Second harmonic generation in nanoparticle arrays

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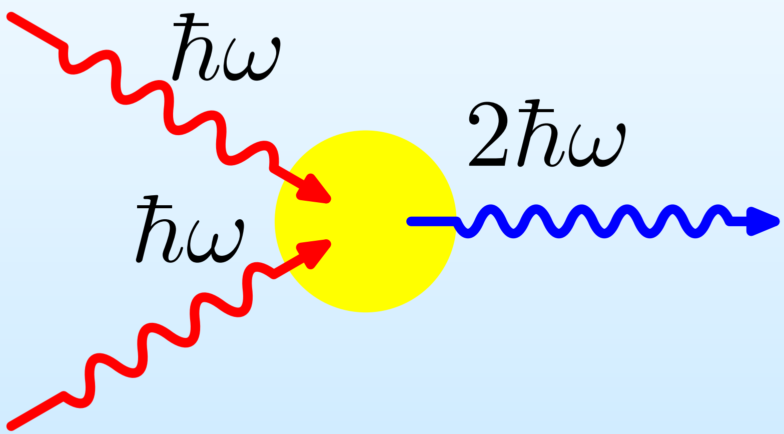
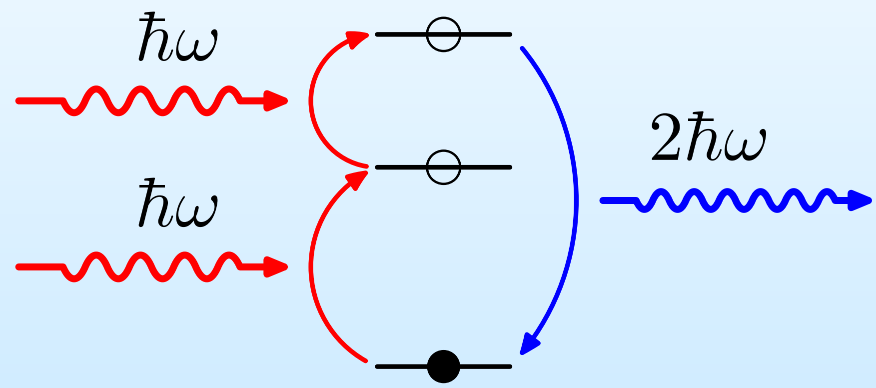
[4]Centro de Investigaciones en Optica

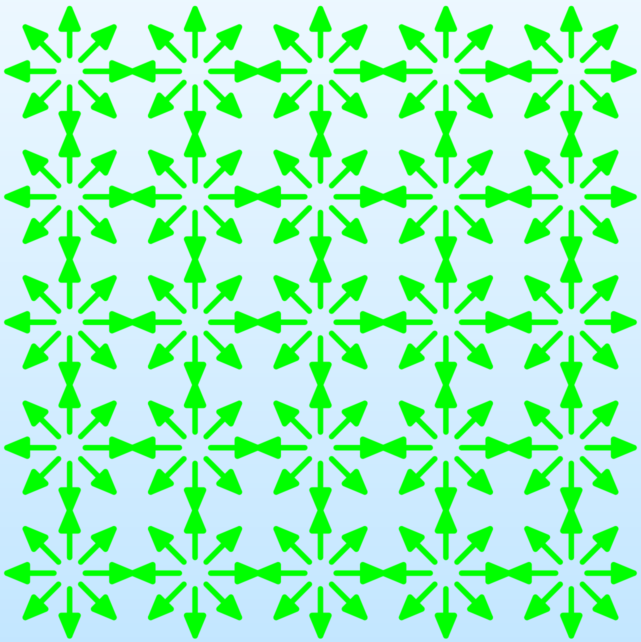
Second Harmonic Generation





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

SHG and Symmetry



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

After an inversion

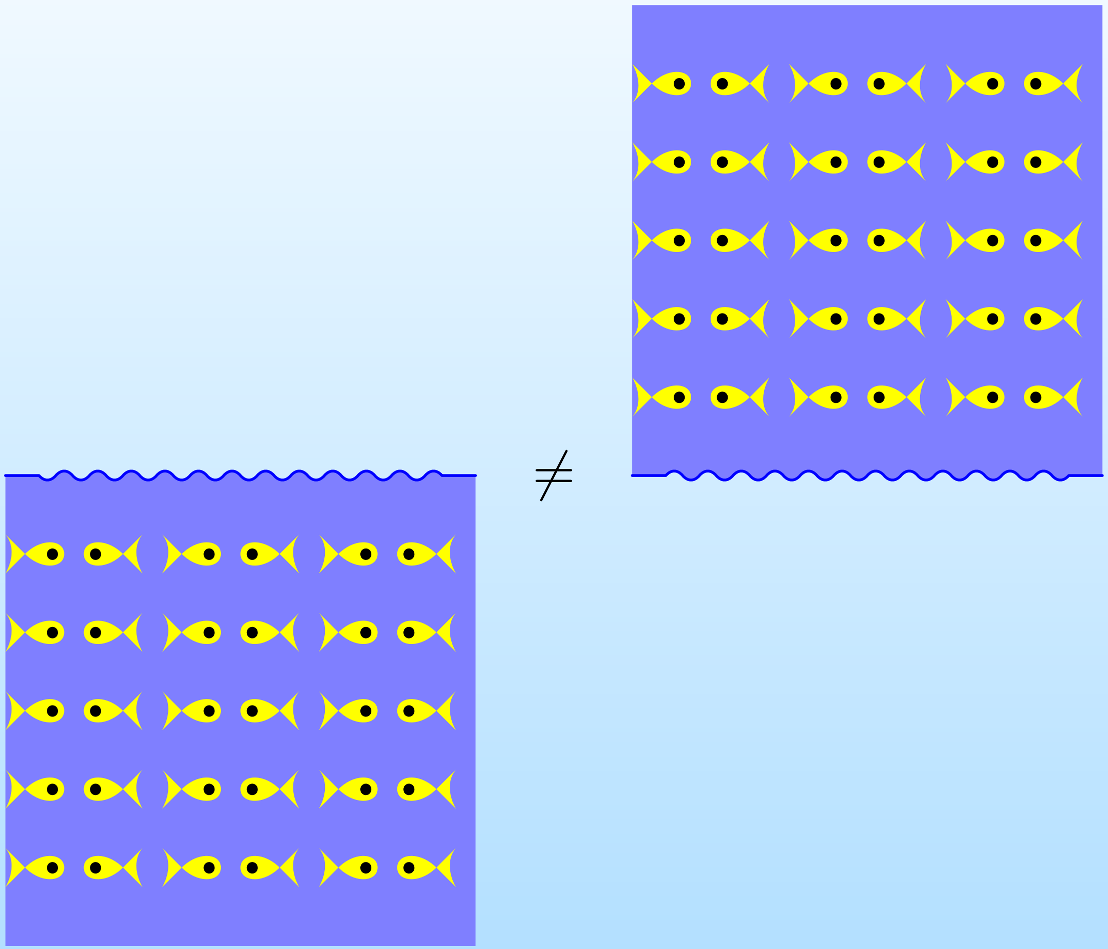
$$-\vec{P}^{(2)} = \chi_I^{(2)}(-\vec{E})(-\vec{E})$$

Centrosymmetry $\Rightarrow$

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

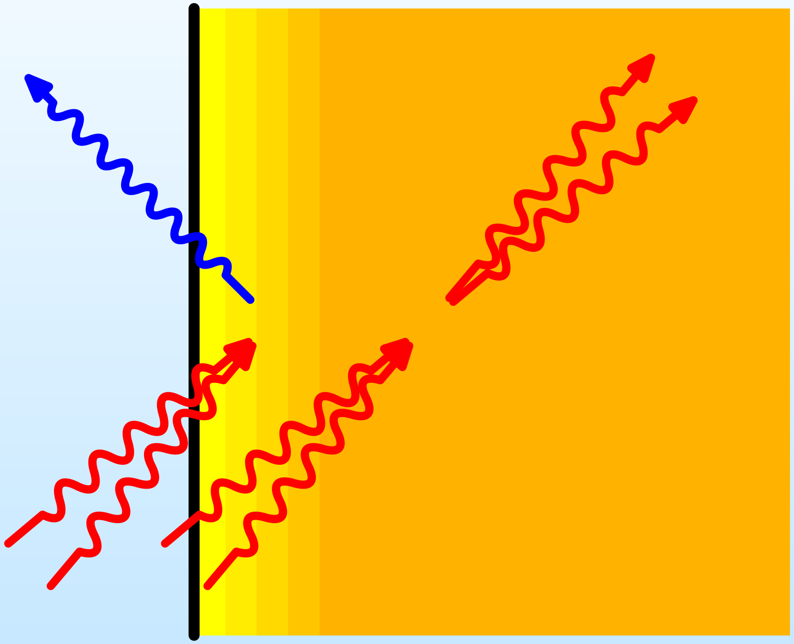
$$\Longrightarrow \vec{P}^{(2)} = 0, \quad \chi^{(2)} = 0$$

Centrosymmetry and Surfaces

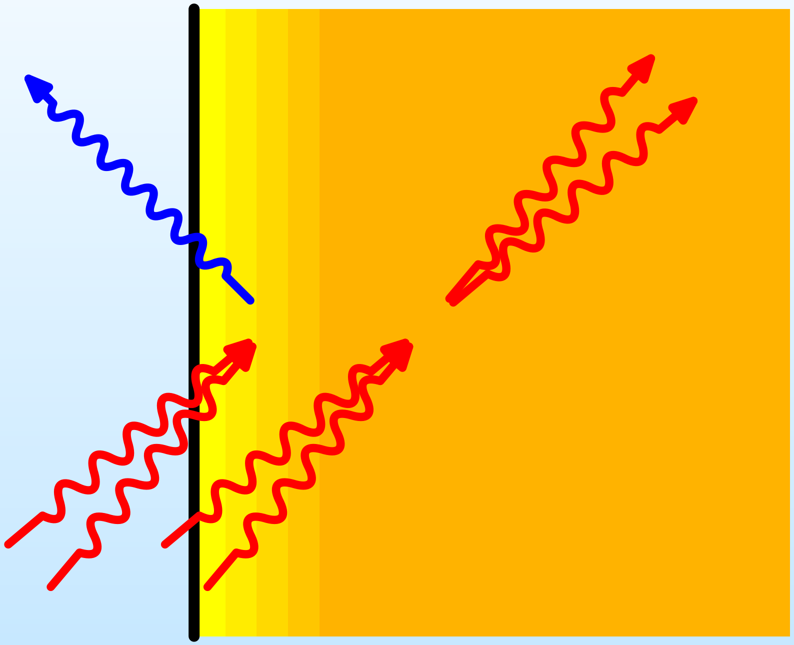


Surfaces are not centrosymmetric!

