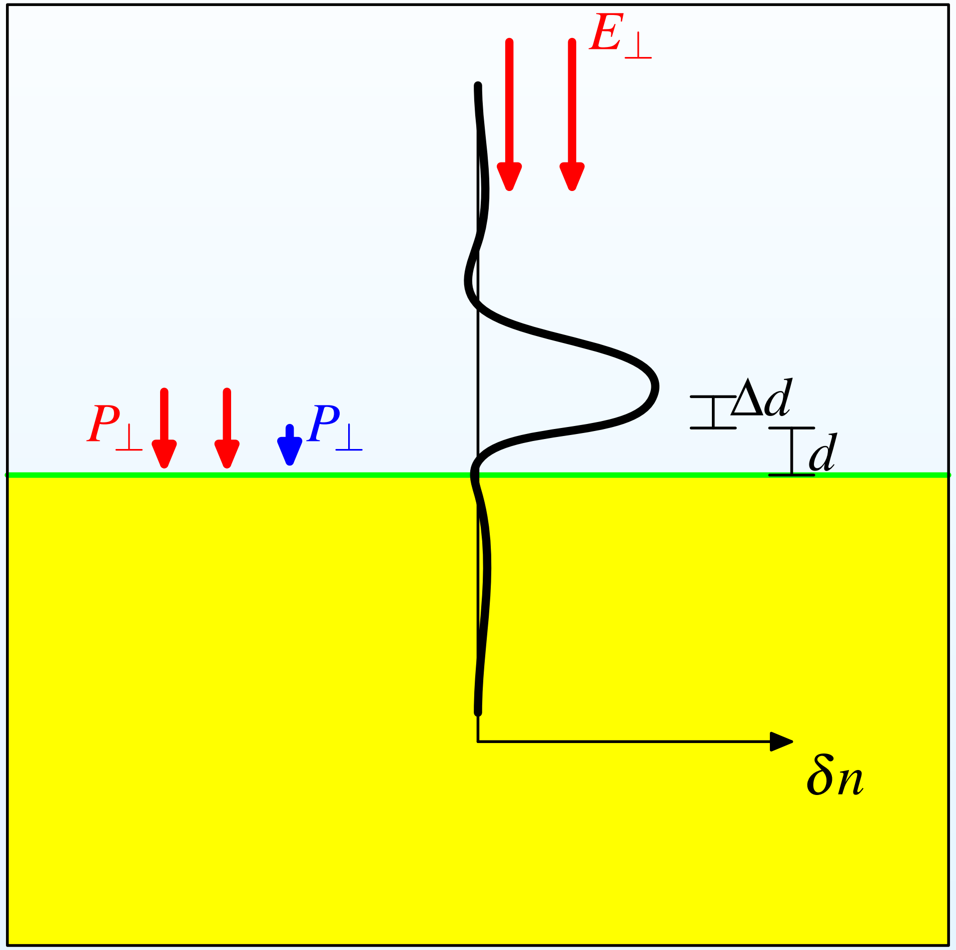

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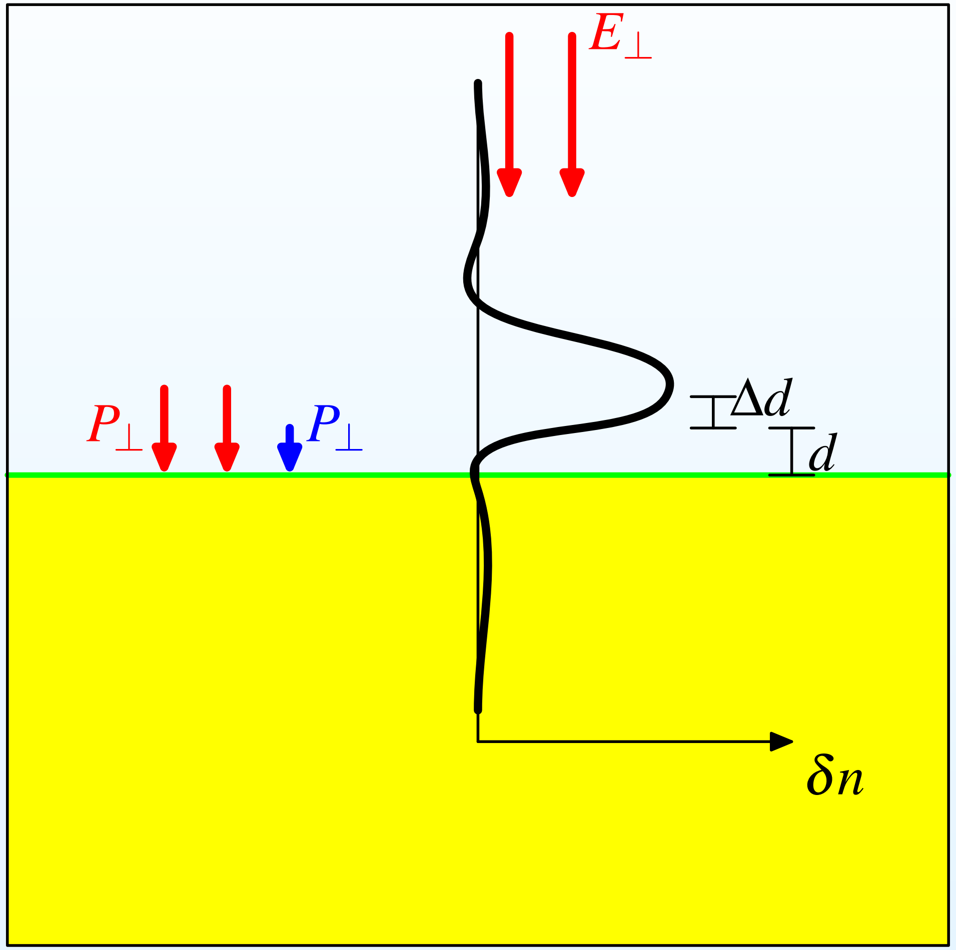

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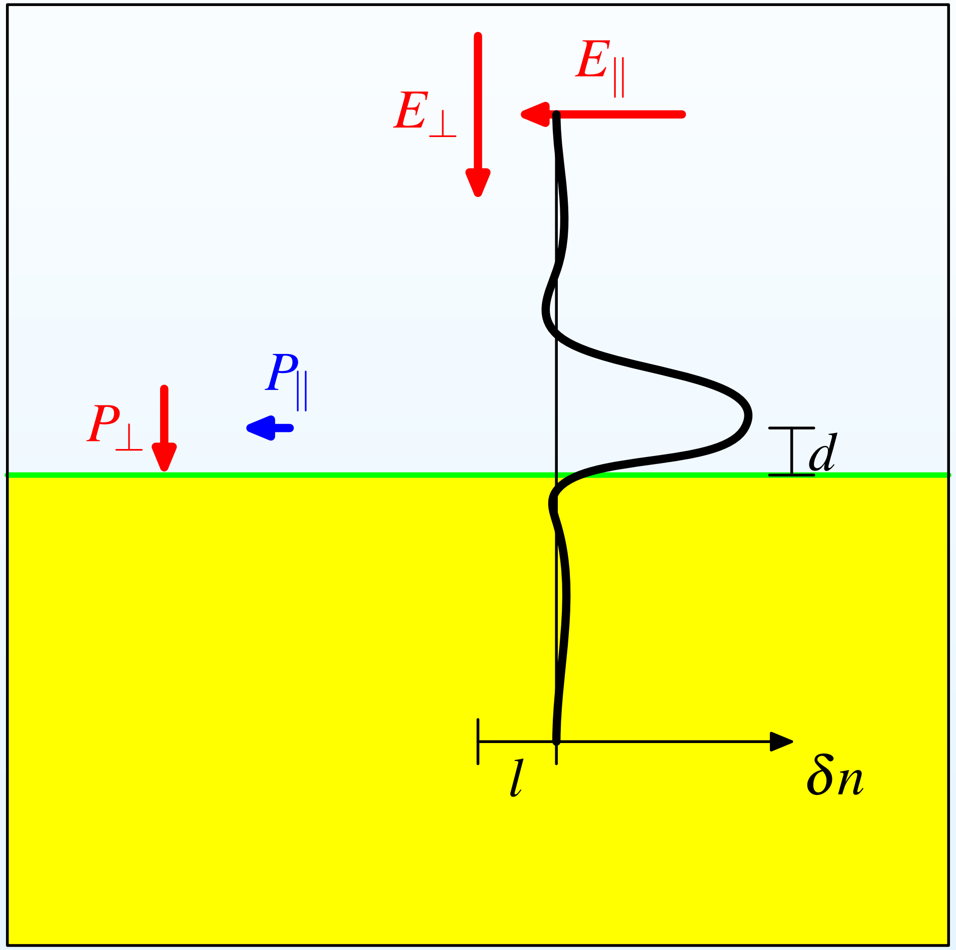
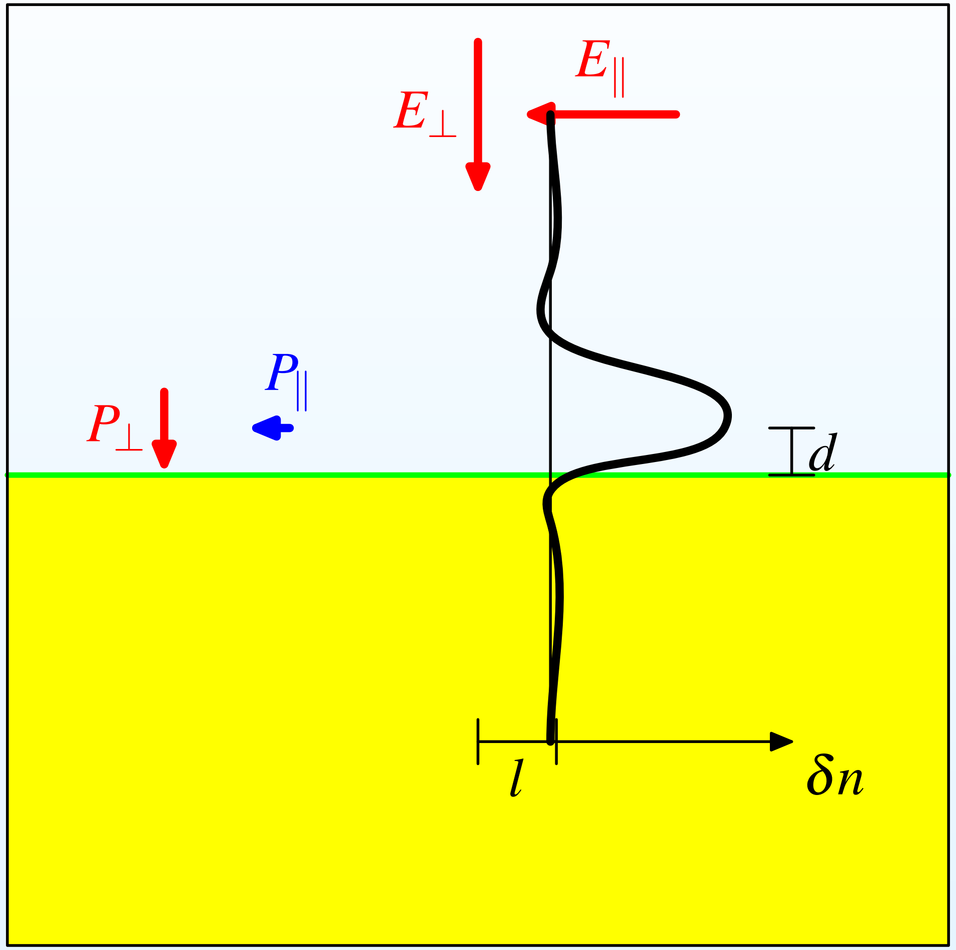
Nonlinear Surface Response: b



$$\chi_{\parallel\perp\parallel} \propto b \propto l$$

Nonlinear Surface Response: b



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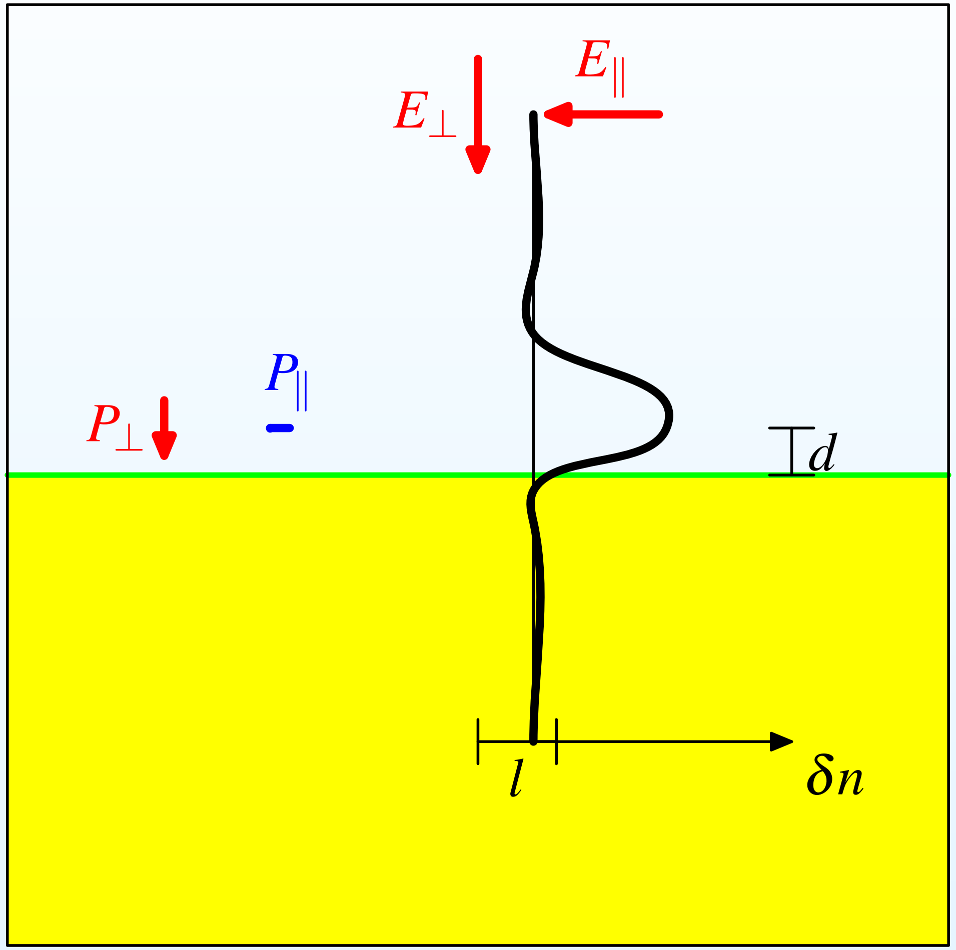