SHG and Surfaces

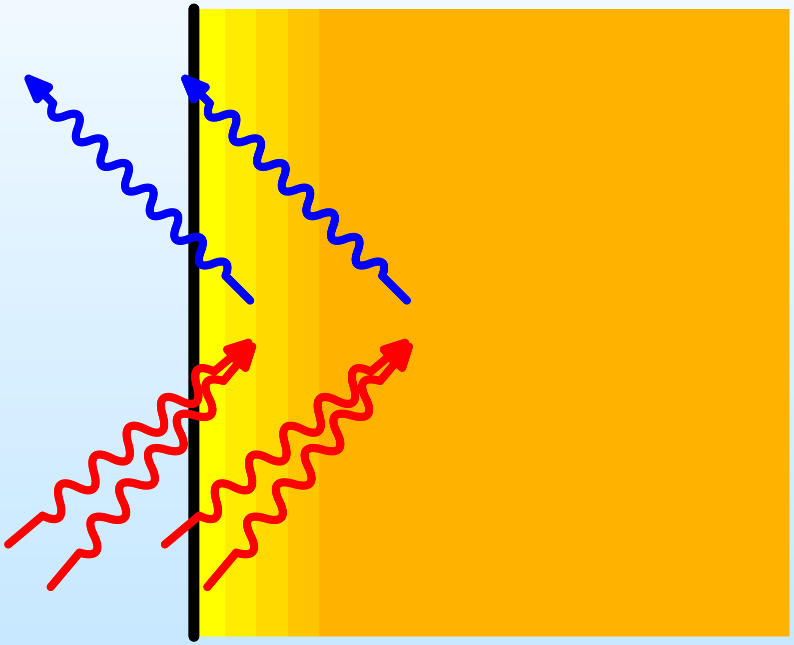


SHG and Surfaces



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

SHG and Surfaces



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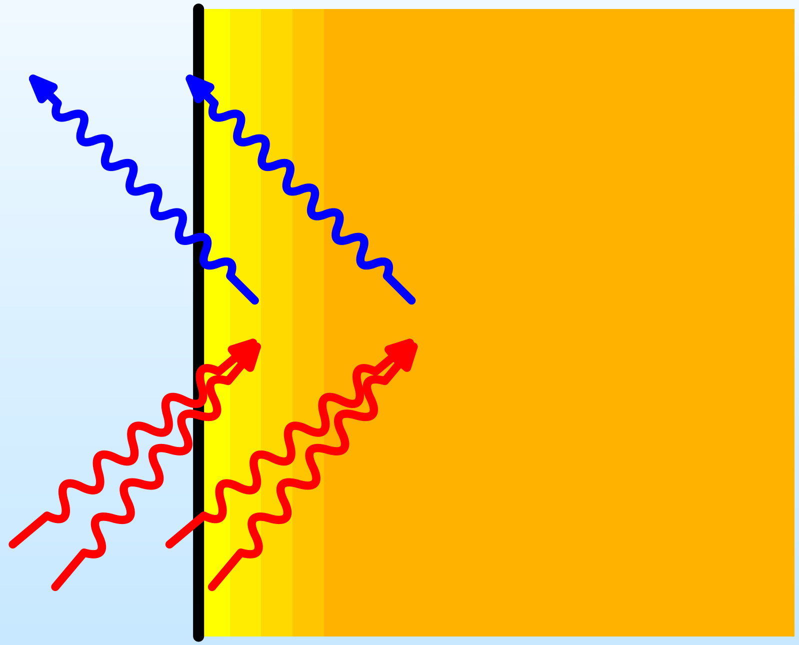
There might be SHG from bulk. . .

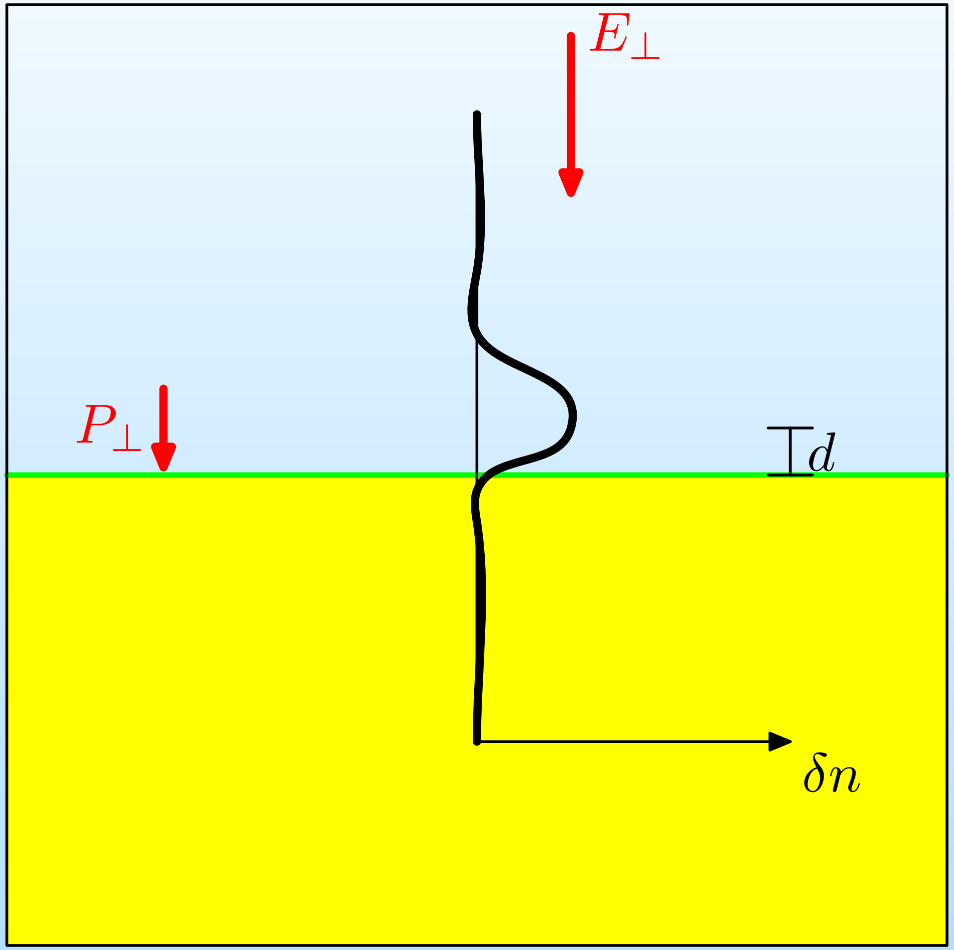
SHG and Surfaces



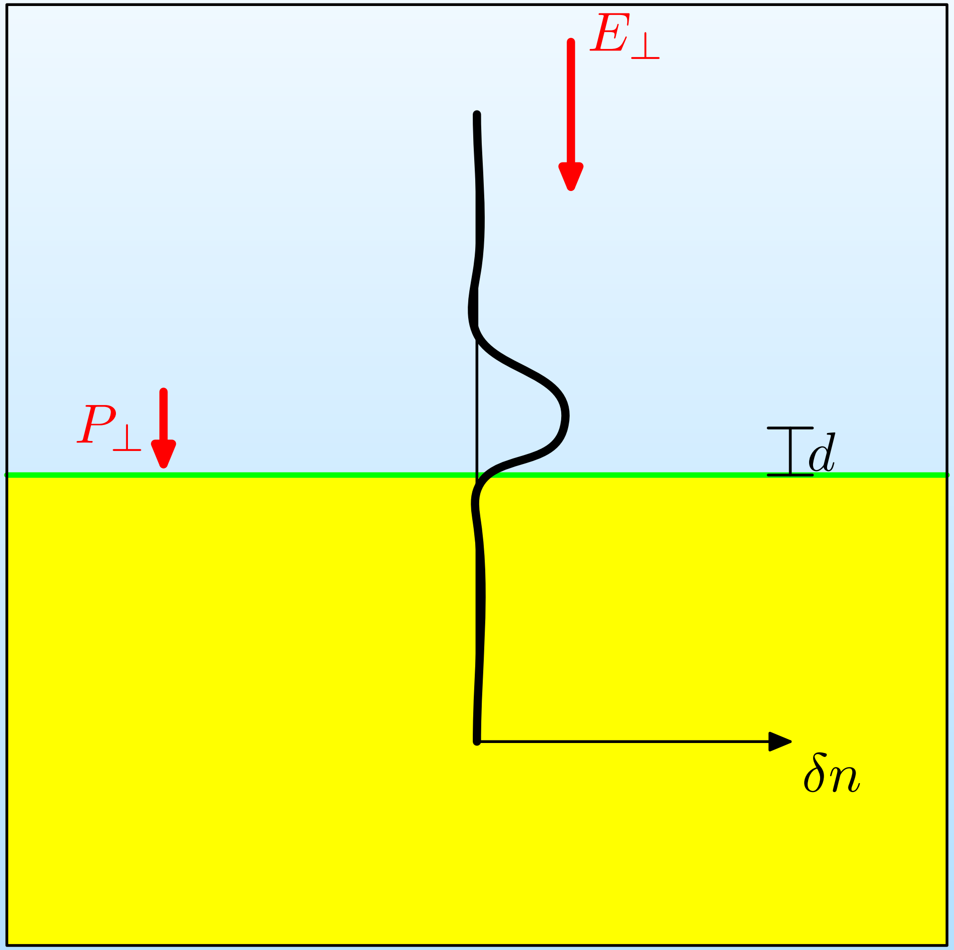
Dipolar SHG $P_i^{(2)} = \chi_{ijk} E_j E_k$ comes from the surface.
There might be SHG from bulk...
but it is *multipolar*

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

Nonlinear Surface Response: a



Nonlinear Surface Response: a



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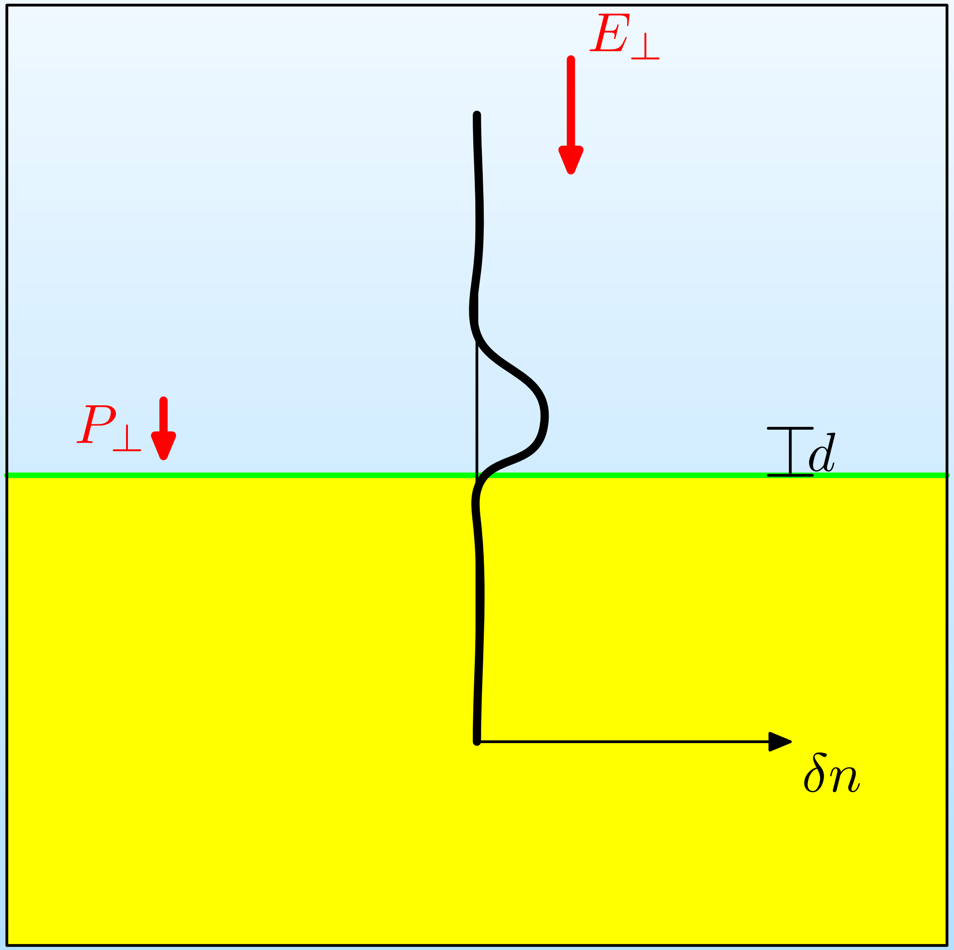

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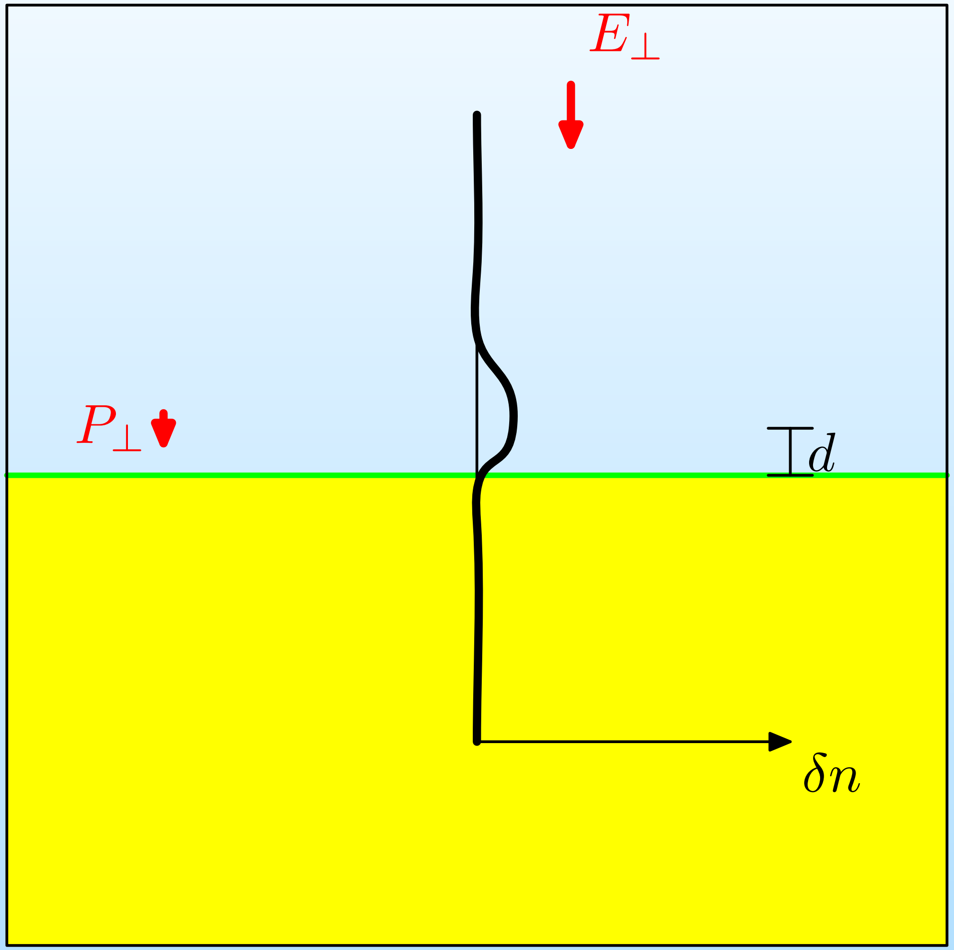

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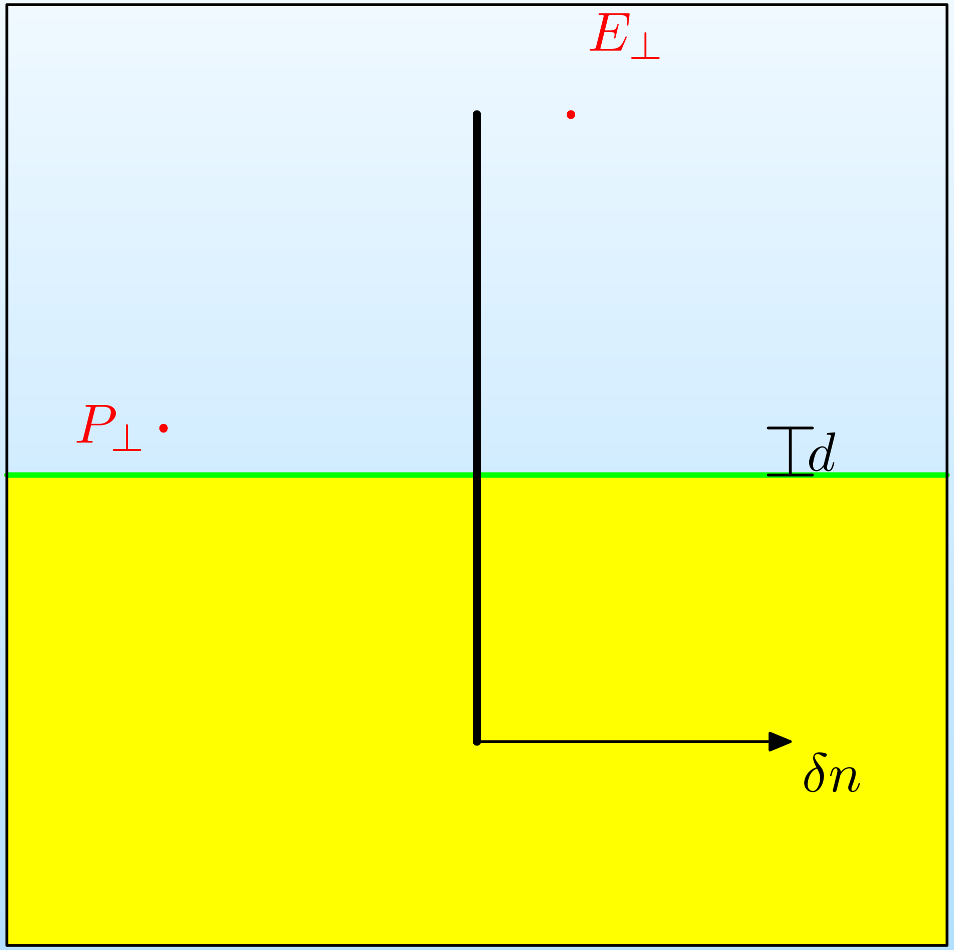

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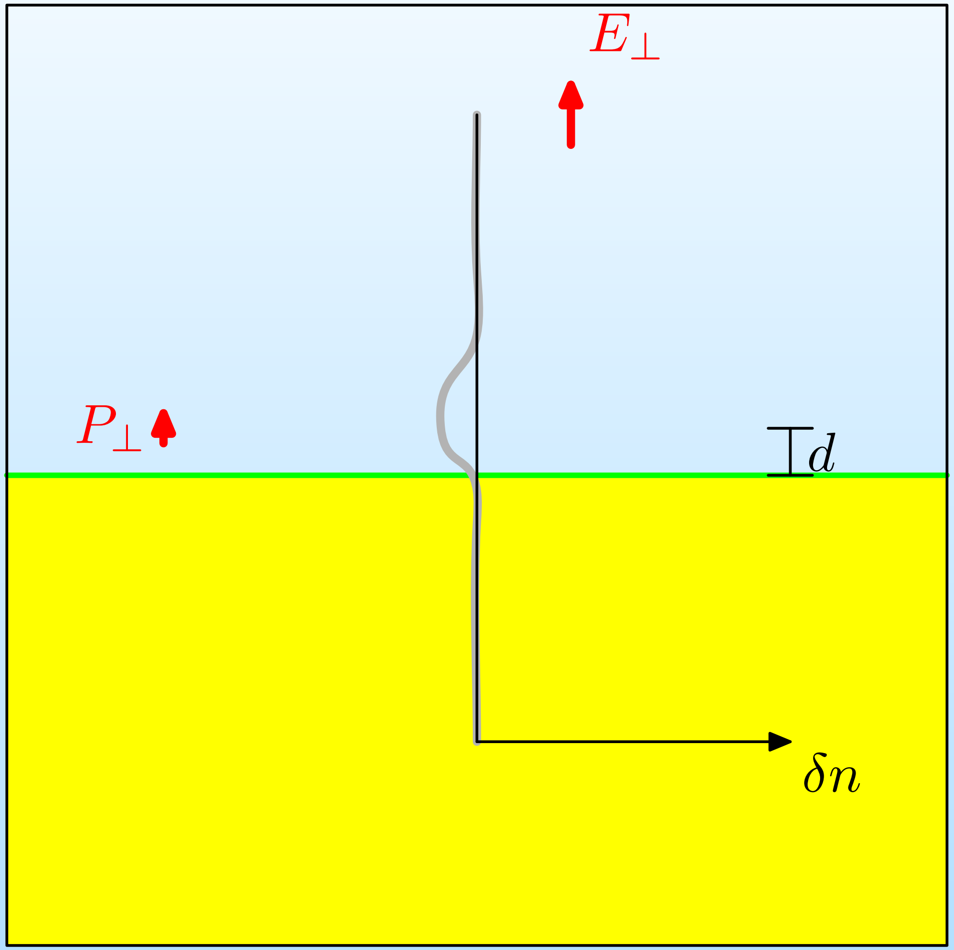

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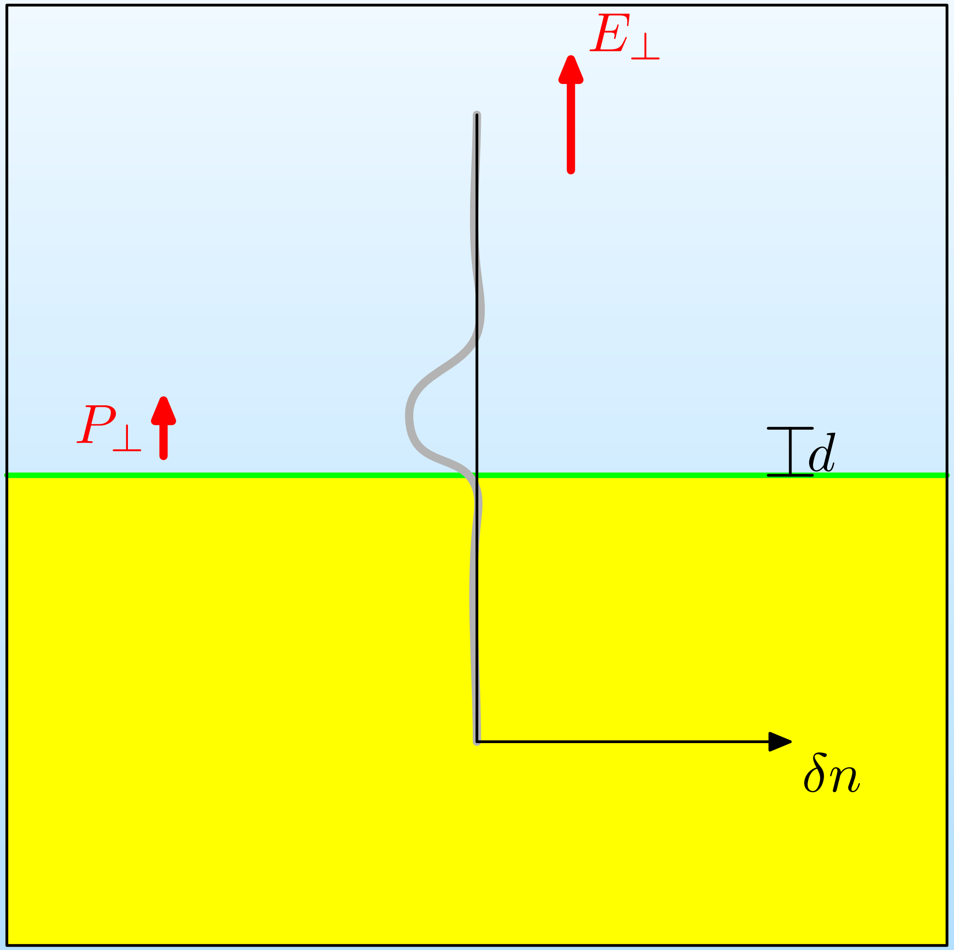

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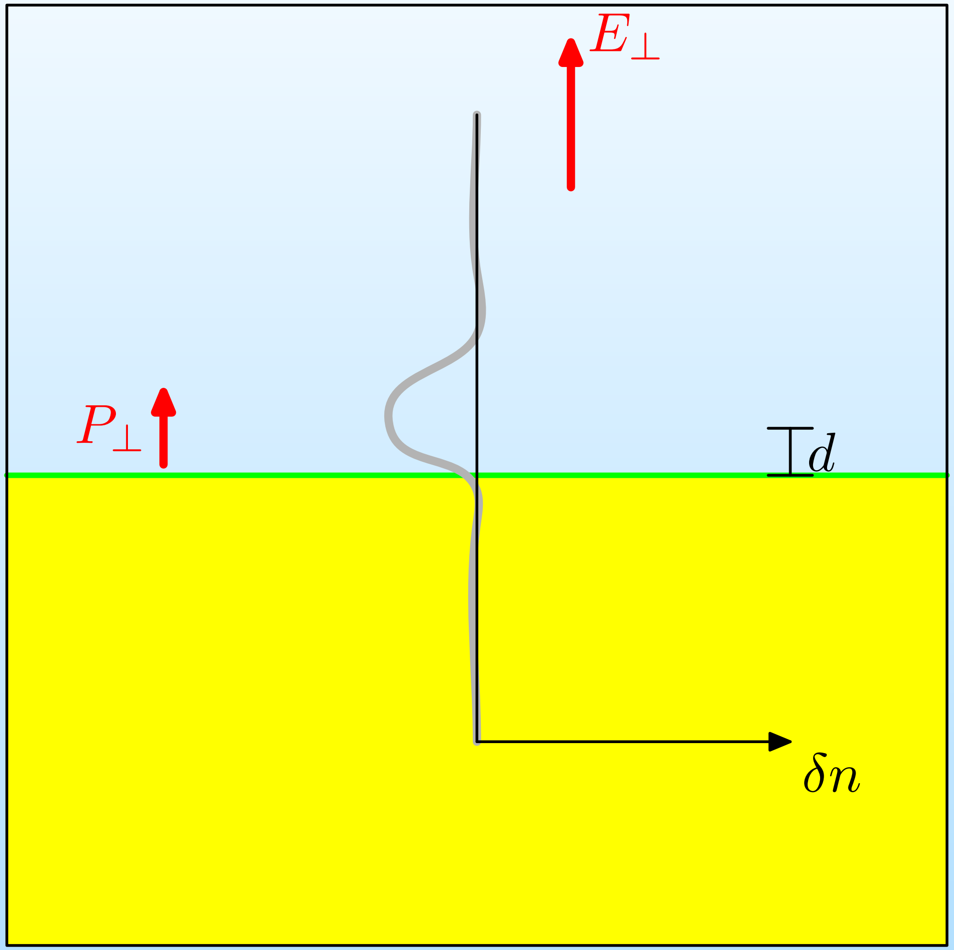