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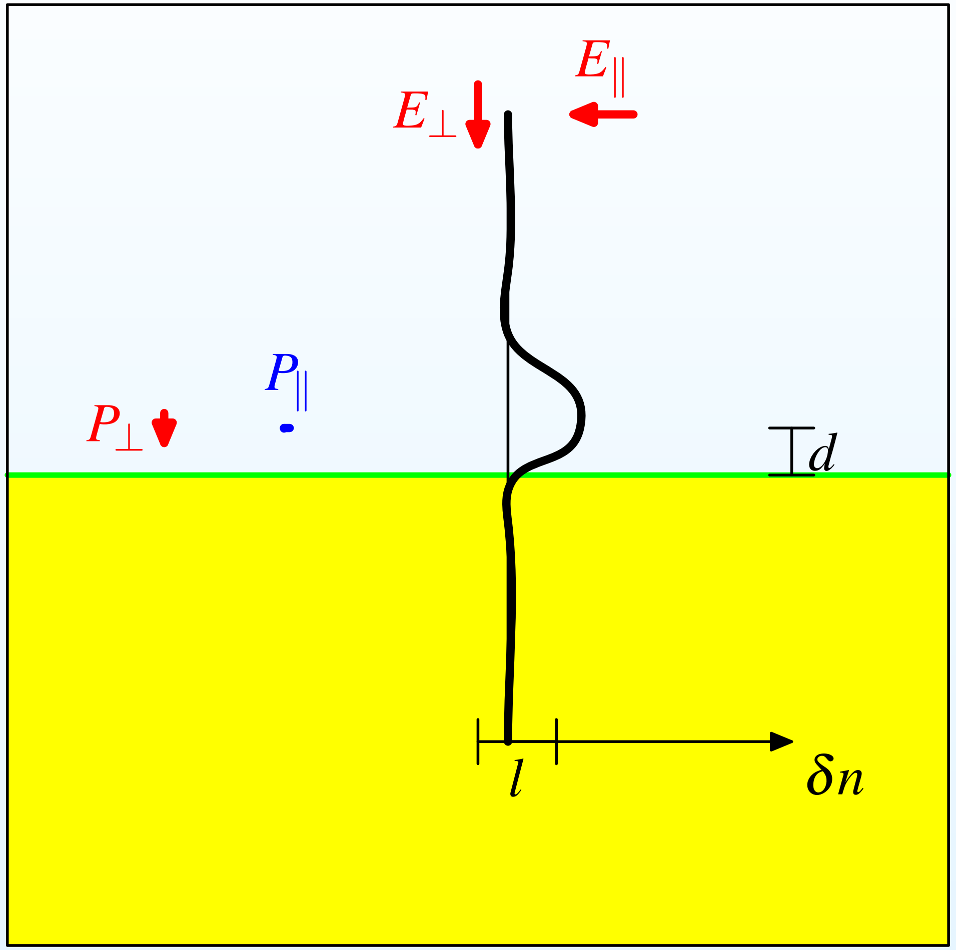

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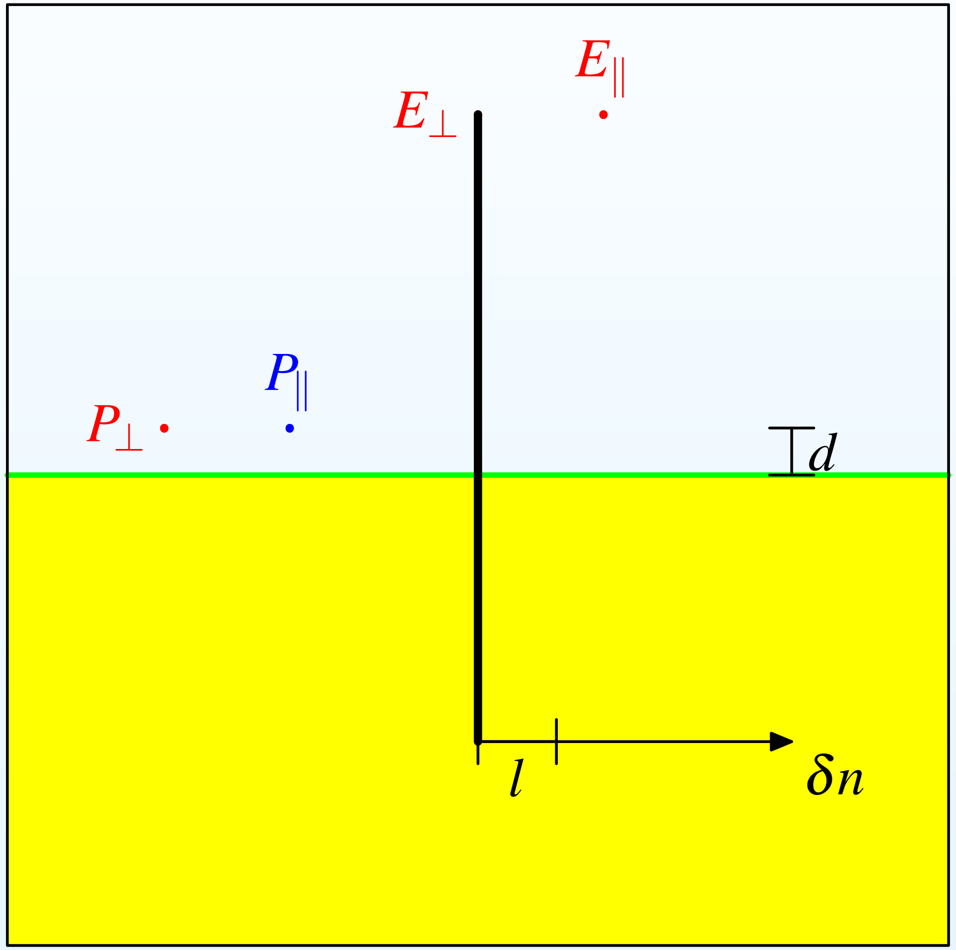

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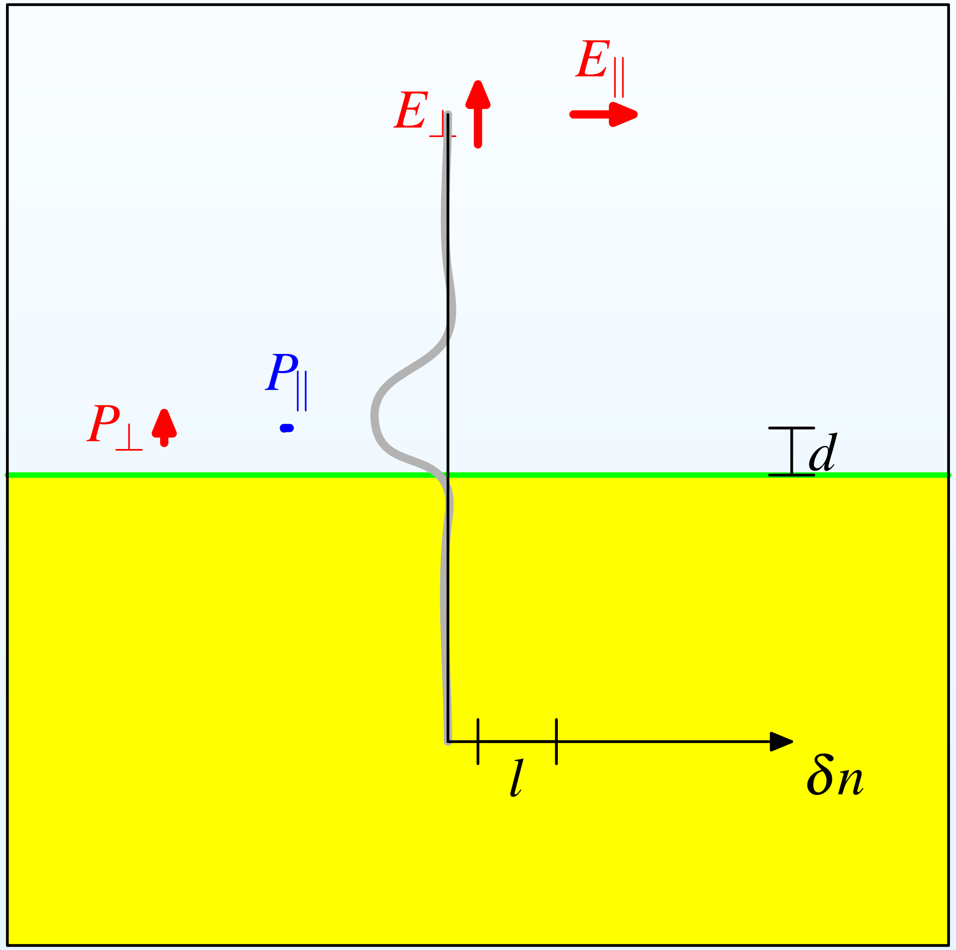

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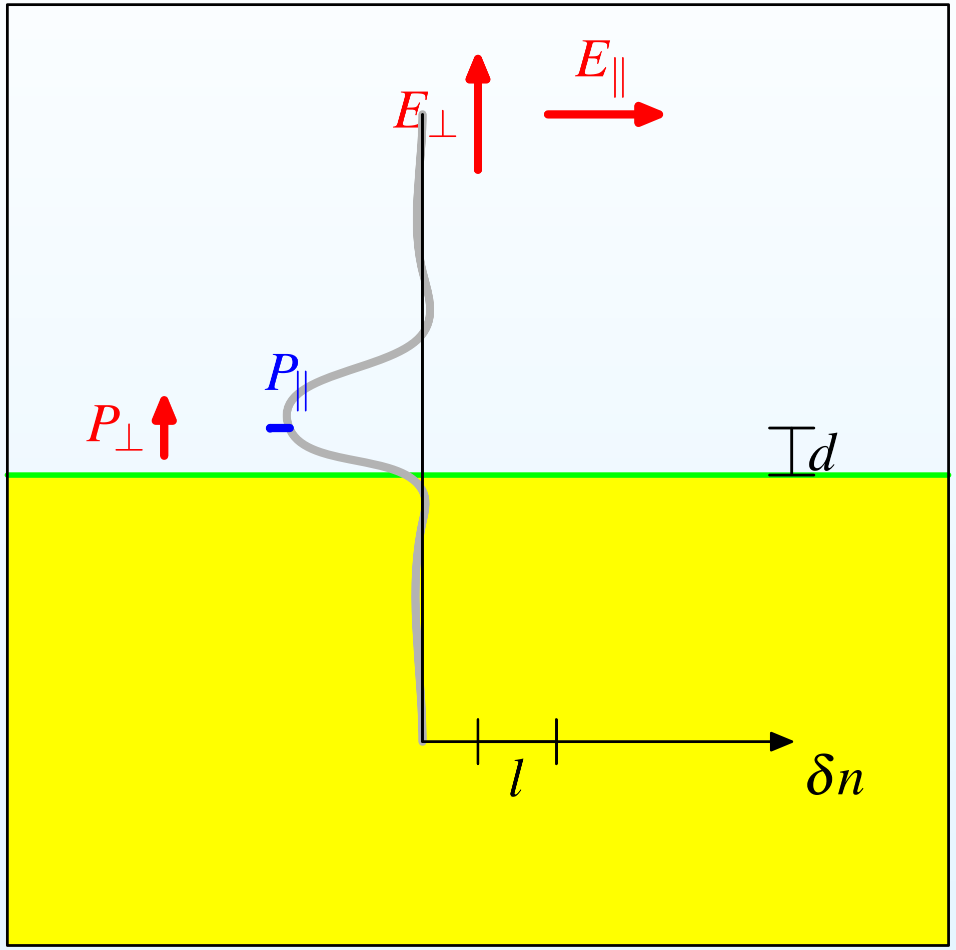

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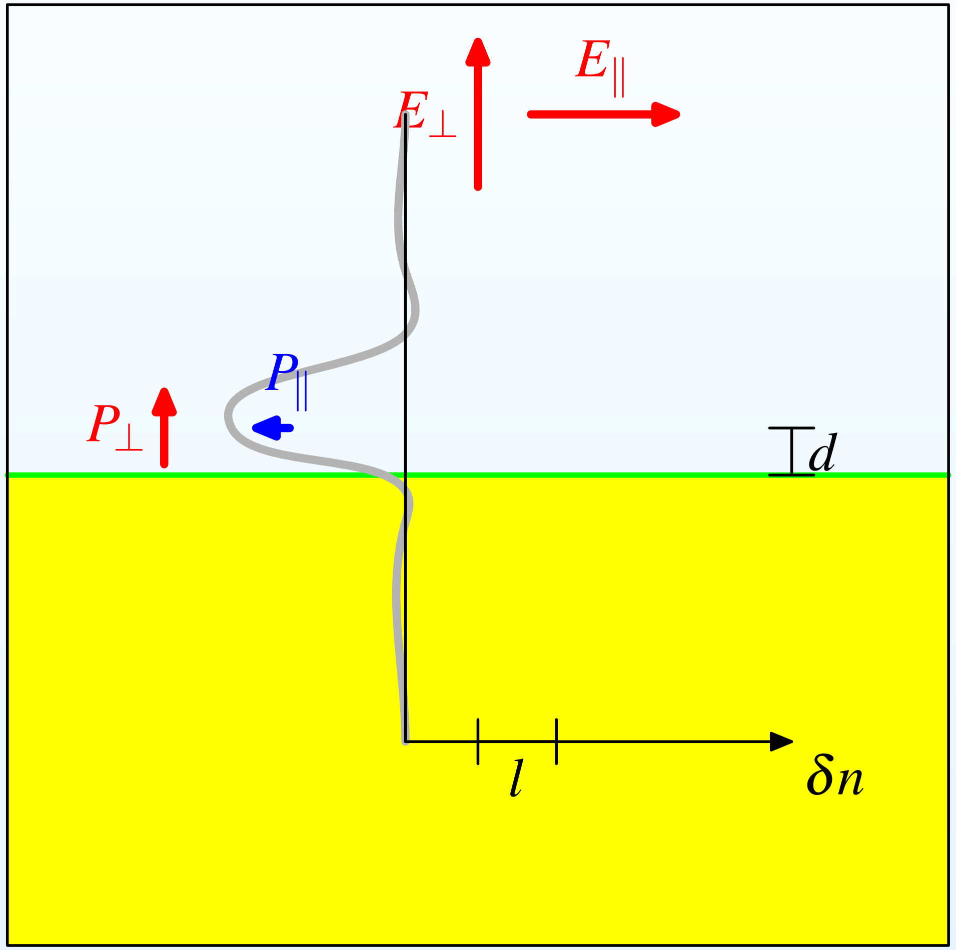

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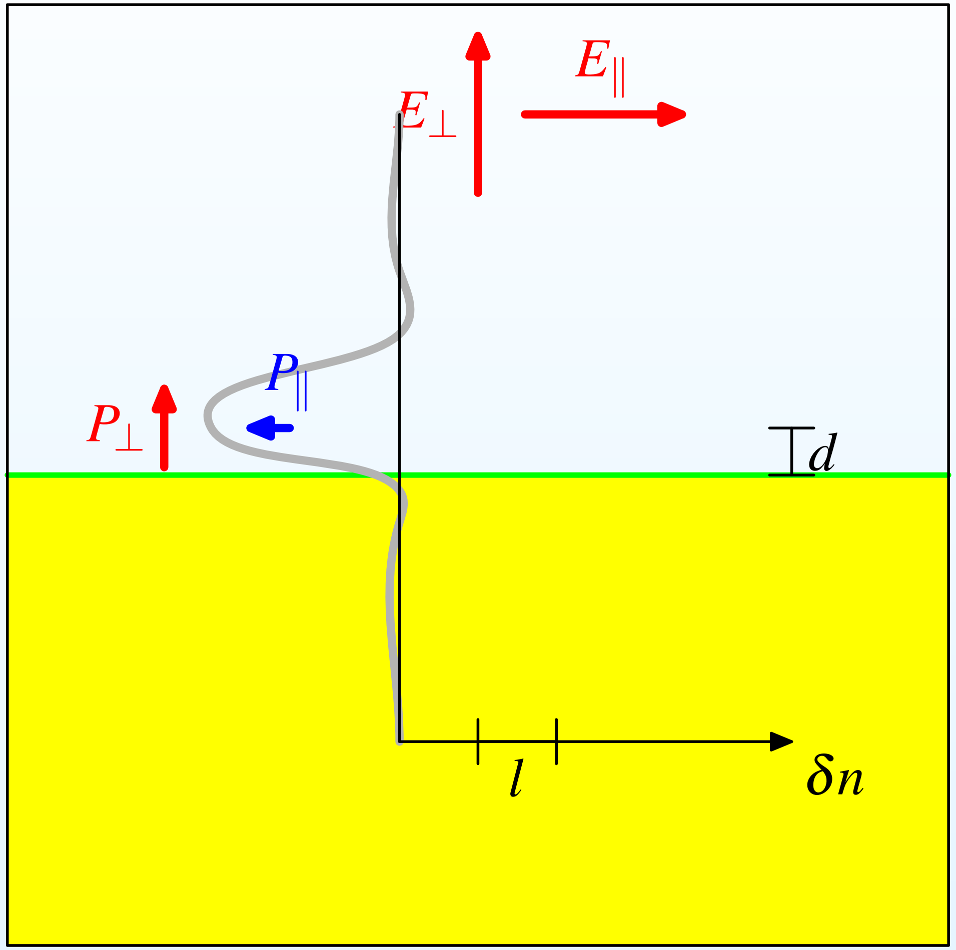