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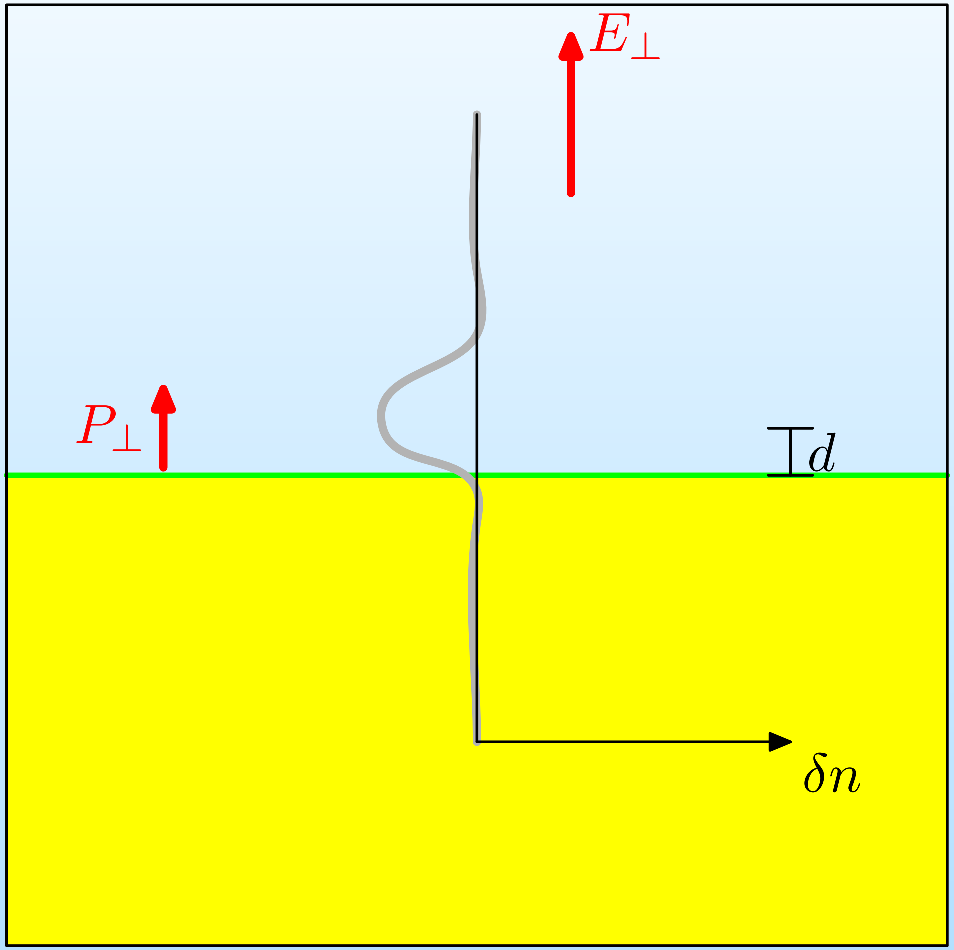

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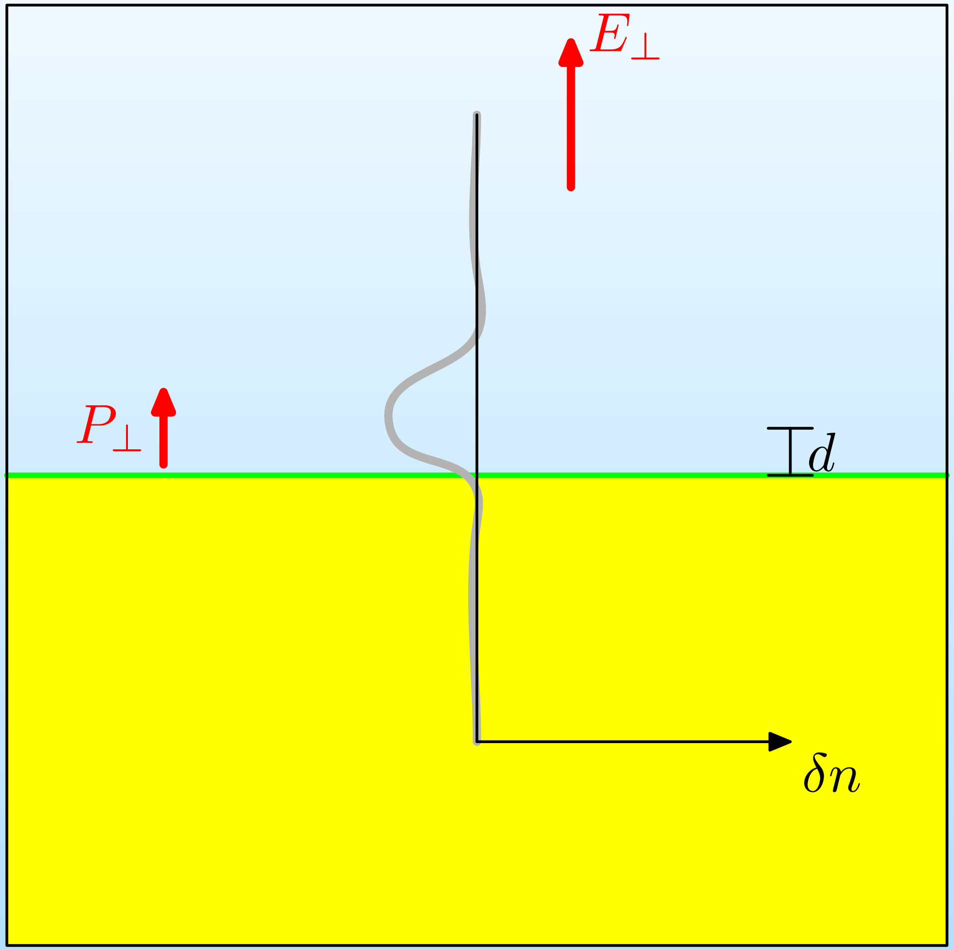

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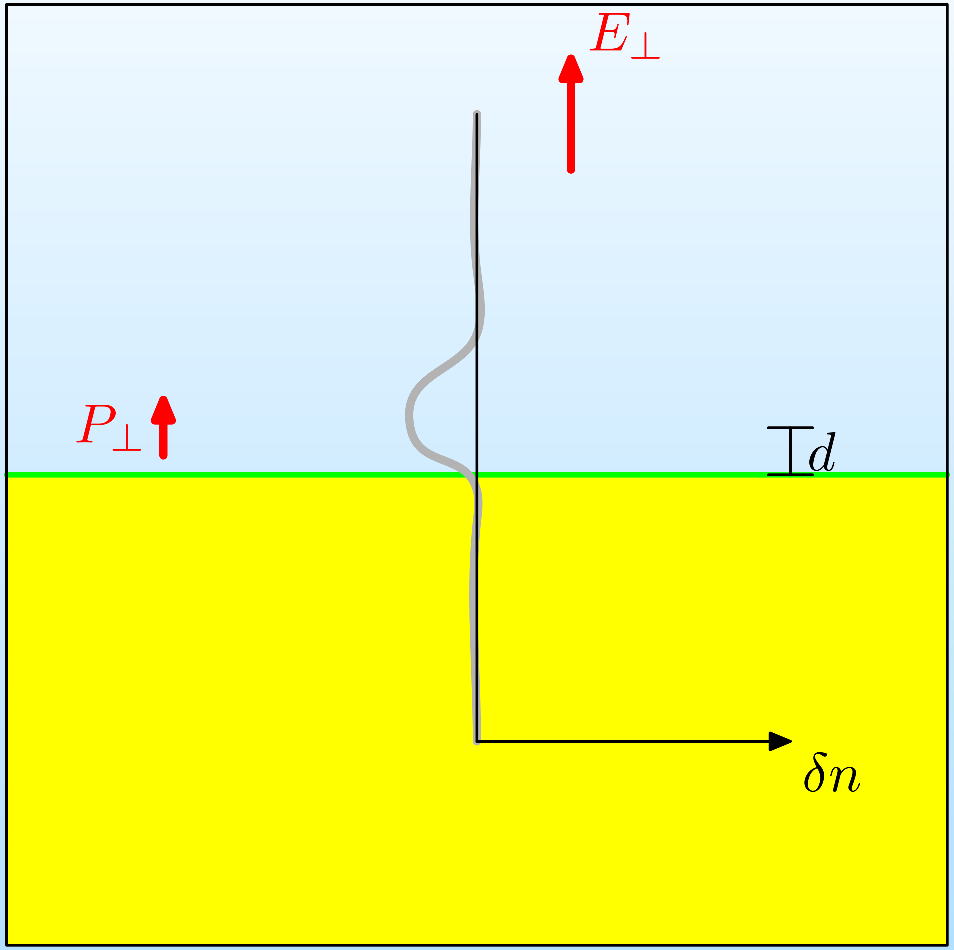

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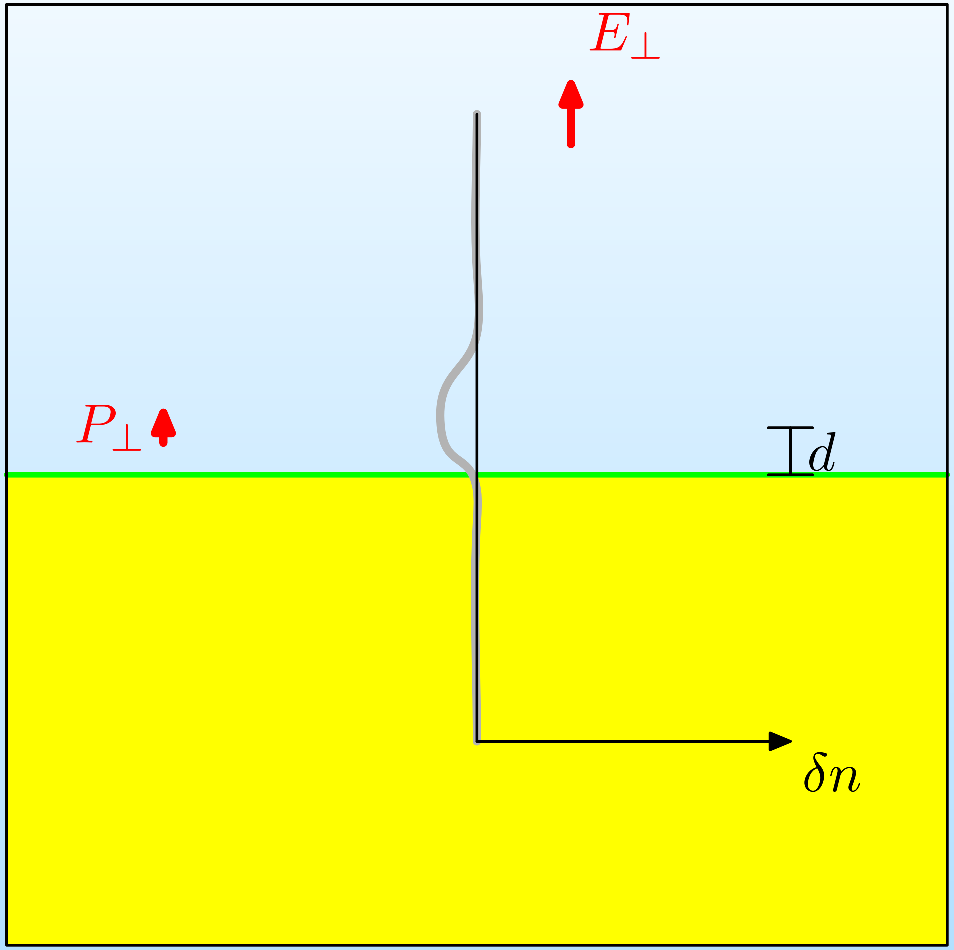