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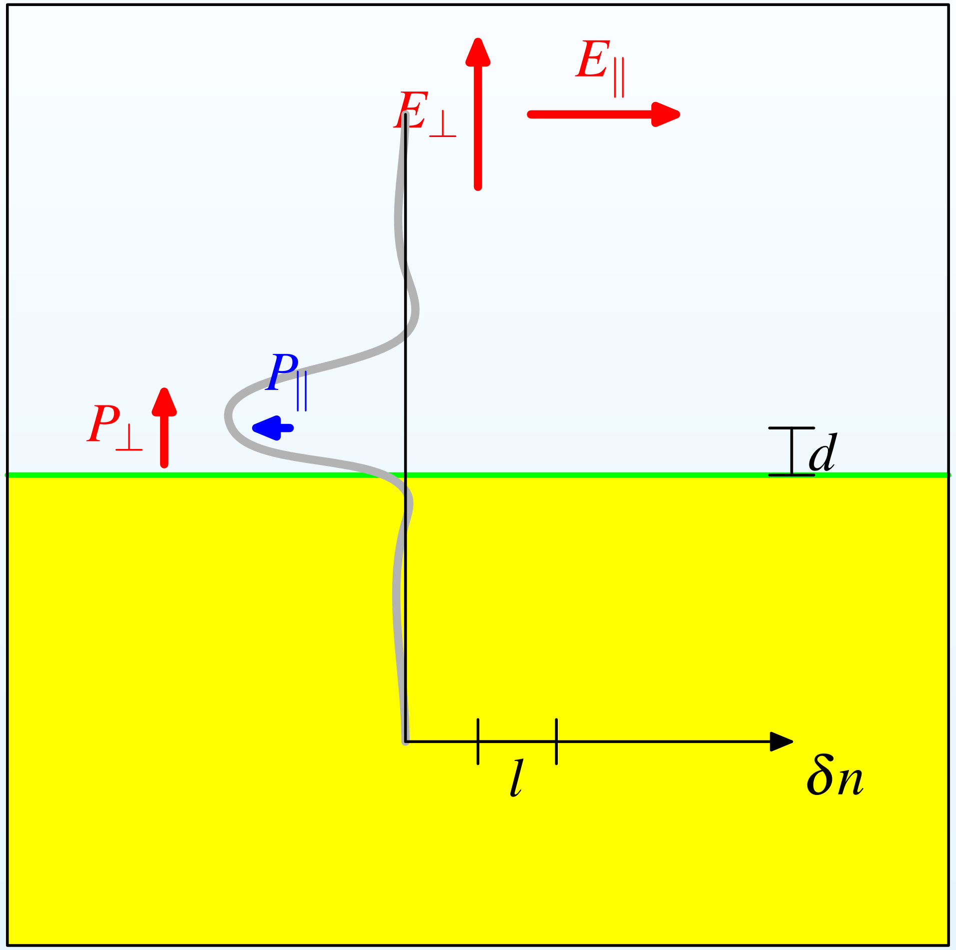

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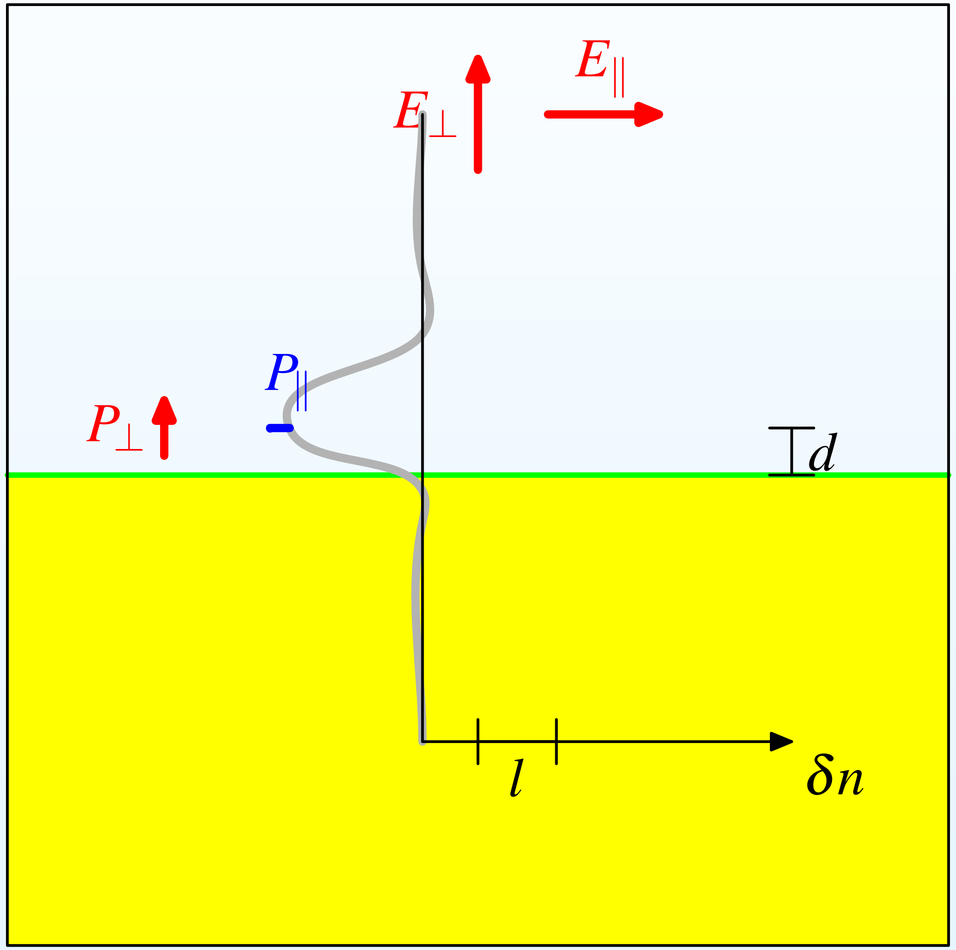

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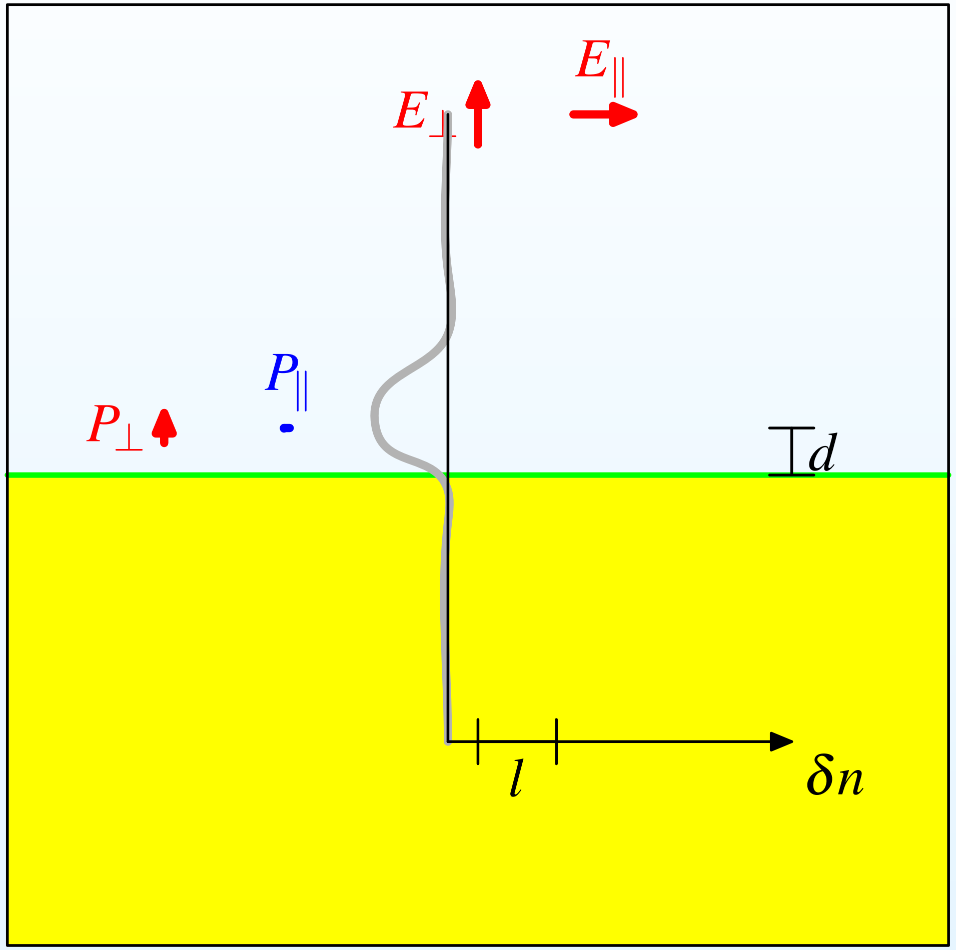

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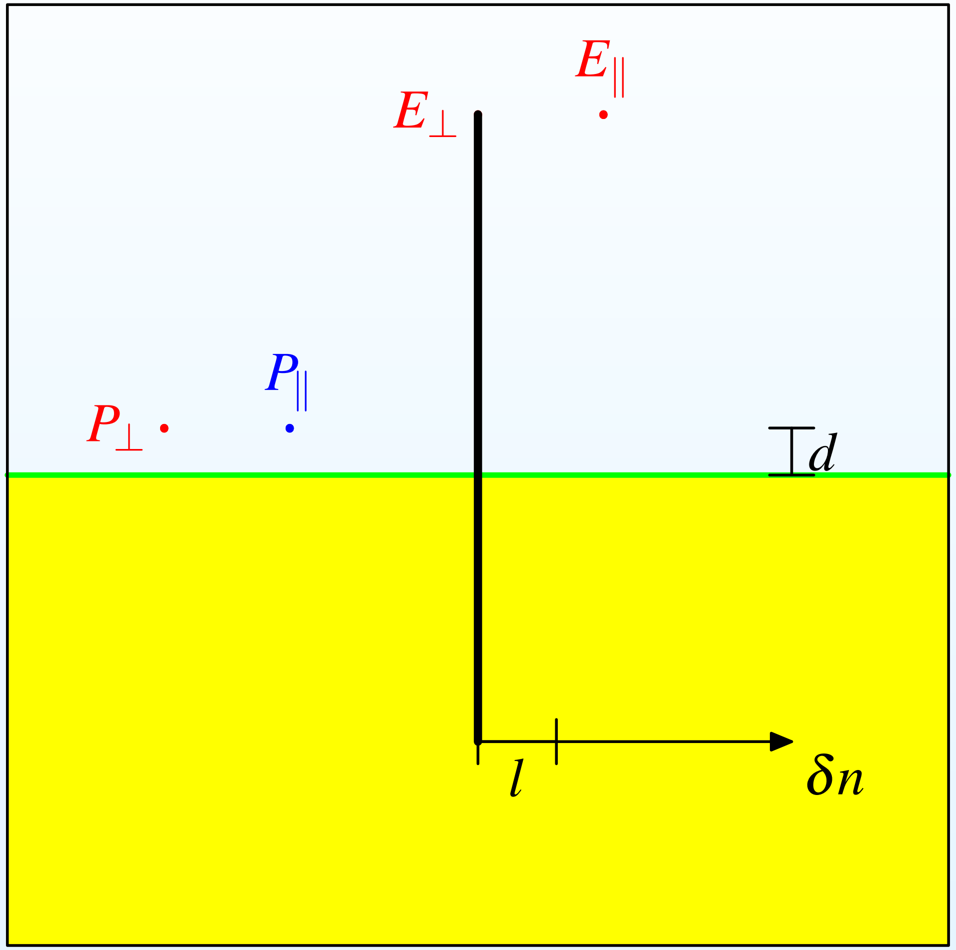
Nonlinear Surface Response: b



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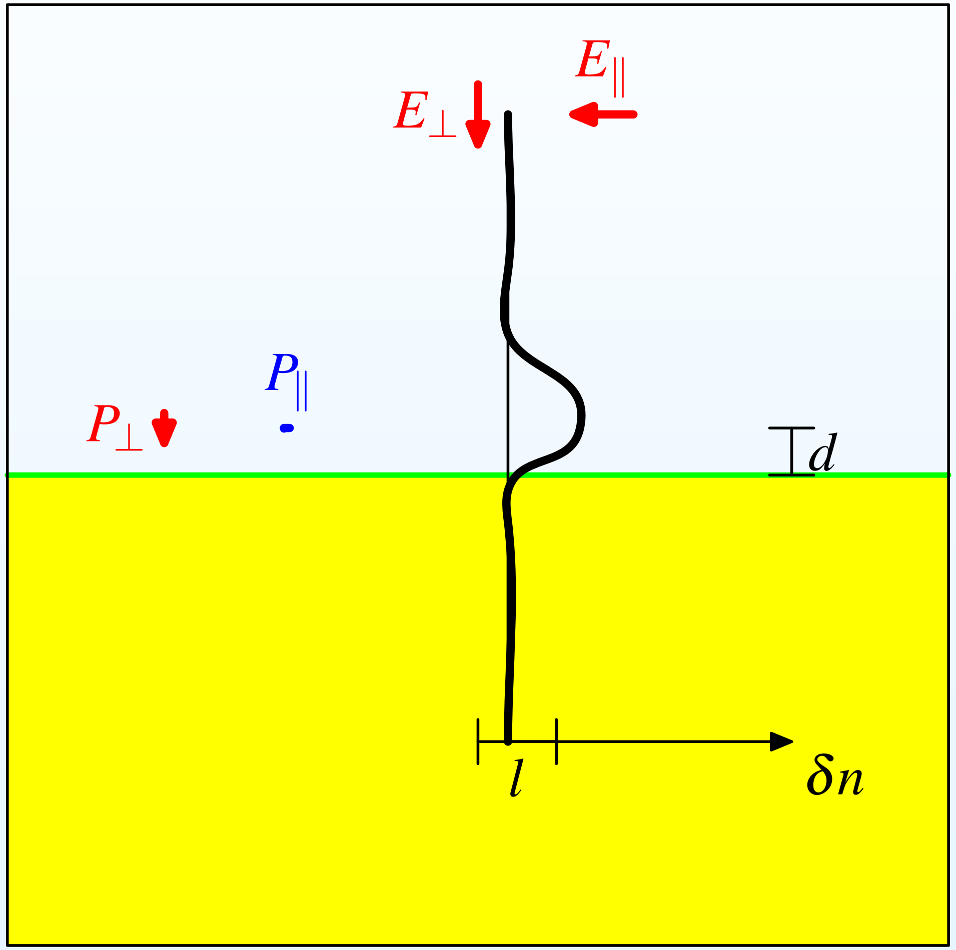