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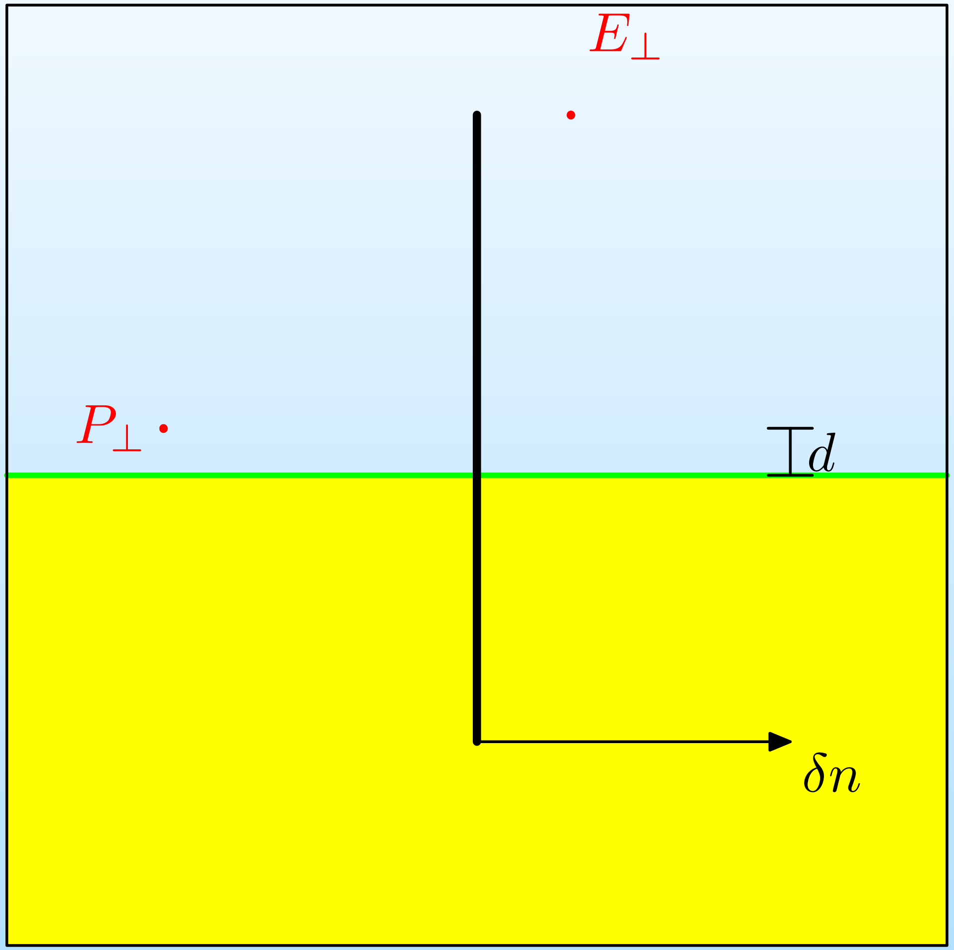

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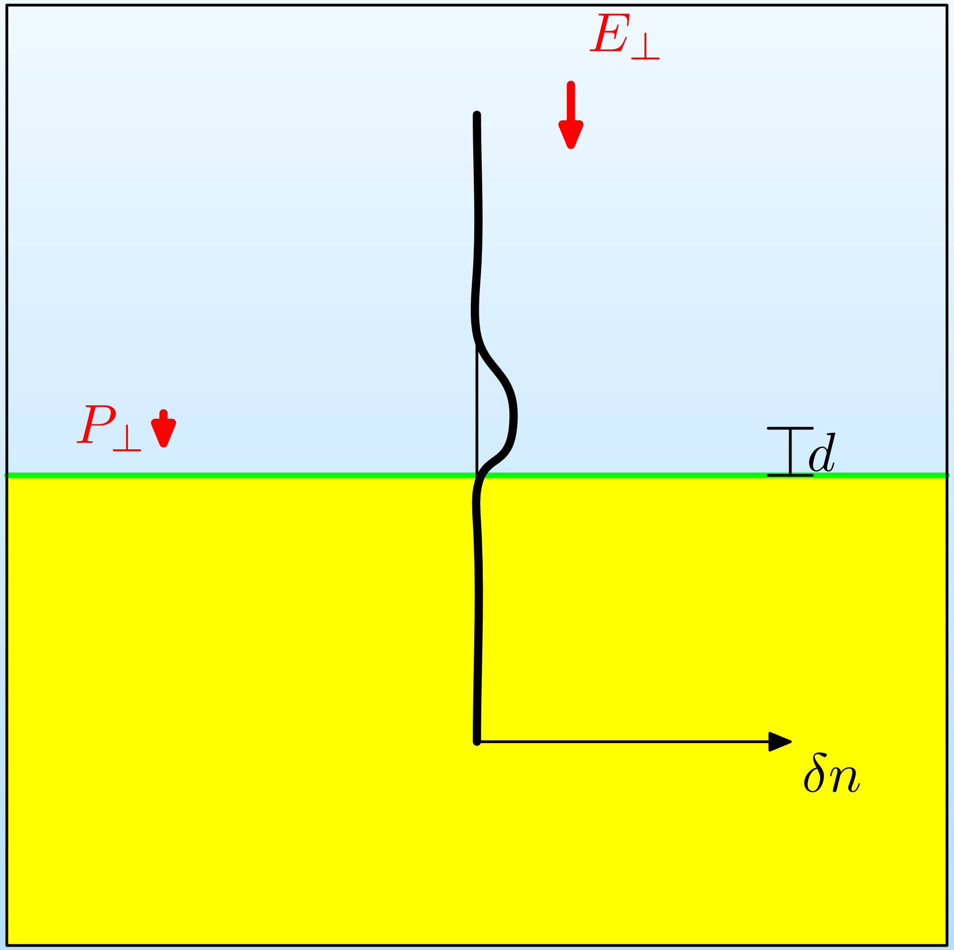

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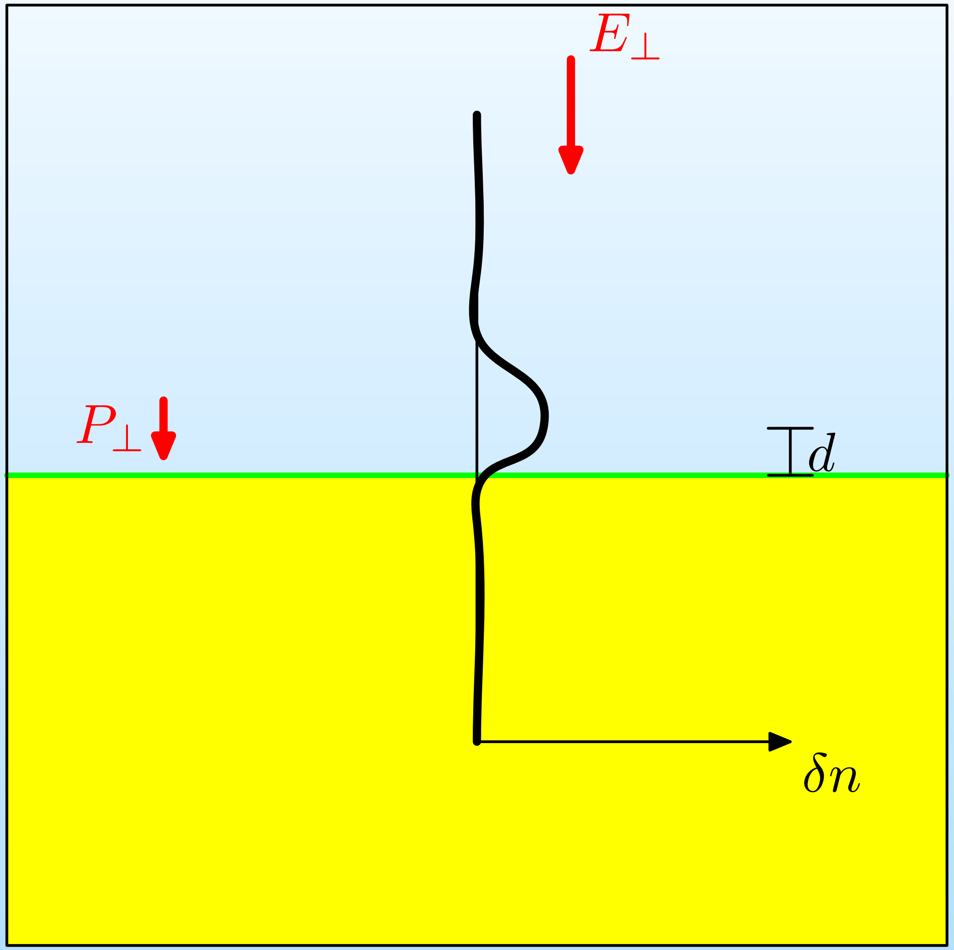

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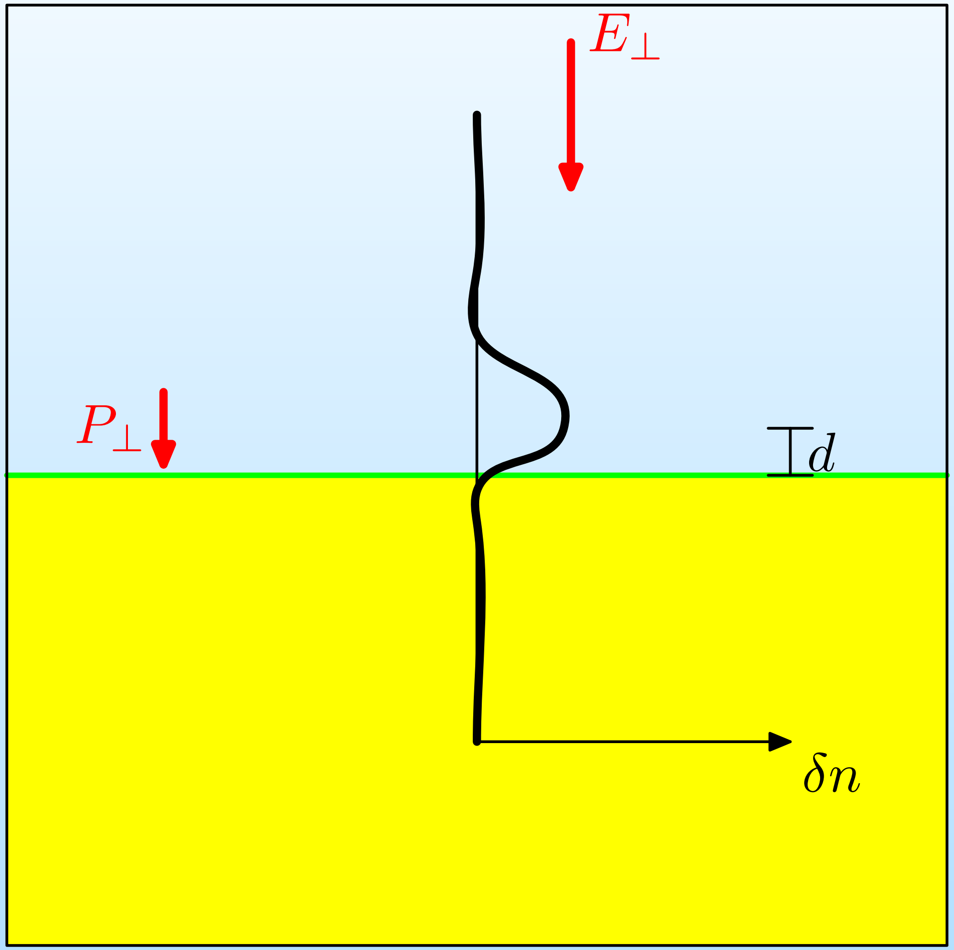