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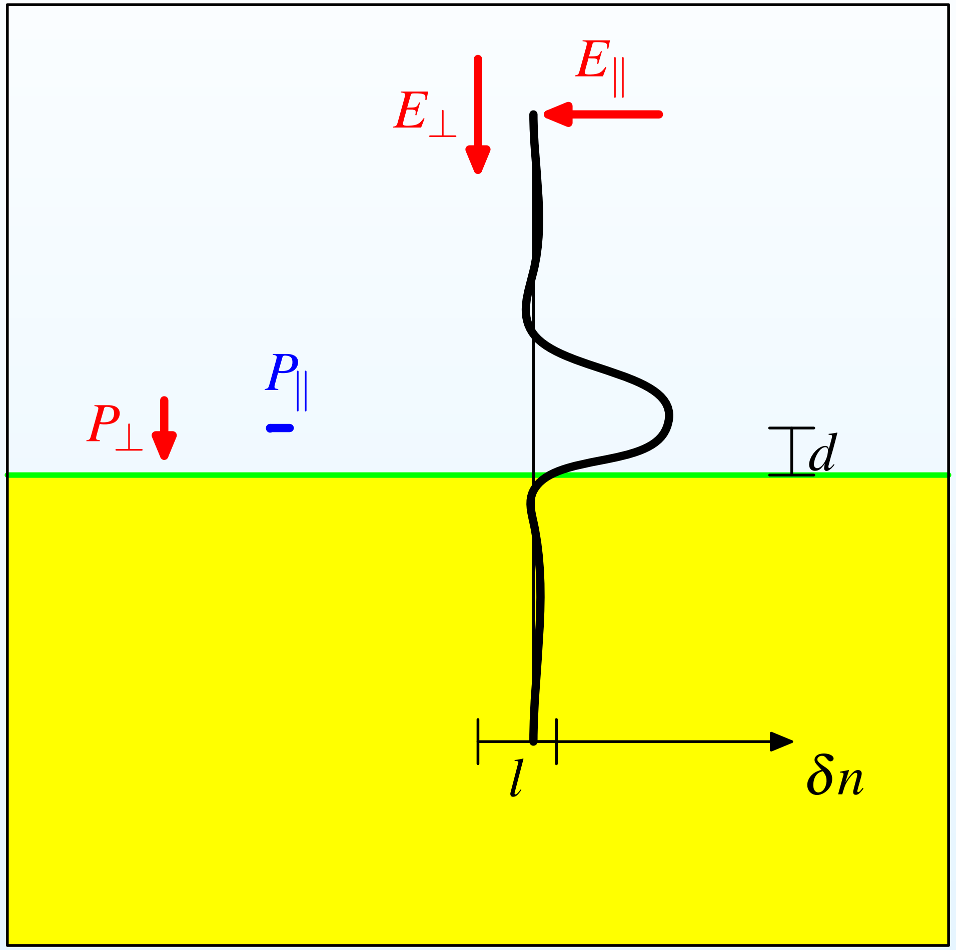

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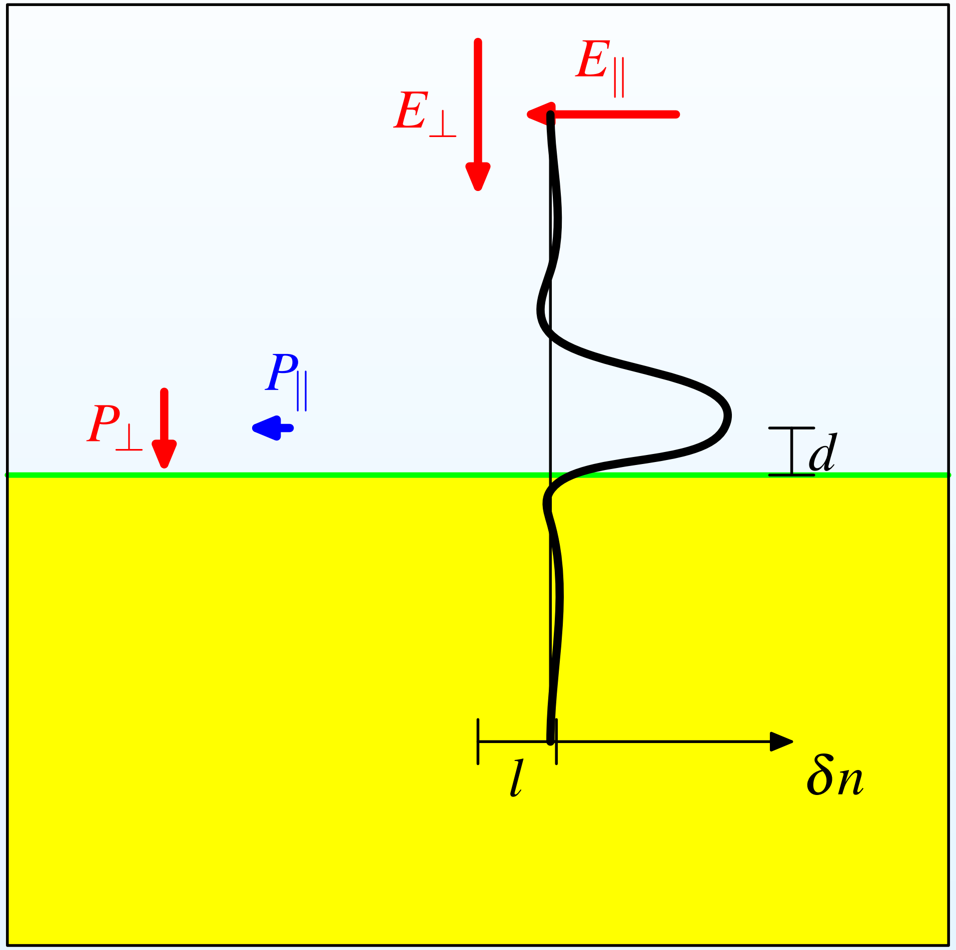

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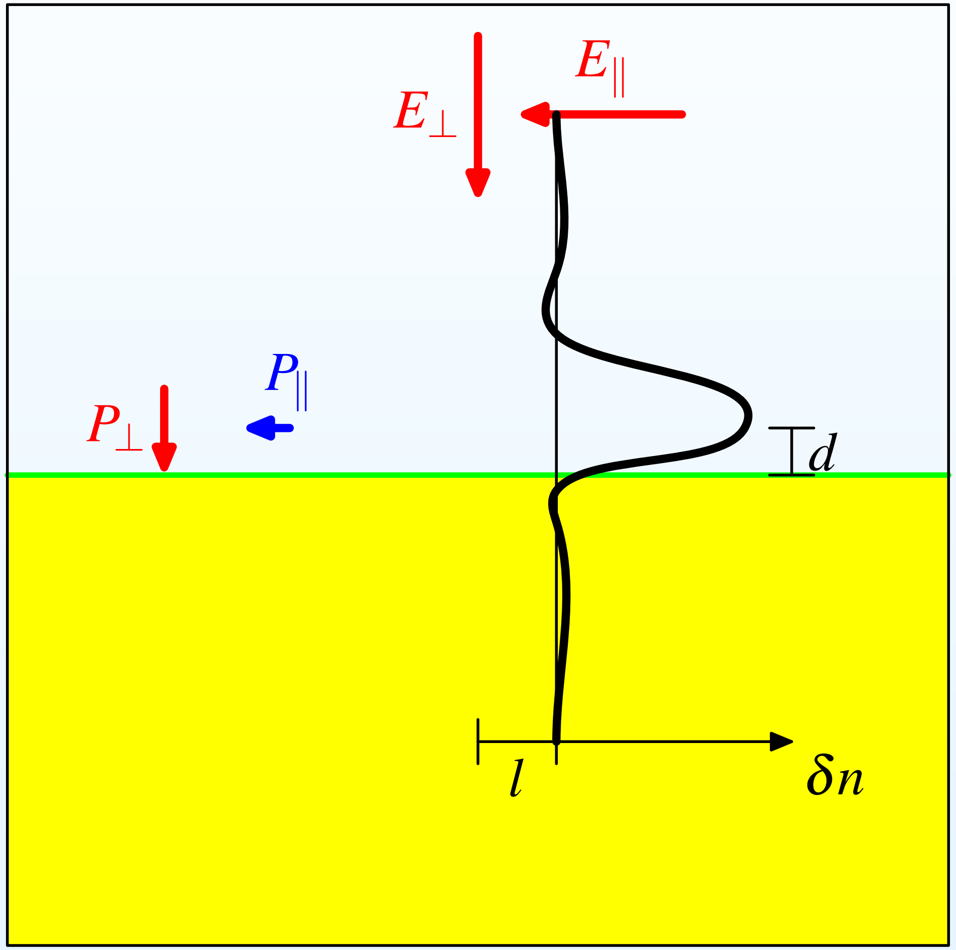
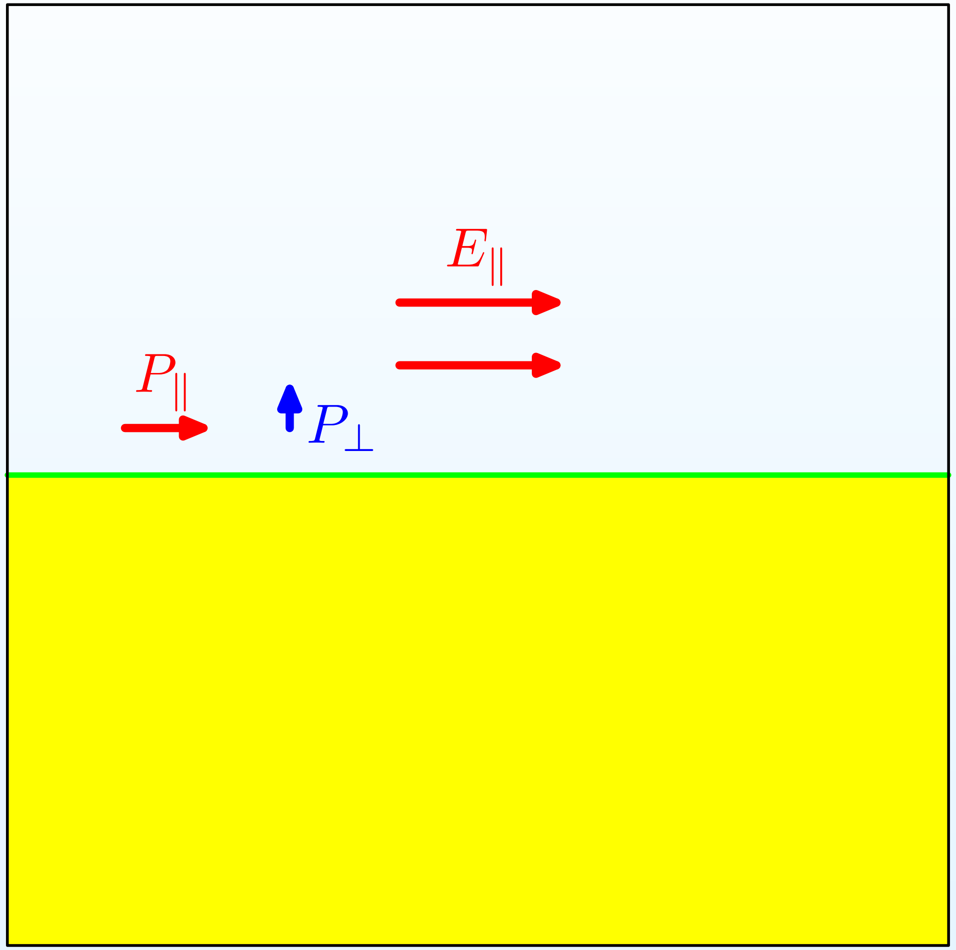
Nonlinear Surface Response: b



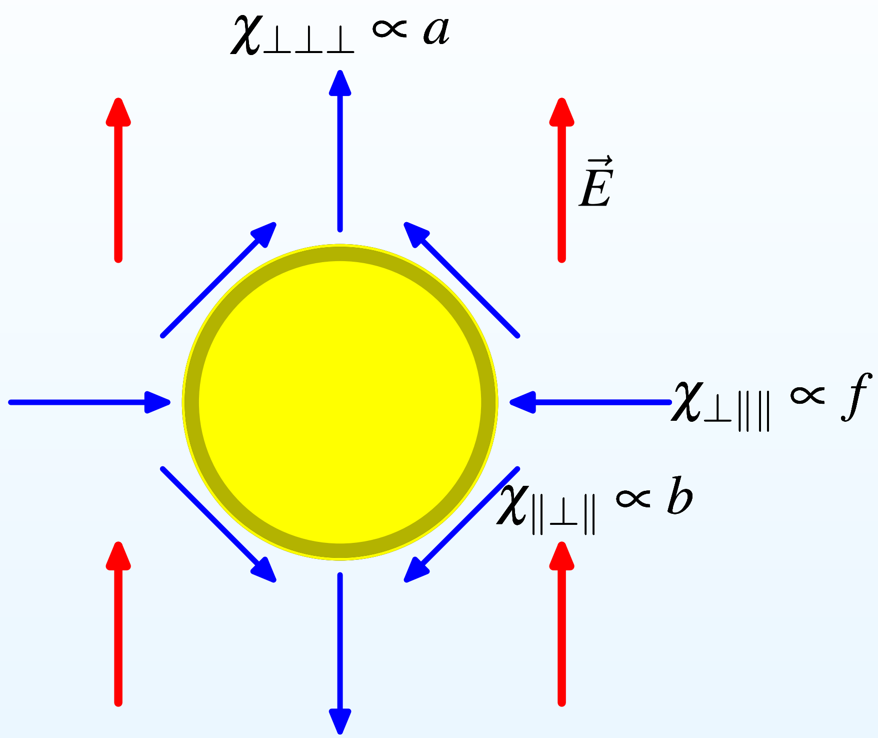
$$\chi_{\parallel\perp\parallel} \propto b \propto l$$