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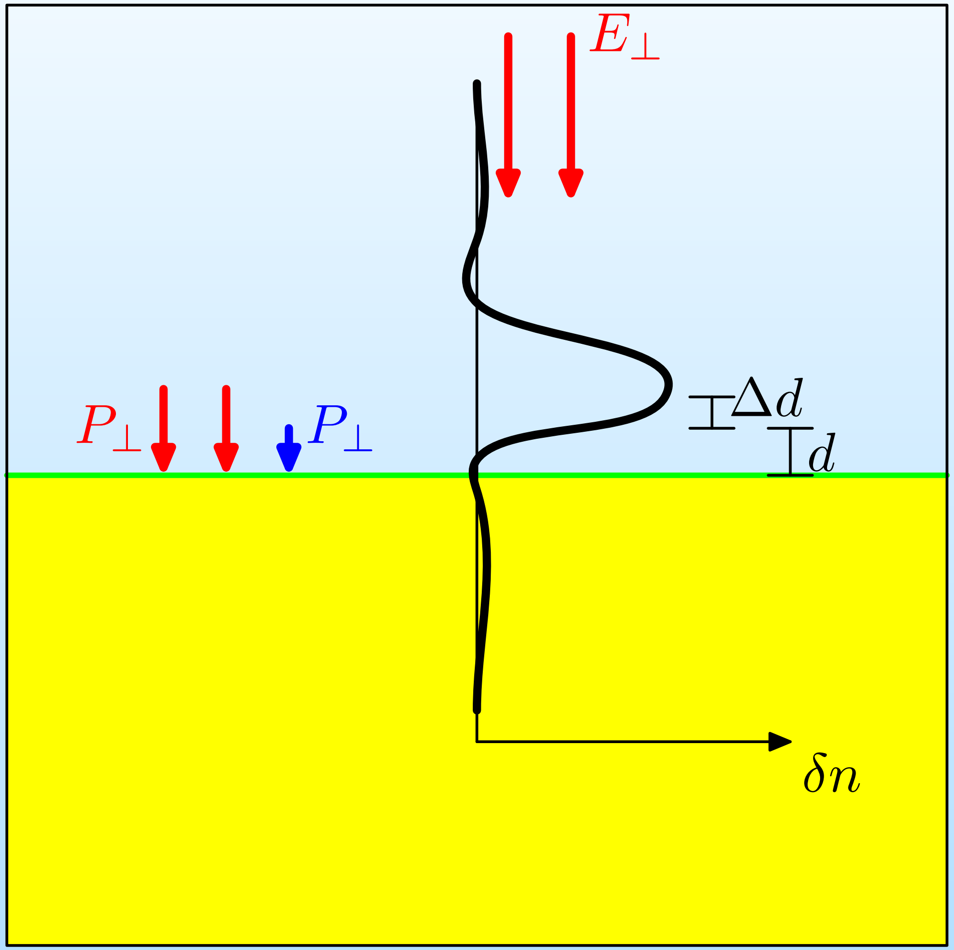

$$\chi_{\perp\perp\perp} \propto a \propto \Delta d$$

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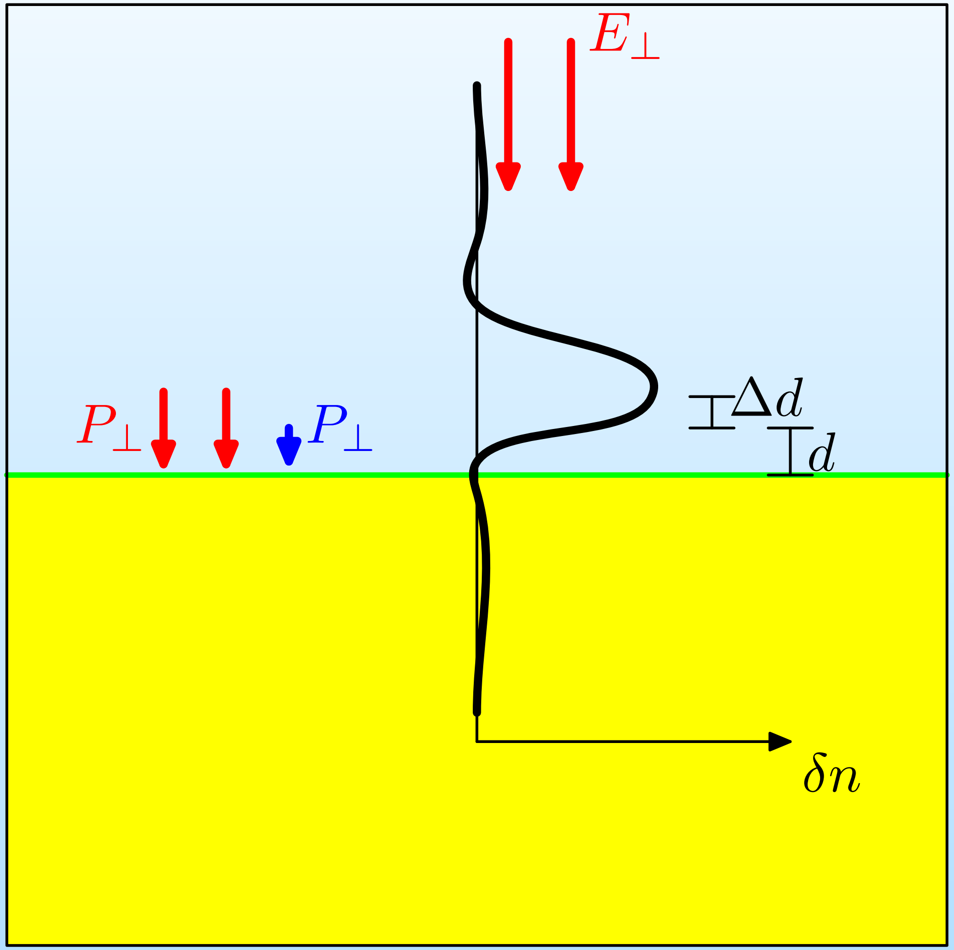

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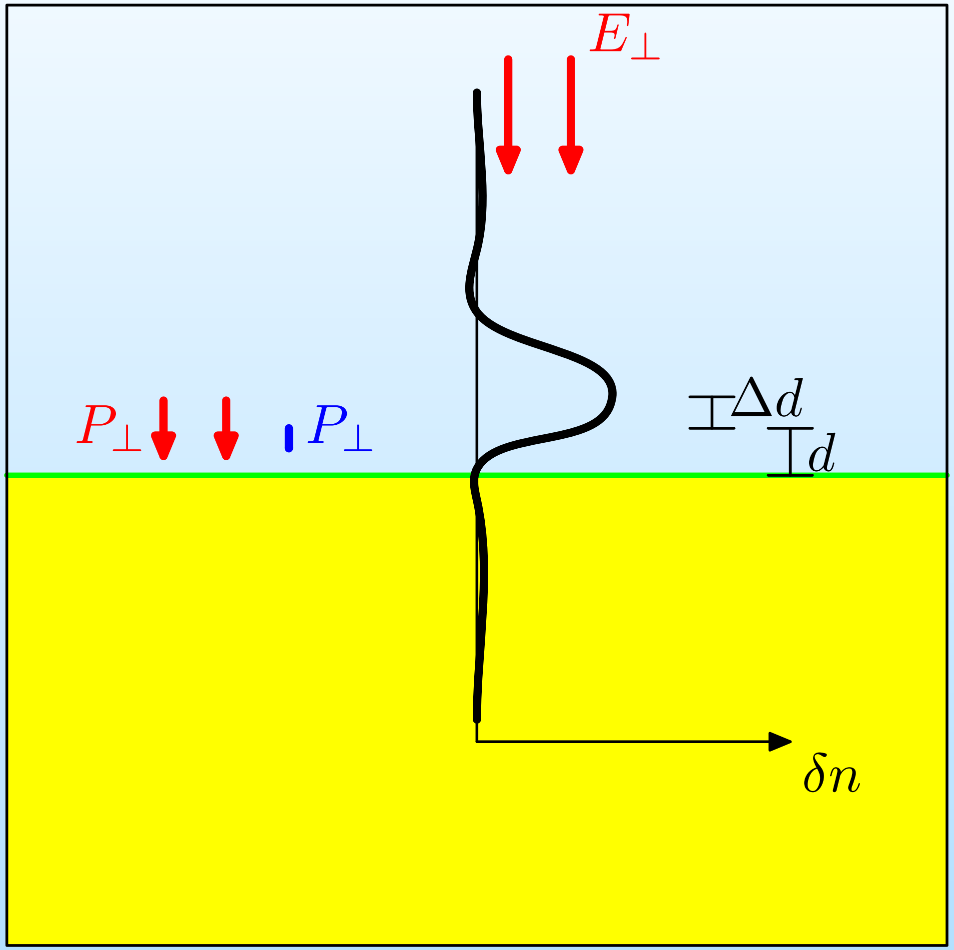

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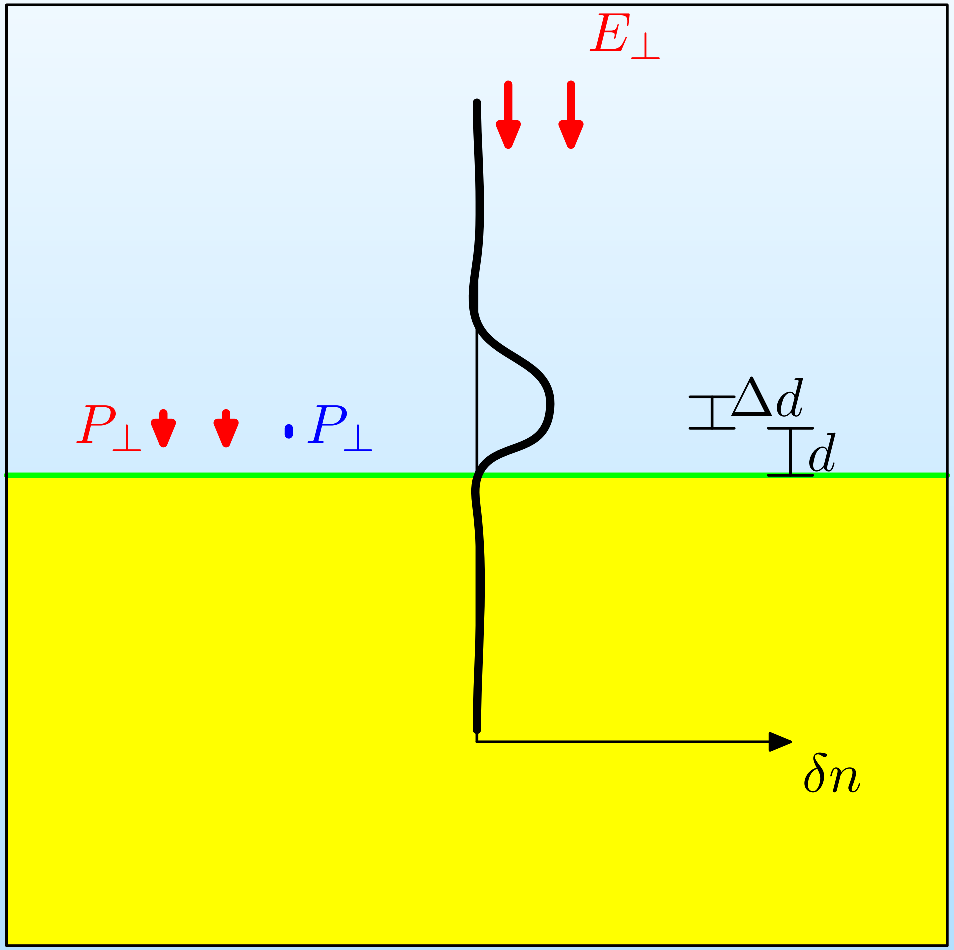

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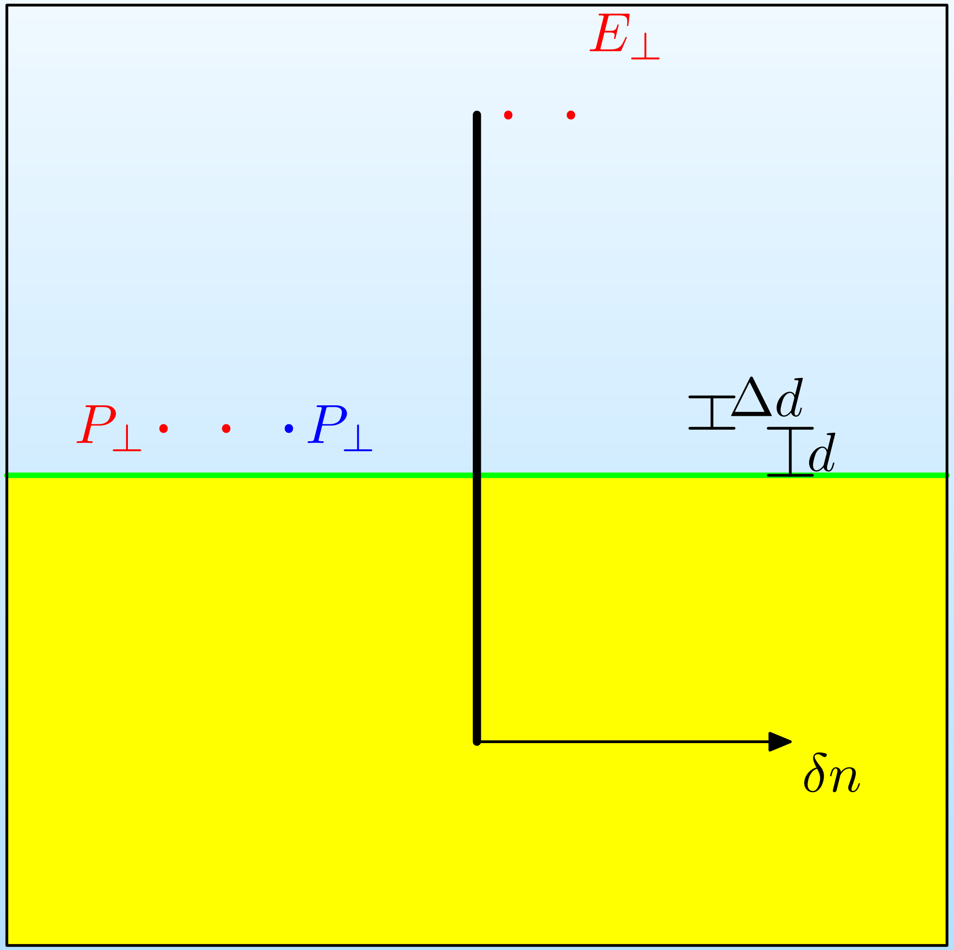