Nonlinear Surface Response: f

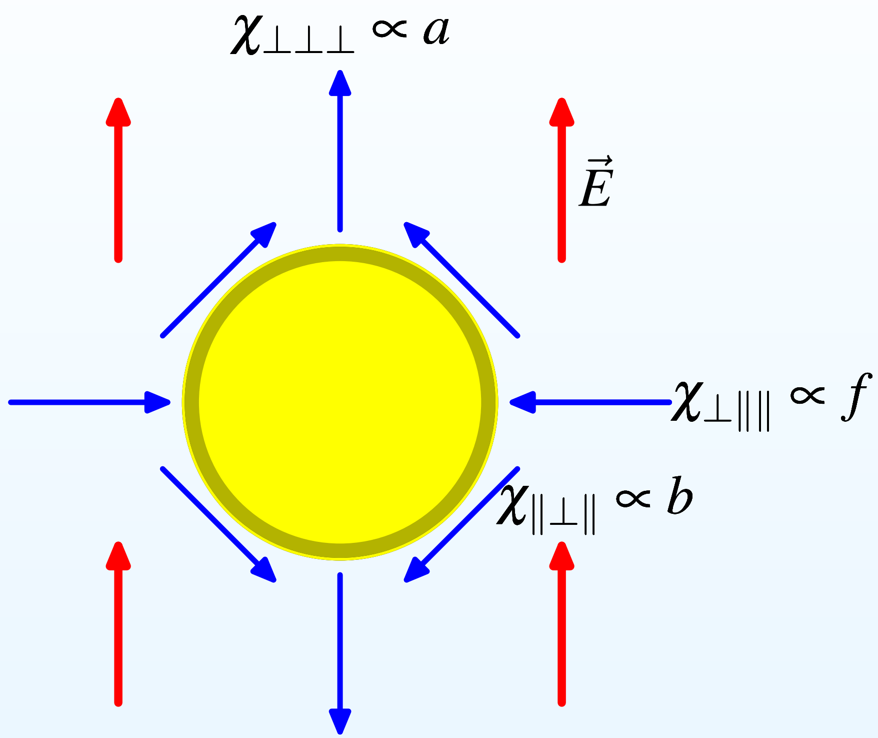


$$\chi_{\perp\parallel\parallel} \propto f$$

Single sphere SHG

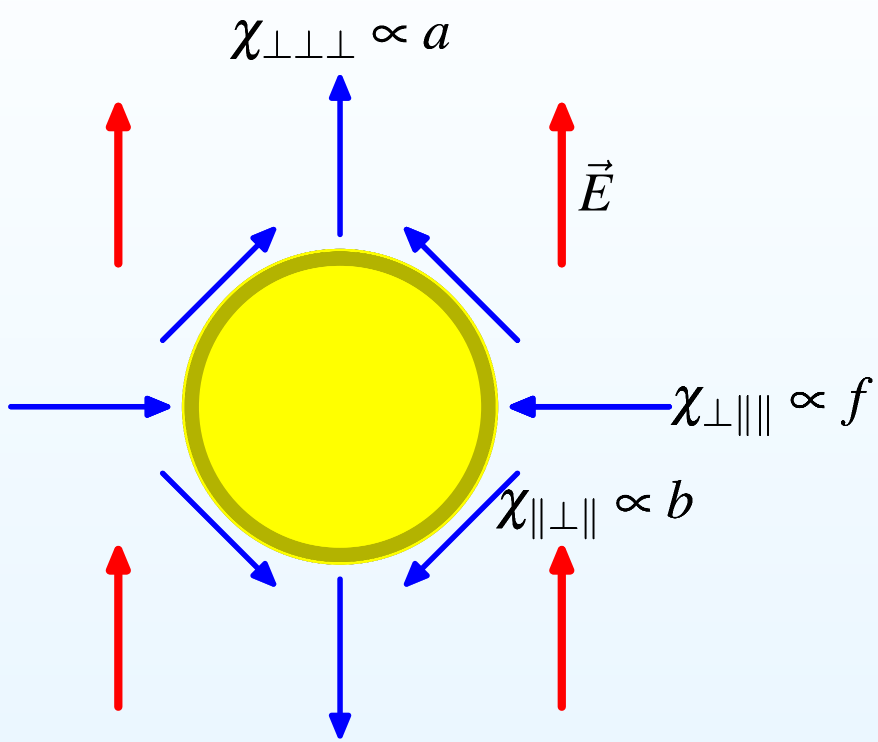


Single sphere SHG



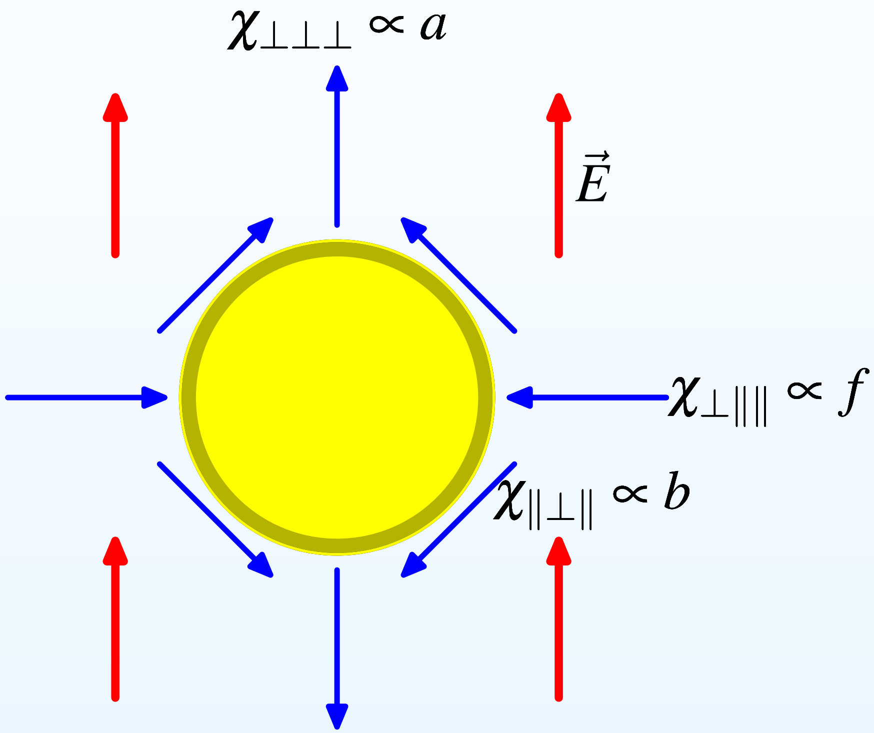
- Centrosymmetry is locally lost. . .

Single sphere SHG



- Centrosymmetry is locally lost. . .
- but globally recovered.
- Total dipole is null. . .

Single sphere SHG



- Centrosymmetry is locally lost. . .

- but globally recovered.
- Total dipole is null. . .
- unless field is inhomogeneous.

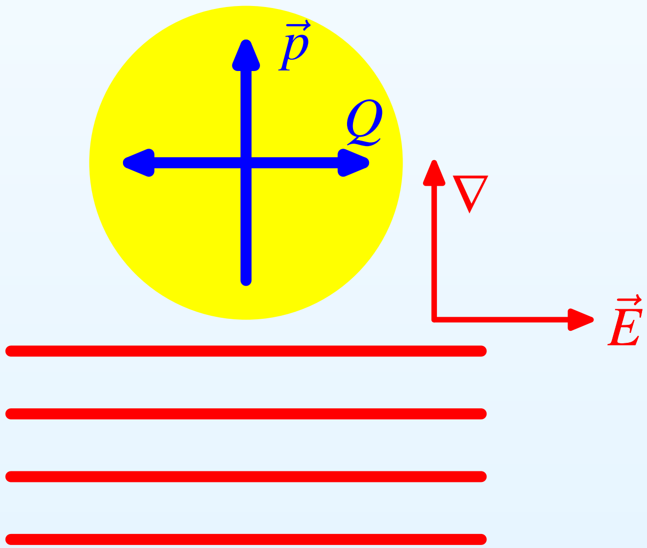
$$\vec{p} = \gamma^e \vec{E}\cdot\nabla\vec{E} + \gamma^m \vec{E}\times(\nabla\times\vec{E})$$

$$\overleftrightarrow{Q} = \gamma^q \vec{E}\vec{E}$$

$$a, b, f, d \longrightarrow \gamma^e, \gamma^m, \gamma^q$$

Radiation patterns

No forward radiation and
wide distribution
vs.
Narrow distribution along
forward direction!



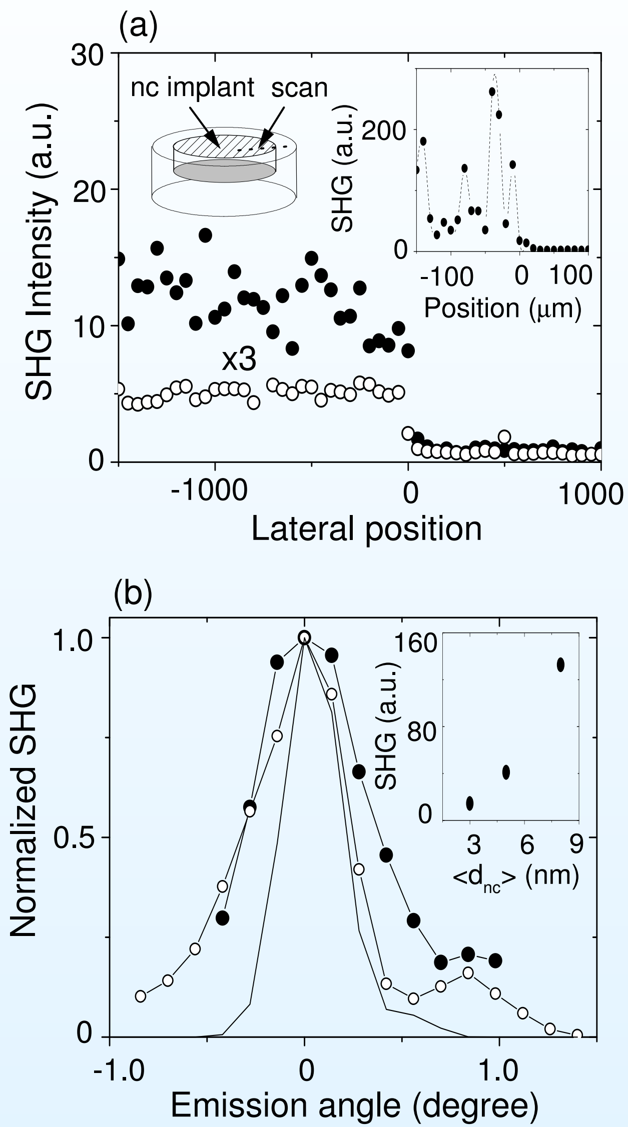
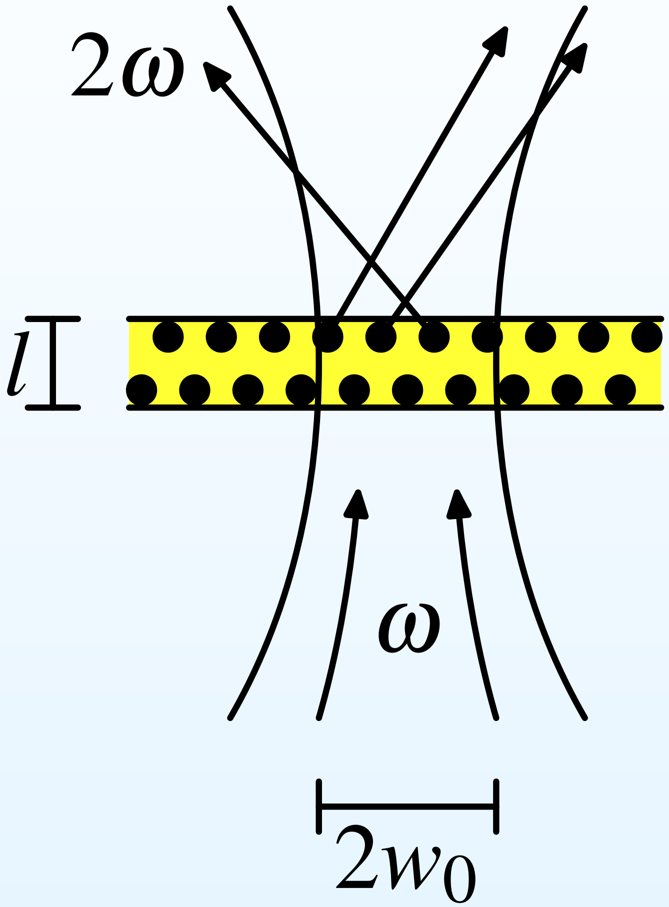
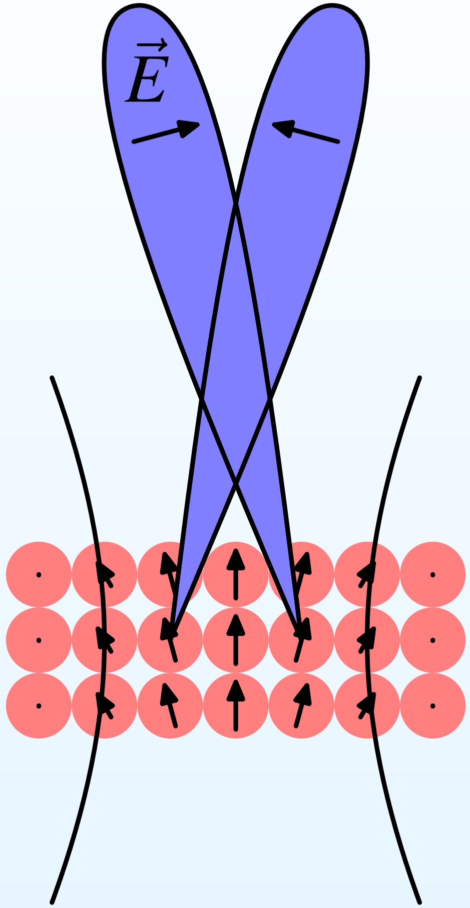


FIG. 3

SHG from composite film





Theory

$$\vec{P}^{nl} = n_s \vec{p}^{(2)} - \frac{1}{6}\nabla \cdot n_s \overleftrightarrow{Q}^{(2)}$$

$$= \Gamma \nabla E^2 + \Delta' \vec{E} \cdot \nabla \vec{E}$$

$$\Gamma = \frac{n_b}{18}(9\gamma^m + \gamma^q - 3\tilde{\gamma}^q)$$

$$\Delta' \equiv n_b(\gamma^e - \gamma^m - \gamma^q/6),$$

$$a,\ b,\ f,\ d \longrightarrow \gamma^e,\ \gamma^m,\ \gamma^q$$

$$\Longrightarrow \vec{j}^{(2)}$$

$$\Longrightarrow \vec{A}^{(2)}$$

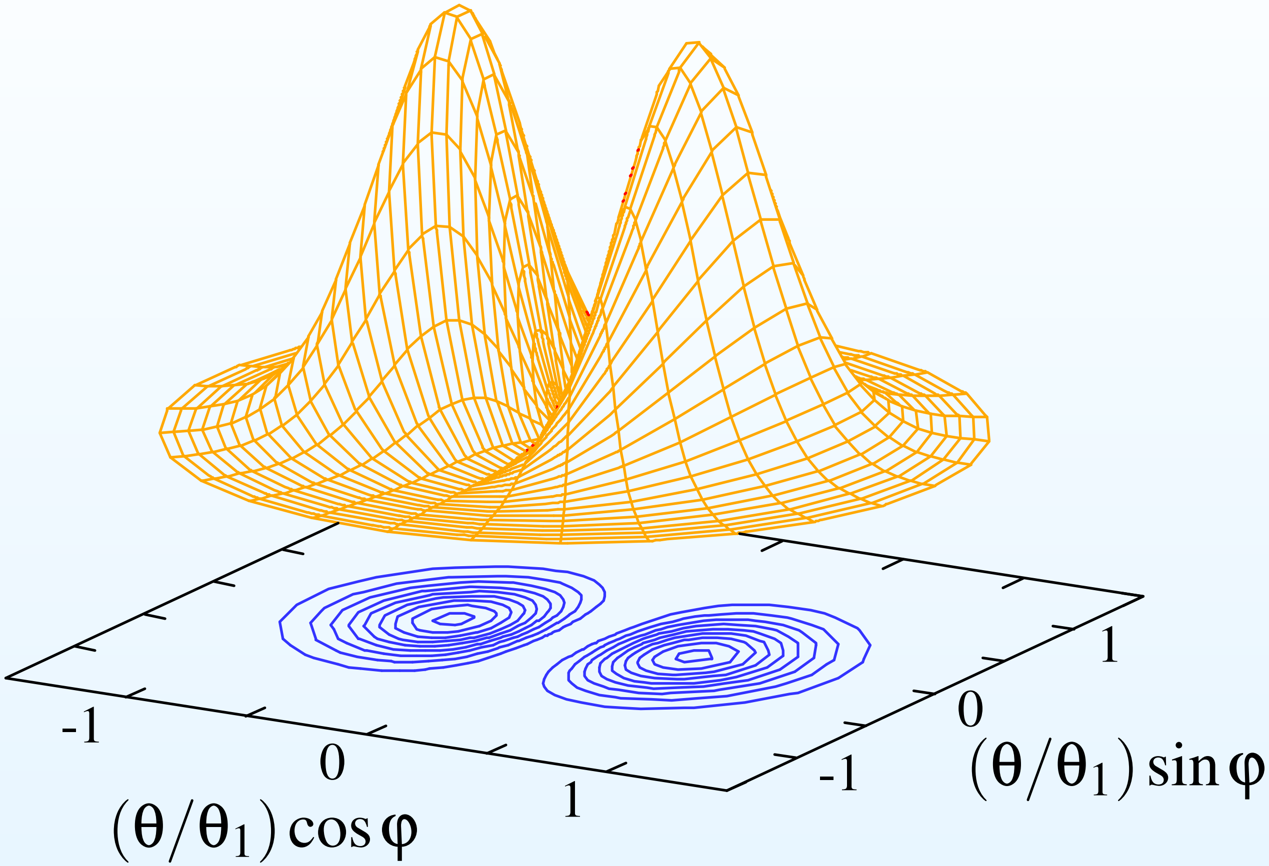
$$\Longrightarrow \vec{E}^{(2)}, \vec{B}^{(2)}$$

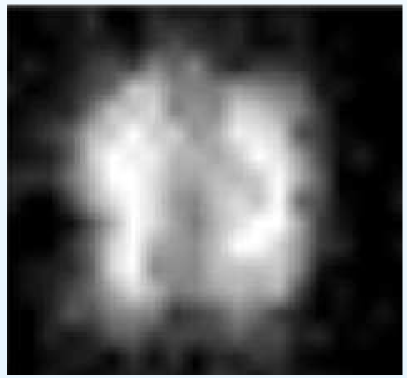
$$\Longrightarrow \vec{S}^{(2)}$$

$$\Longrightarrow \frac{d\mathcal{E}}{d\Omega} = \frac{1}{\mathcal{P}^2}\frac{d\mathcal{P}^{(2)}}{d\Omega}$$

$$\Longrightarrow \mathcal{E}$$

Angular distribution





Figliozzi et al., PRL **94**, 047401 (2005).

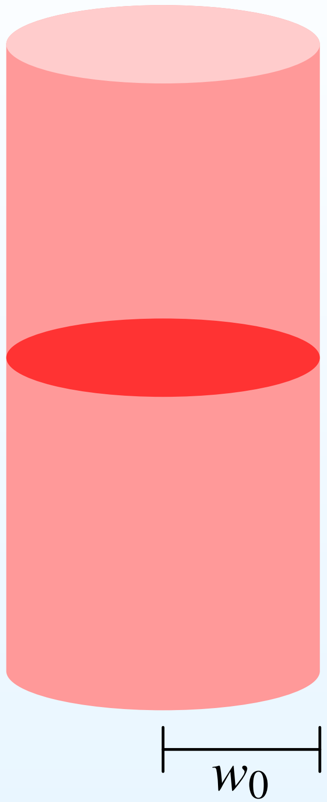
Efficiency

- $\mathcal{E} = \mathcal{P}^{(2)}/\mathcal{P}^2$
- $I^{(2)} \propto I^2 \Rightarrow \mathcal{P}^{(2)} \propto \mathcal{P}^2/w_0^2 \Longrightarrow \mathcal{E} \propto 1/w_0^2, \ldots$
- but, as $\vec{P} \propto \vec{E}\nabla\vec{E} \sim E^2/w_0$, output power is proportional to squared incoming *intensity*!

$$\begin{aligned} \mathcal{E} &= \frac{64\pi^2}{c}\frac{(ql)^2}{w_0^4}|\Delta'|^2 \\ &\approx 10^{-4}\zeta(qa_B)^4(ql)^2 f_b^2\theta_1^4\,\mathrm{W}^{-1} \\ &\approx 10^{-24}\mathrm{W}^{-1}. \end{aligned}$$

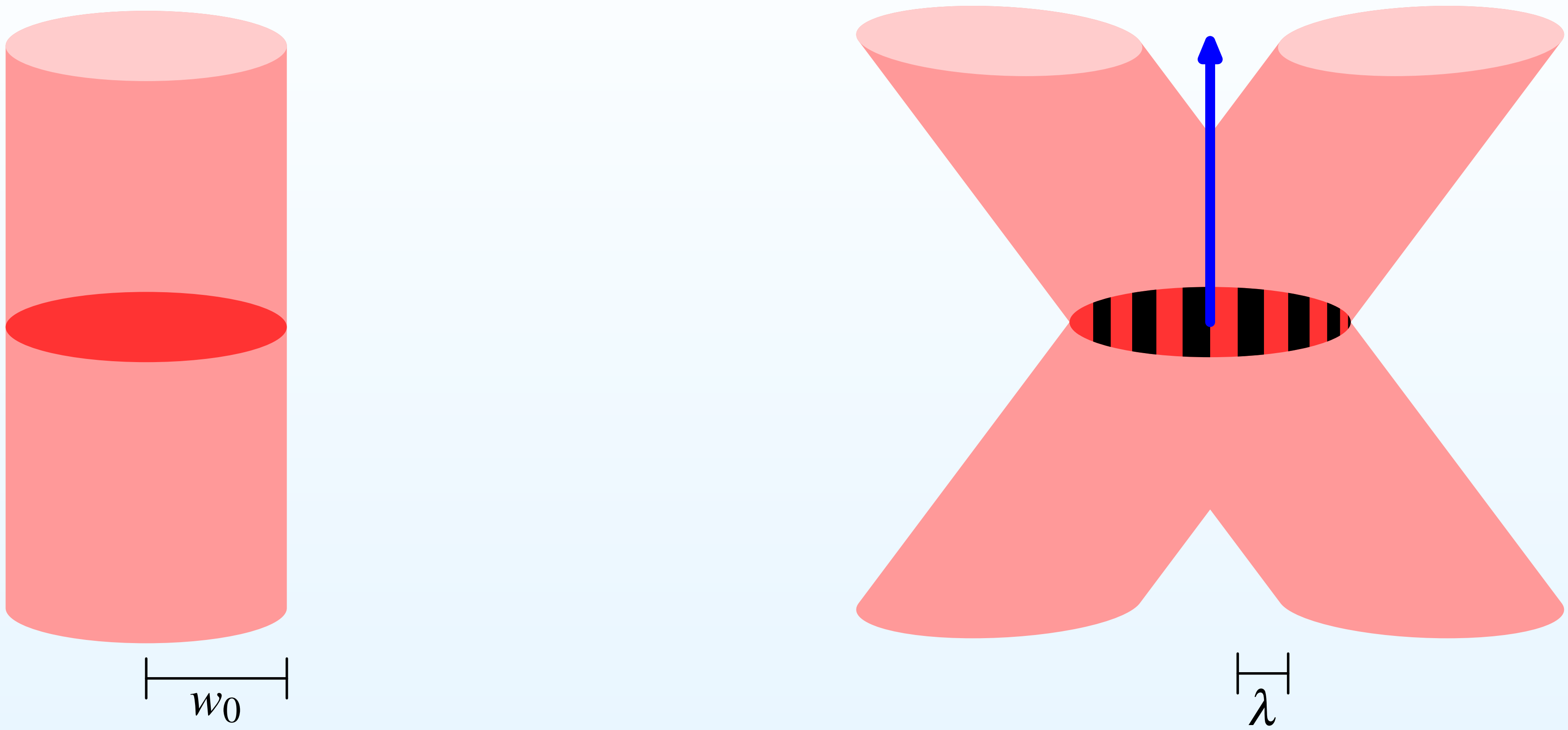
- Larger input power (but bounded intensity) might actually yield less output power!

Two Beam SHG



$\nabla \sim 1/w_0$

Two Beam SHG

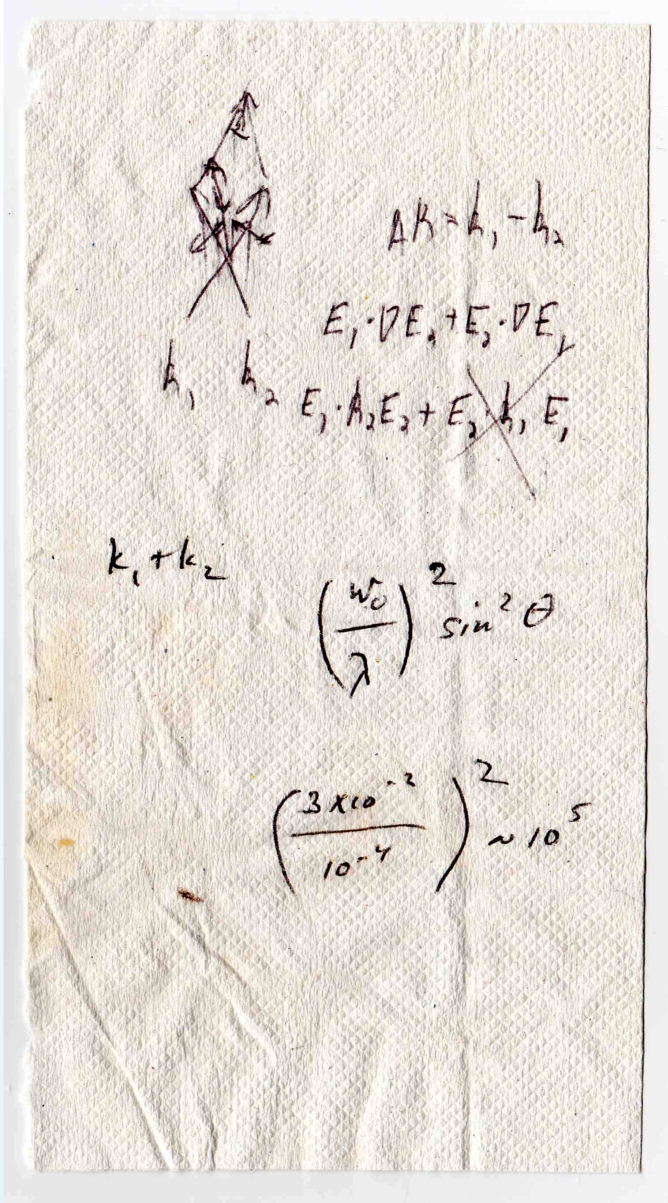


$\nabla \sim 1/w_0$ $\nabla \sim 1/\lambda$

- Solution: Enhance transverse gradients with two beam SHG.

An historical relic

Austin MM 03:



Two Beam SHG

- Expect: $(w_0/\lambda)^2$ enhancement

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- but $\vec{E}_1 \cdot \nabla \vec{E}_2 + \vec{E}_2 \cdot \nabla \vec{E}_1$ is null if both beams are s polarized and longitudinal if both are p polarized $\rightarrow$ no SHG.

Two Beam SHG

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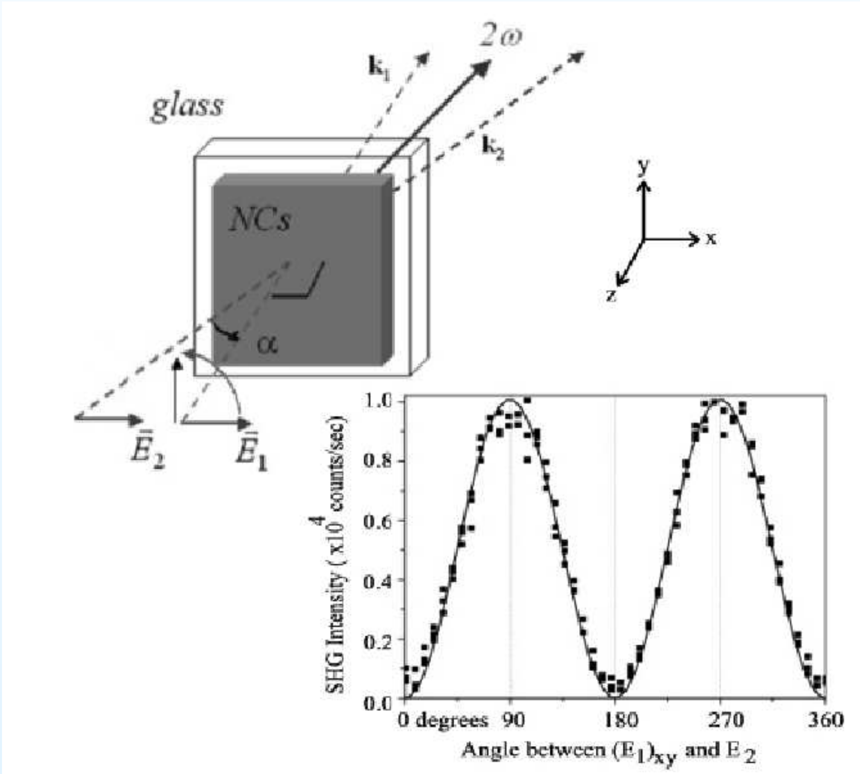
- but $\vec{E}_1 \cdot \nabla \vec{E}_2 + \vec{E}_2 \cdot \nabla \vec{E}_1$ is null if both beams are s polarized and longitudinal if both are p polarized $\rightarrow$ no SHG.

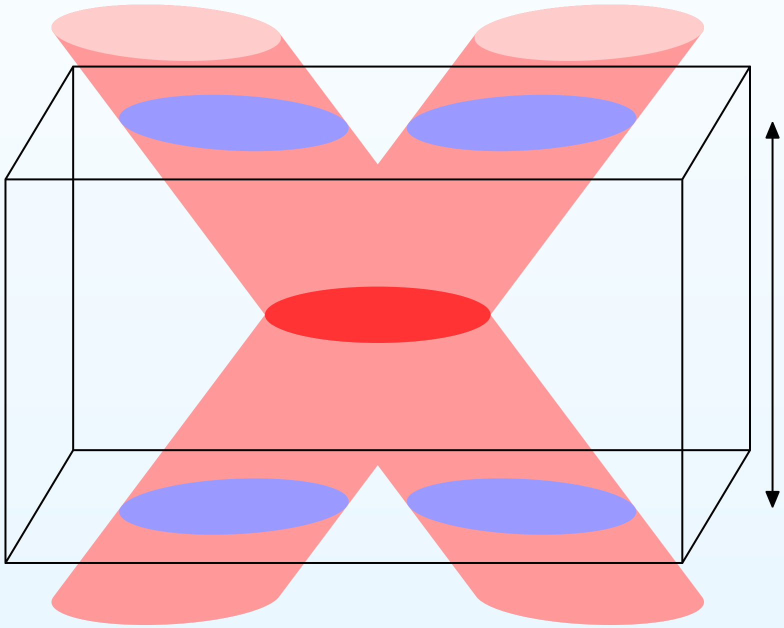
With crossed polarization there is no *intensity* modulation but a polarization modulation that may produce many orders of magnitude enhancement of SHG.