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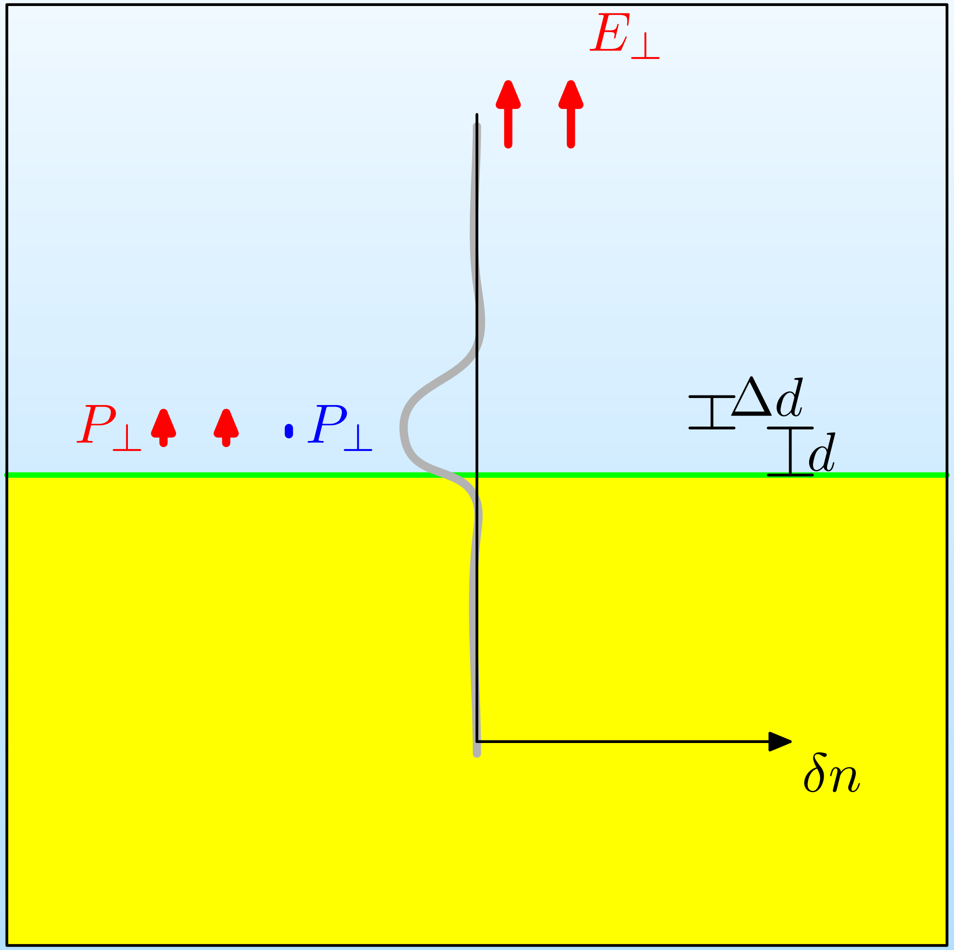

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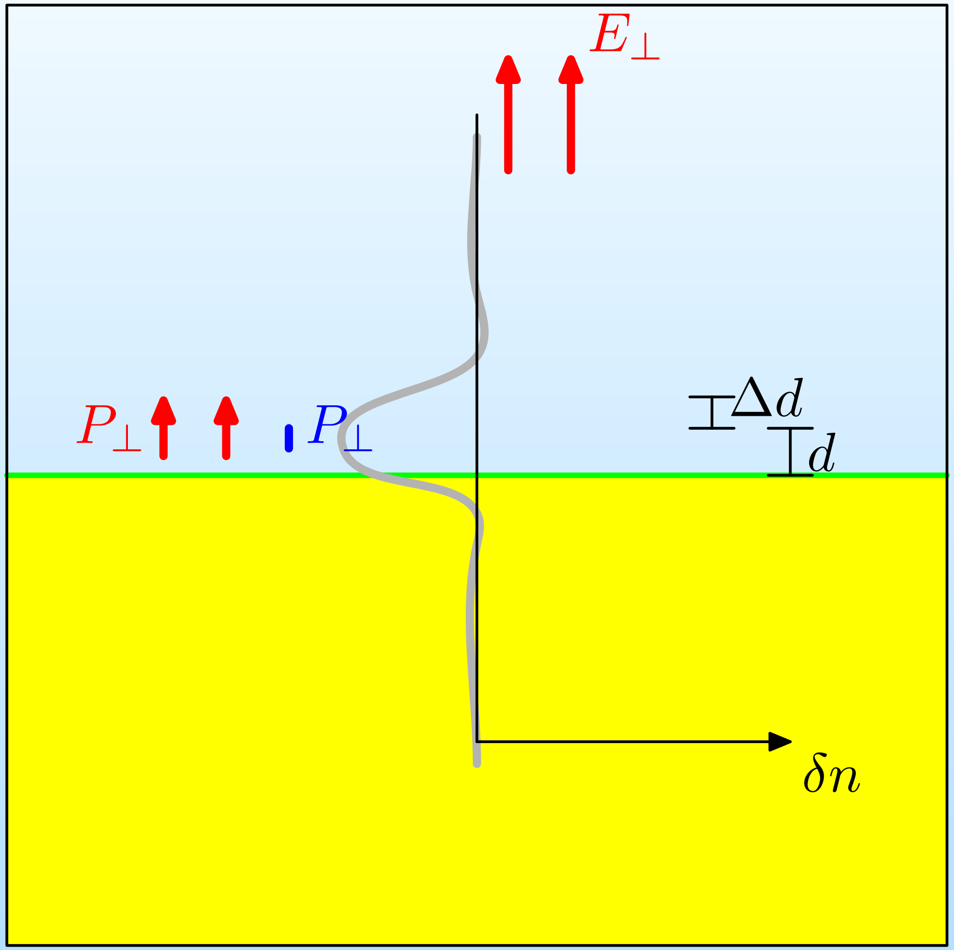

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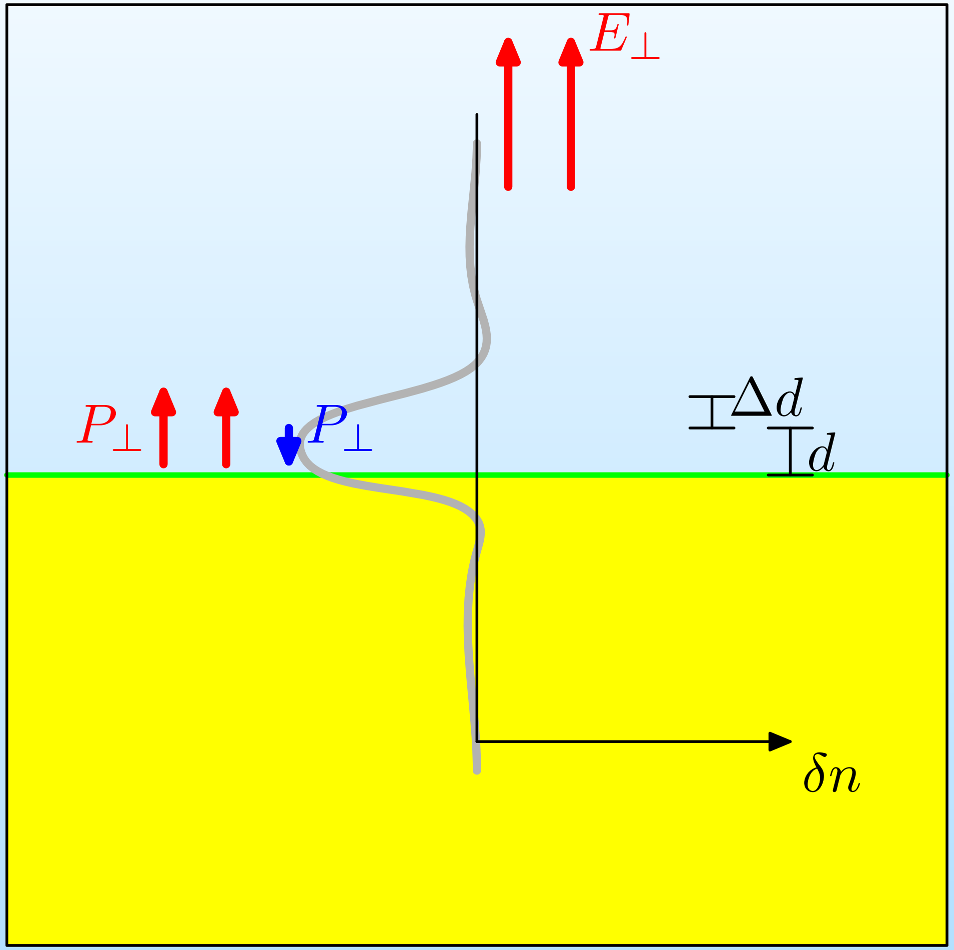

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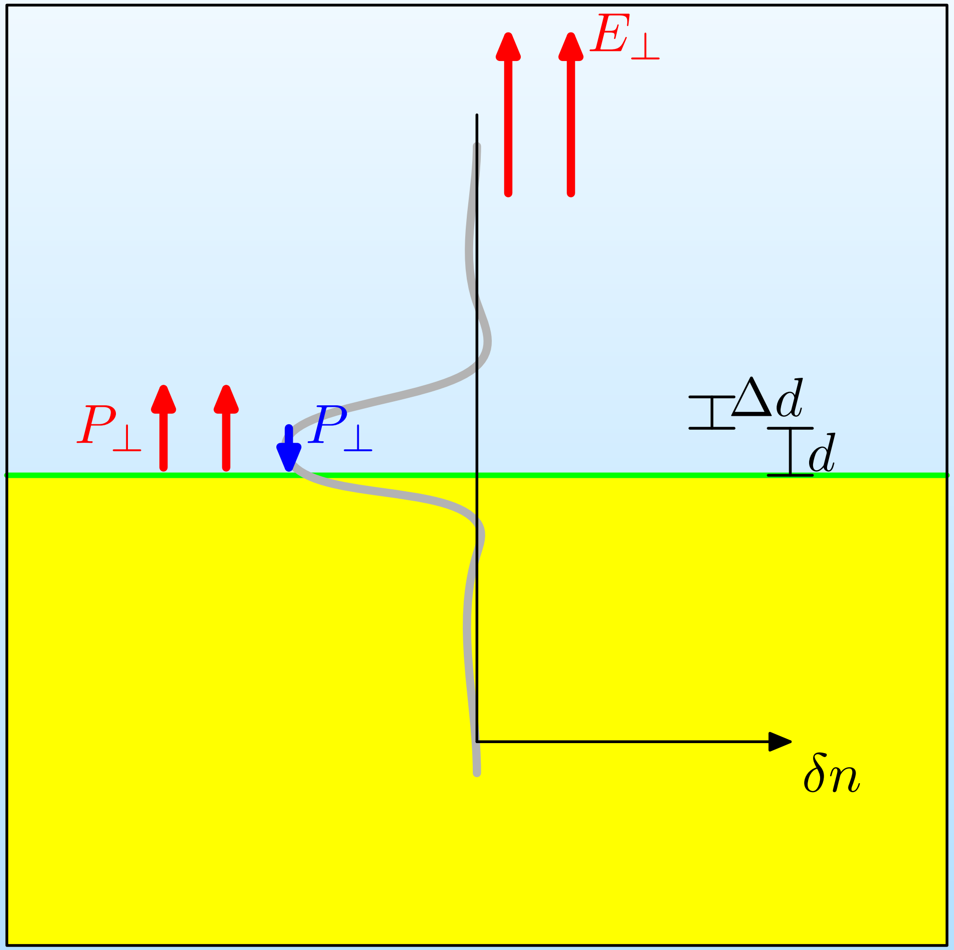