Figliozzi et al., PRL **94**, 047401 (2005)

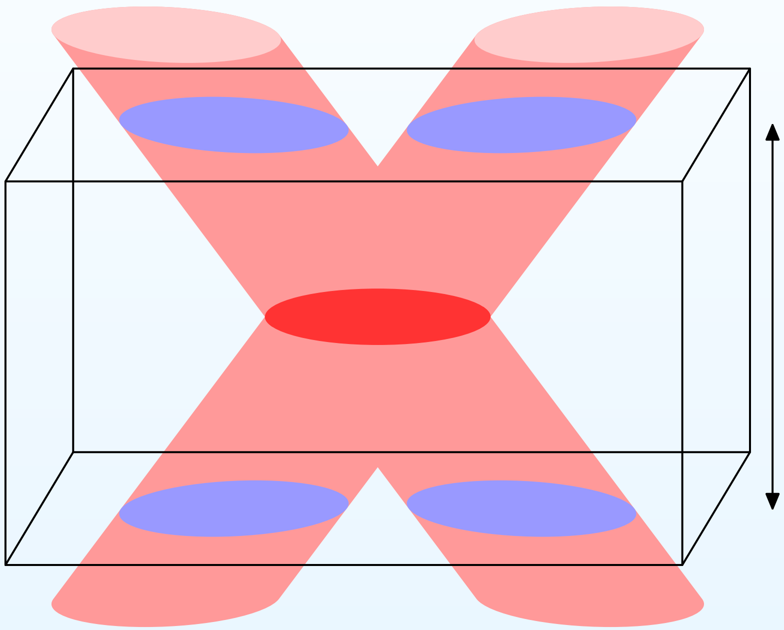
Liangfeng Sun et al., to appear in Optics Lett.

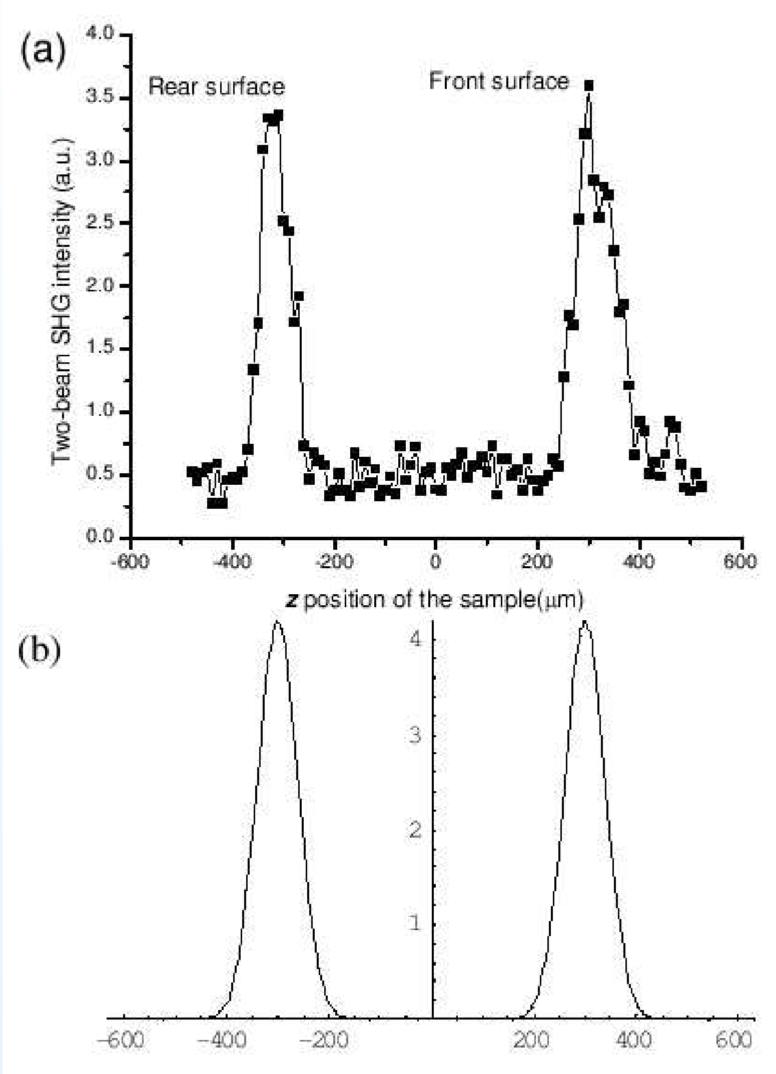


Surface or bulk?



Surface or bulk?





Contrast. . .

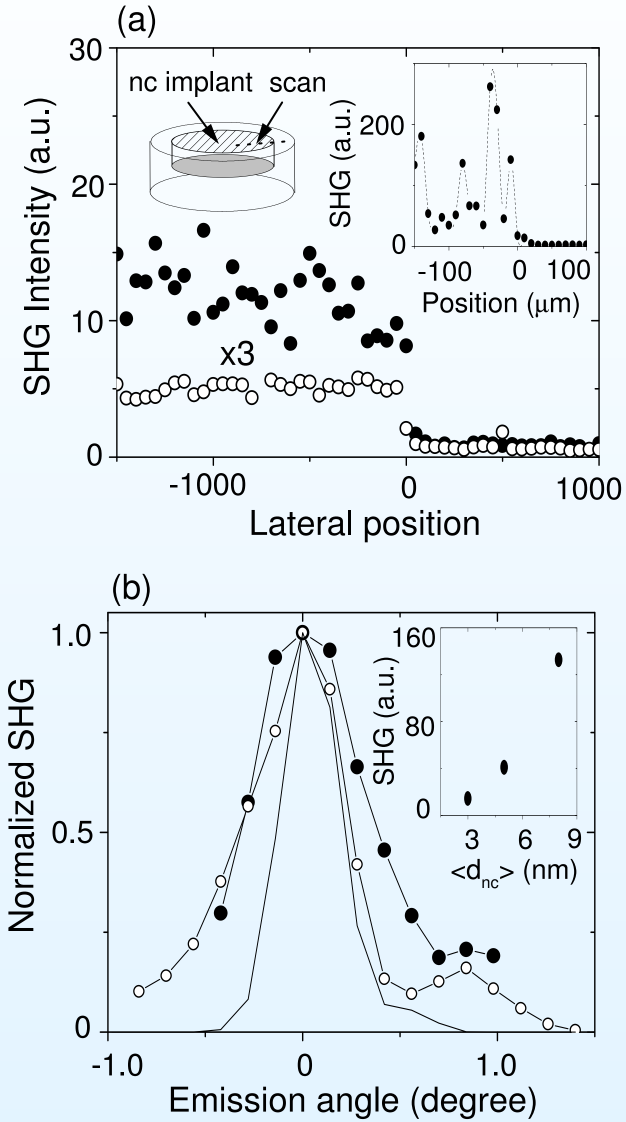
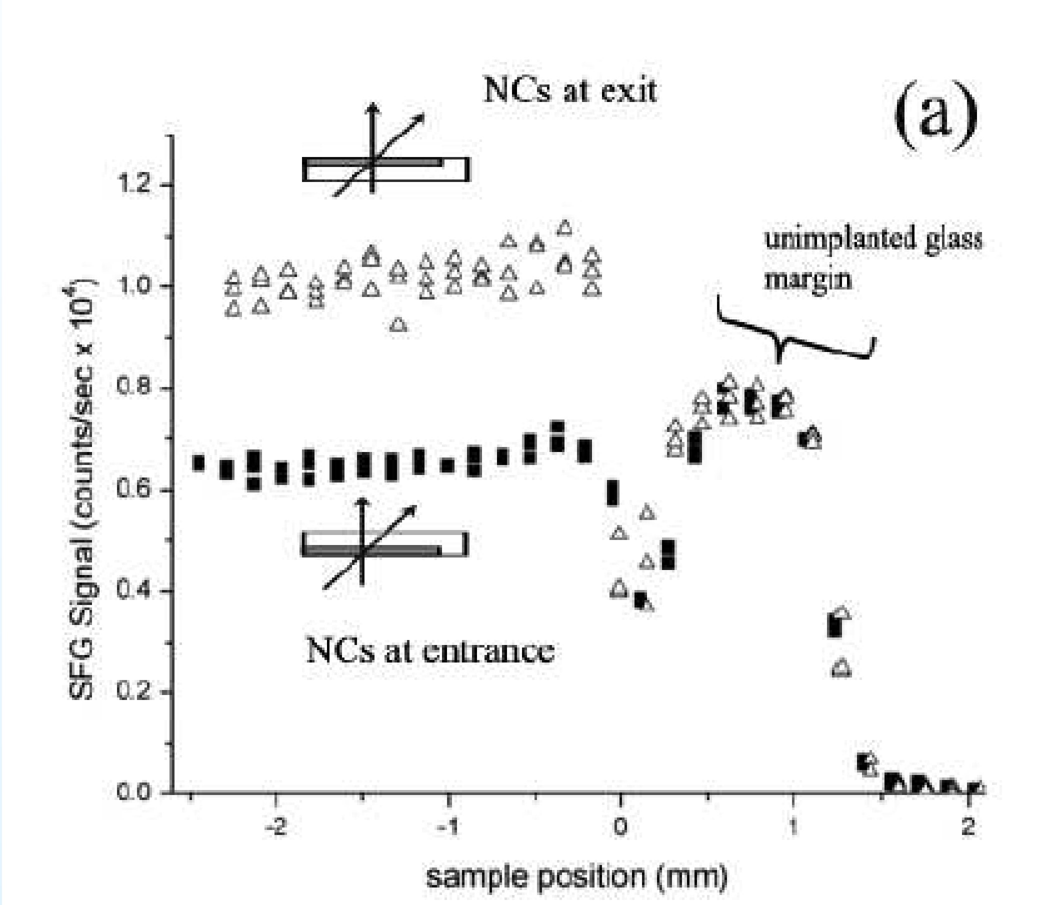


FIG. 3



. . . is gone

Why?

- Nanocrystals

$$\vec{P}_{nc} = \Gamma \nabla E^2 + \Delta' \vec{E} \cdot \nabla \vec{E}$$

Why?

- Nanocrystals

$$\vec{P}_{nc} = \Gamma\nabla E^2 + \Delta'\vec{E}\cdot\nabla\vec{E}$$

- Glass

$$\vec{P}_g = \gamma_g\nabla E^2 + \delta'_g\vec{E}\cdot\nabla\vec{E}$$

Why?

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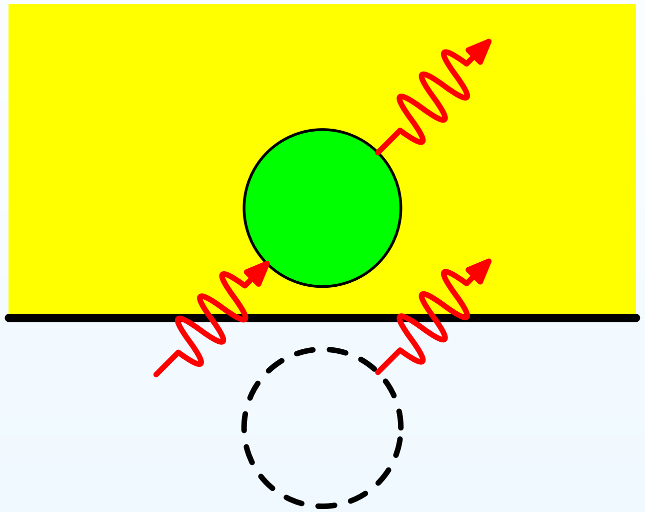
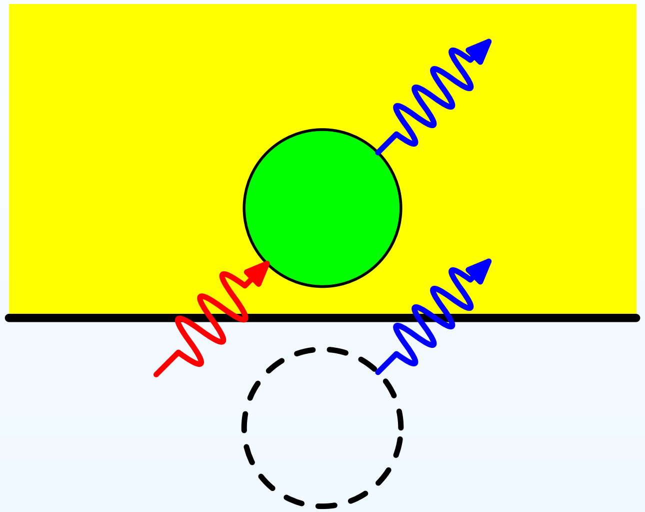
- Glass

$$\vec{P}_g = \gamma_g \nabla E^2 + \delta'_g \vec{E} \cdot \nabla \vec{E}$$

- By increasing $\vec{E} \cdot \nabla \vec{E}$ both contributions should have been enhanced by the same amount. Contrast$= |\Delta'/\delta'_g|^2$.

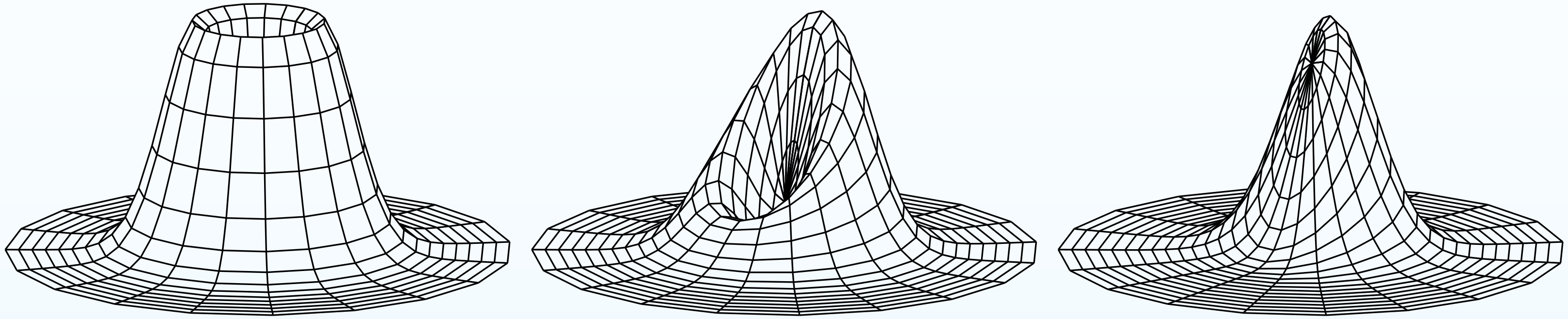
SHG from surface

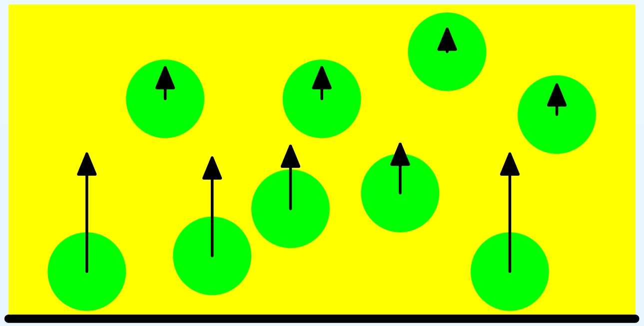




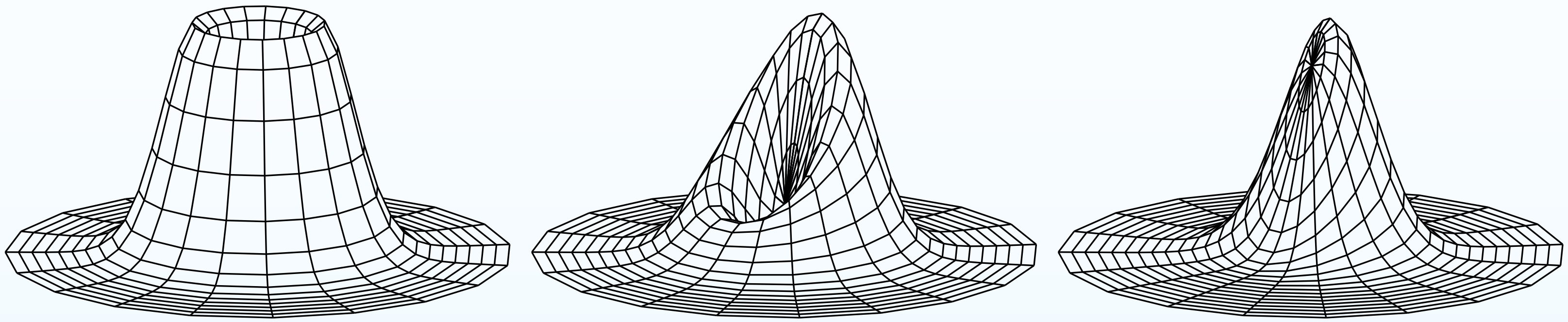
- Large gradient close to surface, independent of beam profile.
- $\vec{p}^{(2)} = \gamma^e \vec{E}_l \cdot \nabla \vec{E}_l + \alpha_2 \overset{\leftrightarrow}{T}{}^I \cdot \vec{p}^{(2)}$.
- Integrate over z and over area to obtain *dipolar* $\chi_s^{(2)}$.

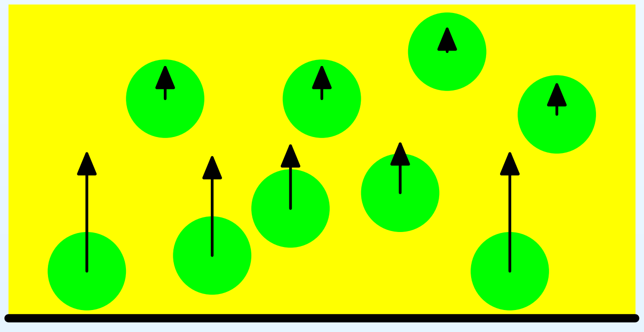
SHG from surface





SHG from surface



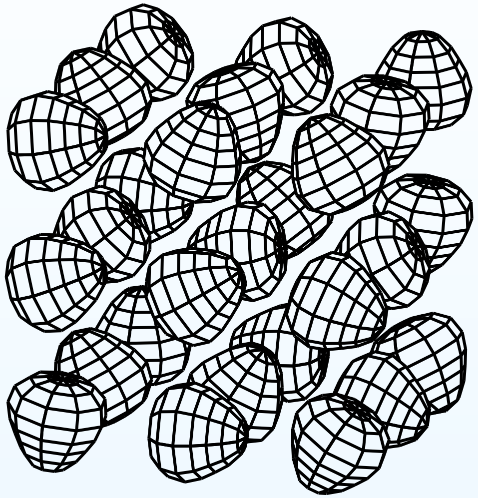


Surface vs. bulk efficiency (s pol.)

$$\frac{\mathcal{E}_s}{\mathcal{E}_B} = \frac{2|\chi^s_{\perp\|\|}|^2}{|\Delta'|^2(q\ell)^2}\left(1+\left(\frac{2\alpha}{\theta_1}\right)^2\right).$$

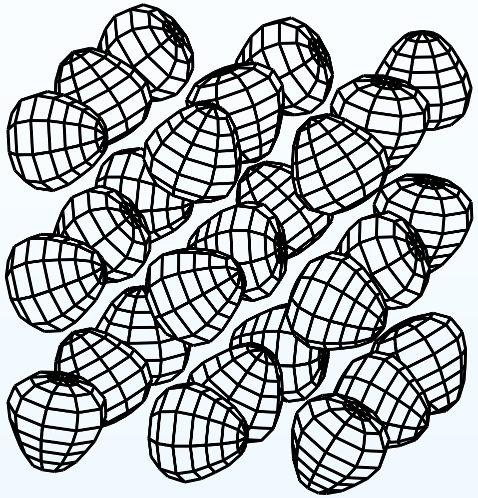
For Si/SiO_2 nanocrystals, $\hbar\omega = 1.55$eV, $\ell = 1\mu$m, $w_0 = 10\mu$m at normal incidence: $\sim 10^{-5}$.

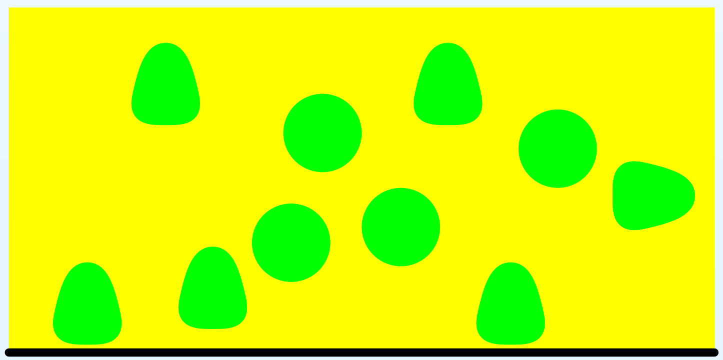
Shapes



- Isotropic *bulk* $\Longrightarrow$ effective spherical shapes

Shapes





- Isotropic *bulk* $\Longrightarrow$ effective spherical shapes
- Anisotropic diffusion at surfaces and edges $\Longrightarrow$ anisotropic, non-spherical shapes

Non spherical particles

- $r = r_0(1 + \sum_{lm} \xi_{lm} Y_{lm})$
- xy isotropy $\Rightarrow m = 0$
- $\xi_{00} = 0$ if r_0 =average radius.
- $\xi_{10} \Rightarrow$ C.M. translation.
- $\xi_{20} \Rightarrow$ centrosymmetric spheroidal deformation.
- ξ_{30} is the lowest order deformation that breaks centrosymmetry and produces dipolar SH.
- $r_0 = \left\langle \frac{1}{4\pi} \int d\Omega\, r(\hat{\Omega}) \right\rangle.$
- $\xi = \left\langle \int d\Omega\, r(\hat{\Omega}) Y_{30}(\hat{\Omega}) \right\rangle.$
- $r(\hat{\Omega}) = r_0(1 + \xi Y_{30}(\hat{\Omega}))$
- Assume small ξ.

Dipole moment

- Surface polarization

$$\vec{P}_s = \chi_s \left[\frac{a}{\epsilon_1^2} \hat{n}(\hat{n} \cdot \vec{D})^2 + \frac{2b}{\epsilon_1} (\vec{E} - \hat{n}\hat{n} \cdot \vec{E}) \hat{n} \cdot \vec{D} + \hat{f} \hat{n} (E^2 - (\hat{n} \cdot \vec{E})^2) \right]$$

- Surface normal $\hat{n} = \hat{r} - \hat{\theta} \xi \, dY_{30}/d\theta$.
- Screened linear field $\vec{E} = L_{11} \vec{E}_a$.
- $L_{lw} = (2l+1)/(l\epsilon_w + l + 1)$.
- Total dipole $\vec{p} = \int da \vec{P}_s \quad + \quad$ linear screening at 2ω.

Non linear polarizability

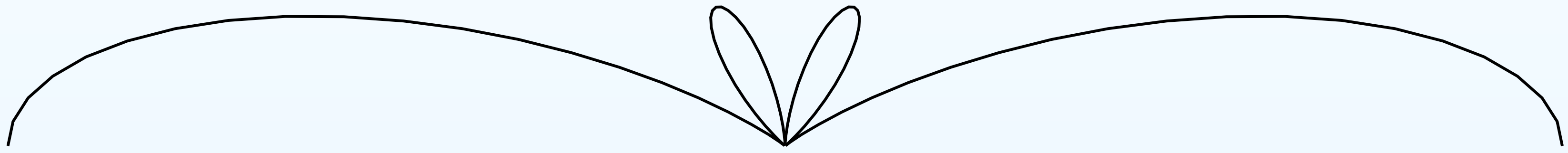
- $\vec{p}_i = \alpha_{ijk} E^a_j E^a_k$
- $\alpha_{zzz} = -2A$,
- $\alpha_{zxx} = \alpha_{xxz} = \alpha_{xzx} = A$,
- $\alpha_{ijk} = 0$ if not equivalent to above.
- $A = \xi r_0^2 \sqrt{\pi/7} \chi_s (4\epsilon_2 a - 8b - 4\epsilon_2 f) L_{11}^2 L_{12}$

Surface susceptibility of composite

- $\chi_{ijk} = nd\alpha_{ijk}$
- $\chi_{\perp\perp\perp} = -2X$
- $\chi_{\perp\|\|} = X$
- $\chi_{\|\|\perp} = \chi_{\|\perp\|} = X,$
- $X = n(d/r_0)\xi r_0^3\sqrt{\pi/7}\chi_s(4\epsilon_2 a - 8b - 4\epsilon_2 f)L_{11}^2 L_{12}$

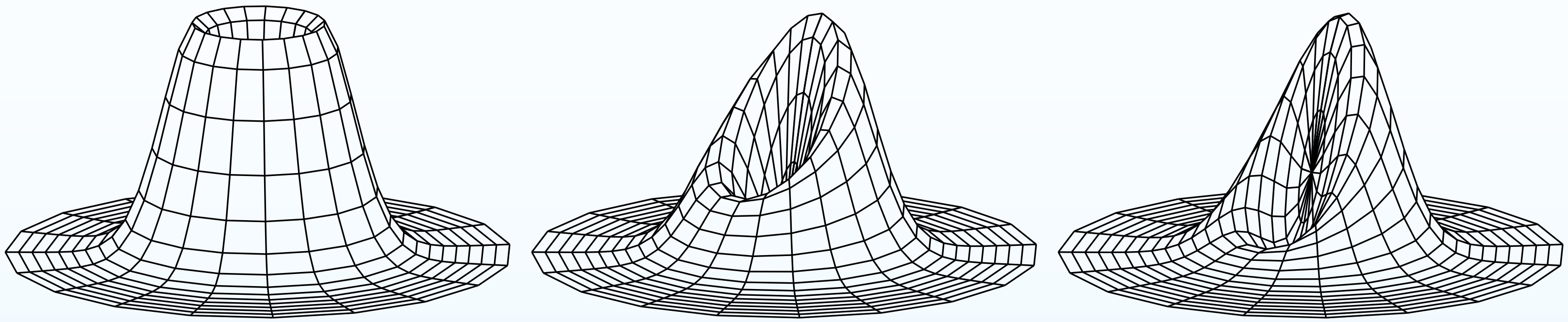
Angular dependence-large angles

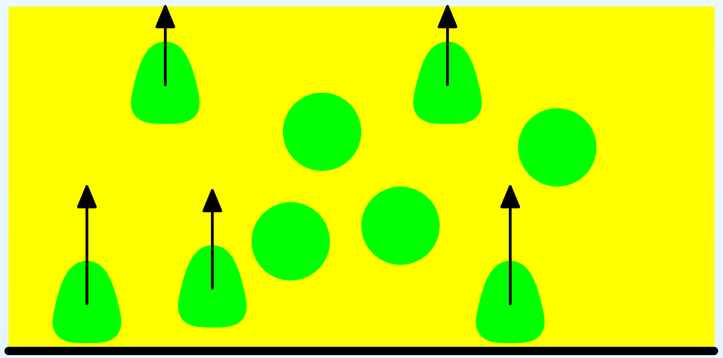
- $\chi_{\perp\|\|} = \chi_{\|\|\perp} = \chi_{\|\perp\|} = -\chi_{\perp\perp\perp}/2$
- p polarization



- Maximum for transmission angle $= \tan^{-1}(1/2)$.

Angular dependence-small angles, finite beam, p input





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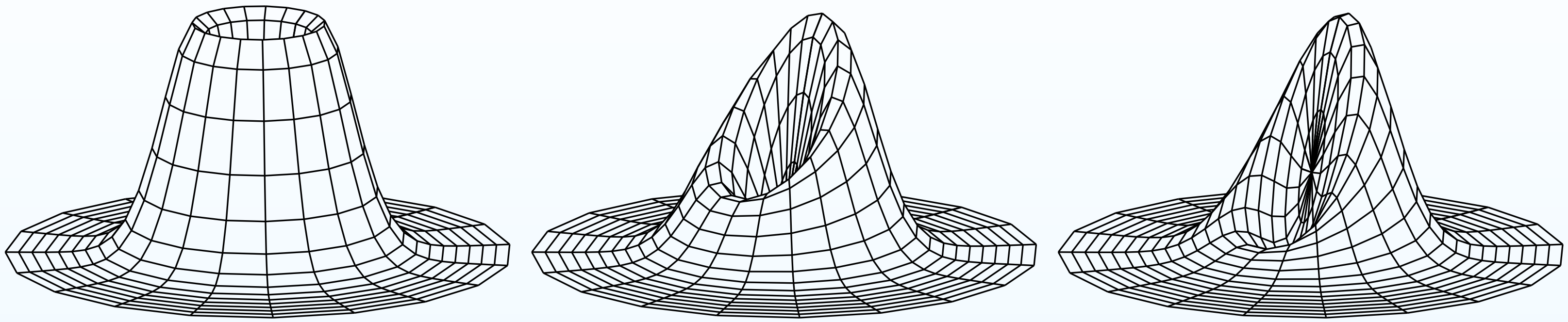

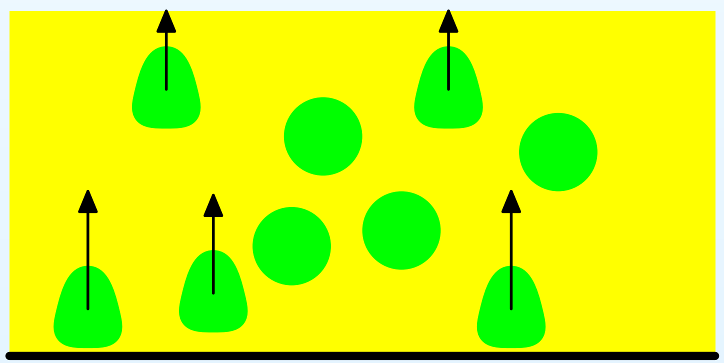

Surface vs. bulk efficiency (p pol.)

$$\frac{\mathcal{E}_s}{\mathcal{E}_B} = \frac{2|X|^2}{|\Delta'|^2(q\ell)^2}\left(1+\left(\frac{36\alpha}{\theta_1}\right)^2\right).$$

For Si/SiO_2 nanocrystals, $\hbar\omega = 1.55$eV, $\ell = 1\mu$m, $w_0 = 10\mu$m, $N\xi = 2$ at normal incidence: ~ 10.

Conclusions

- The surface of nanoparticles buried within composites may be observed with SHG.
- There is no forward radiation, but there is nearly forward coherent SHG from composites illuminated by finite beams.
- Output power cannot be boosted simply by increasing input power.
- SHG may be enhanced orders of magnitude using two cross-polarized beams.
- *Surface* SHG wouldn't be enhanced $\Rightarrow$ Si nc/glass contrast.
- Local field gradients seem too small, but shape modifications might explain the change of contrast.