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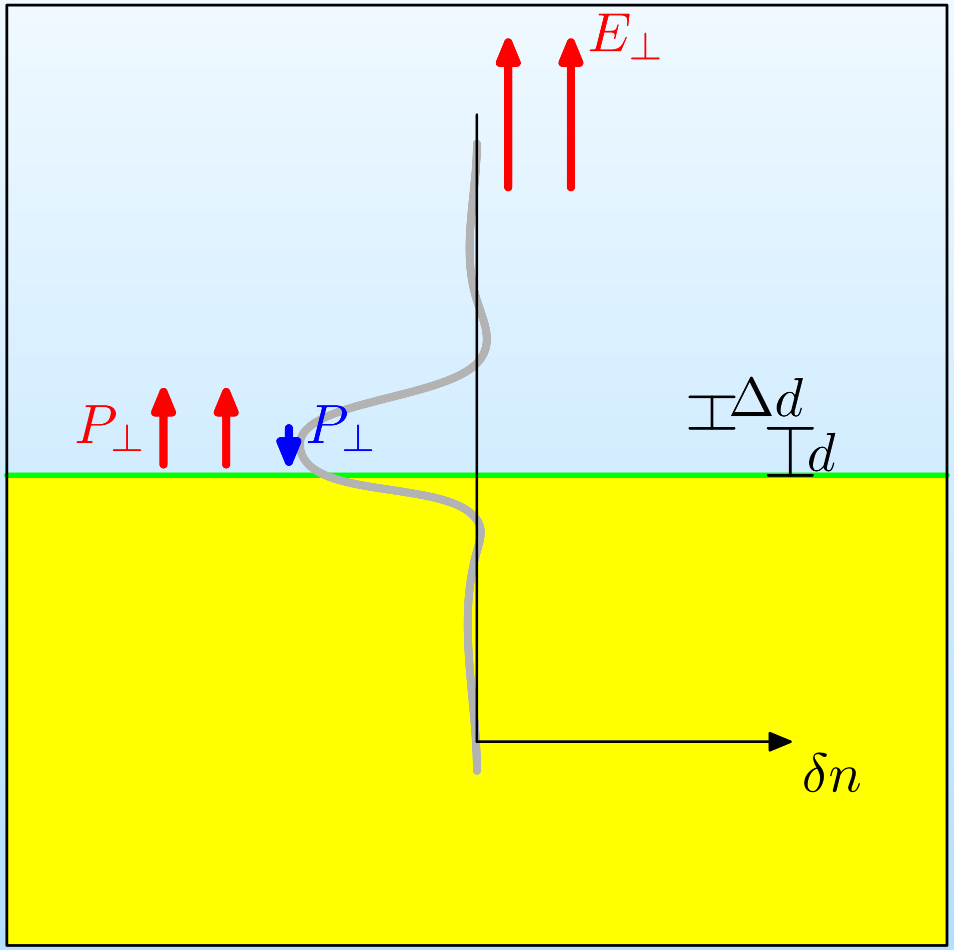

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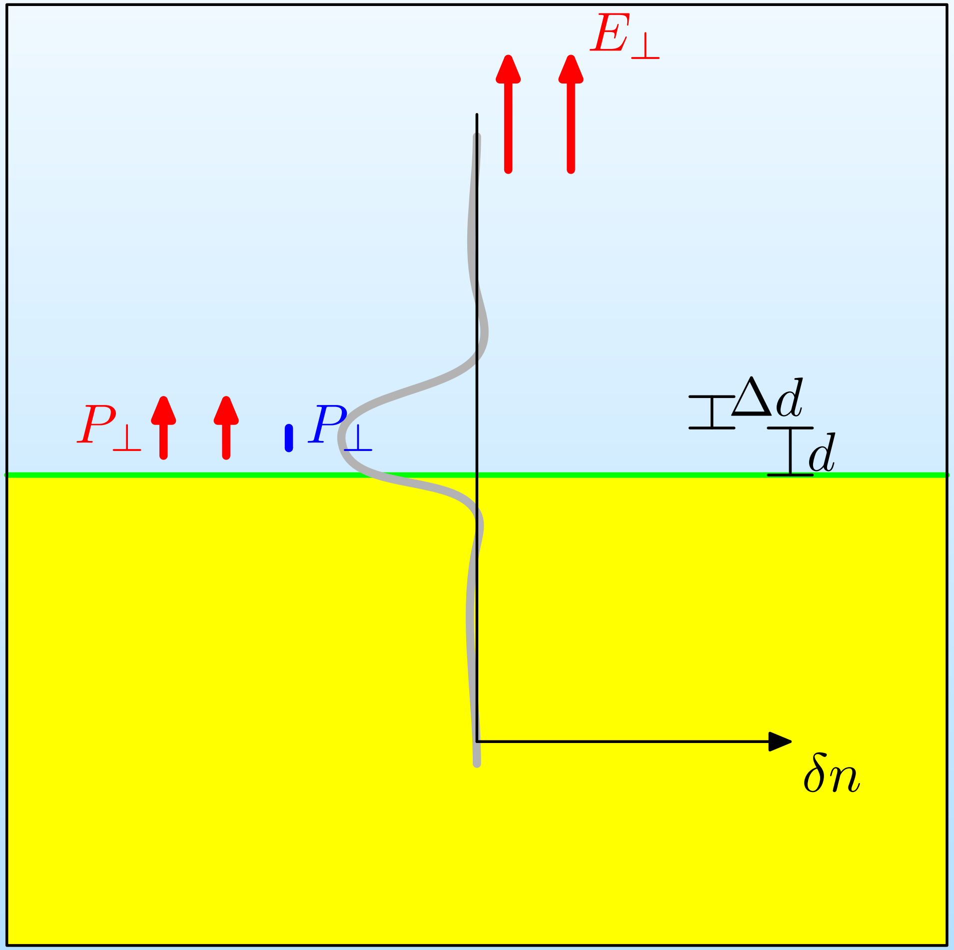

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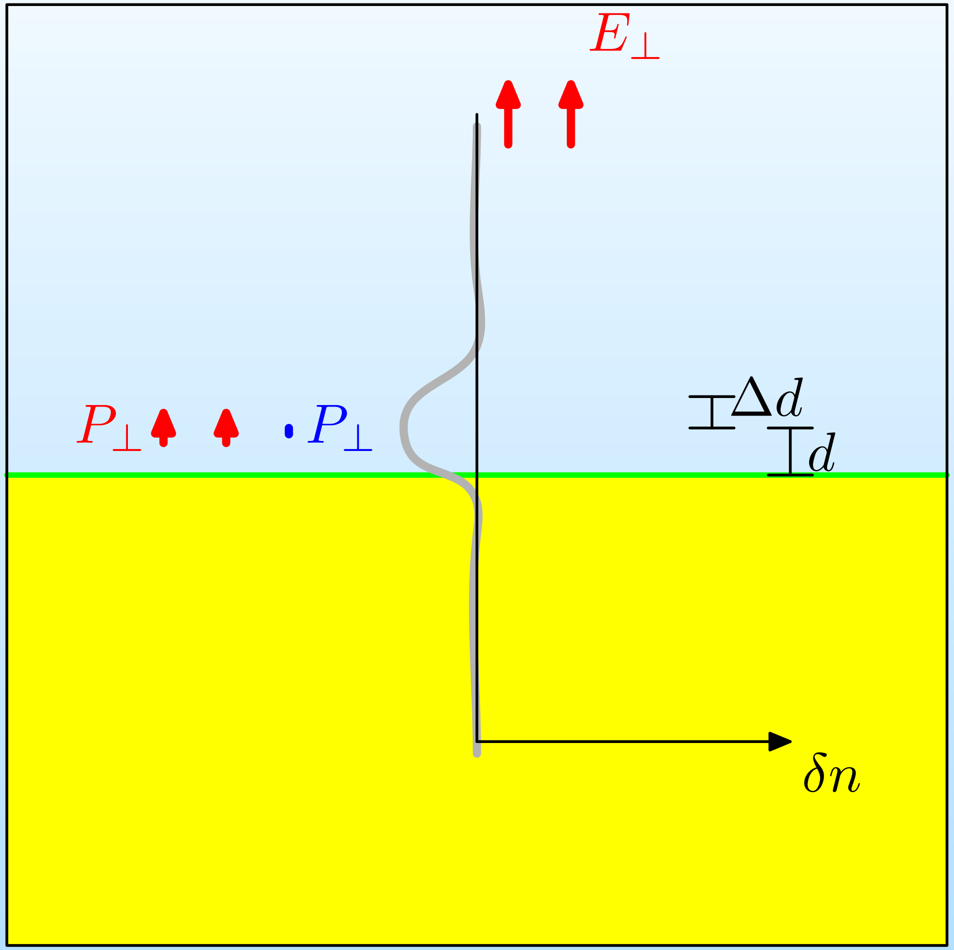

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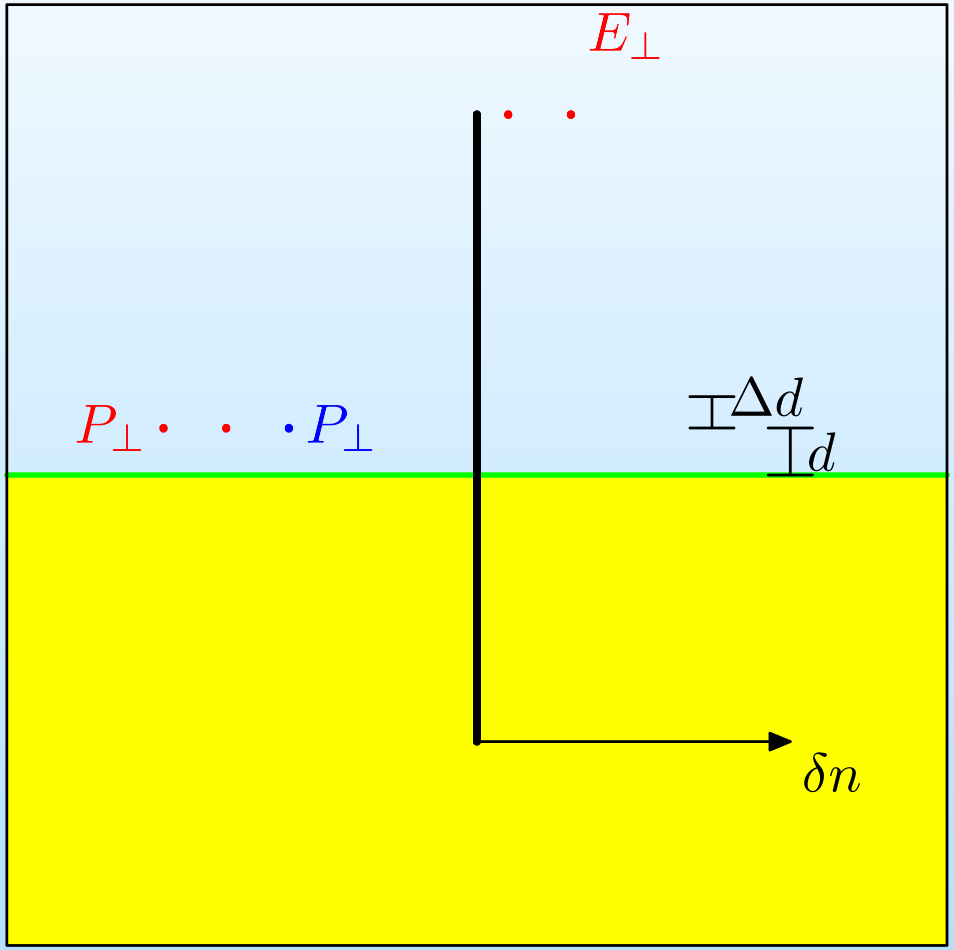

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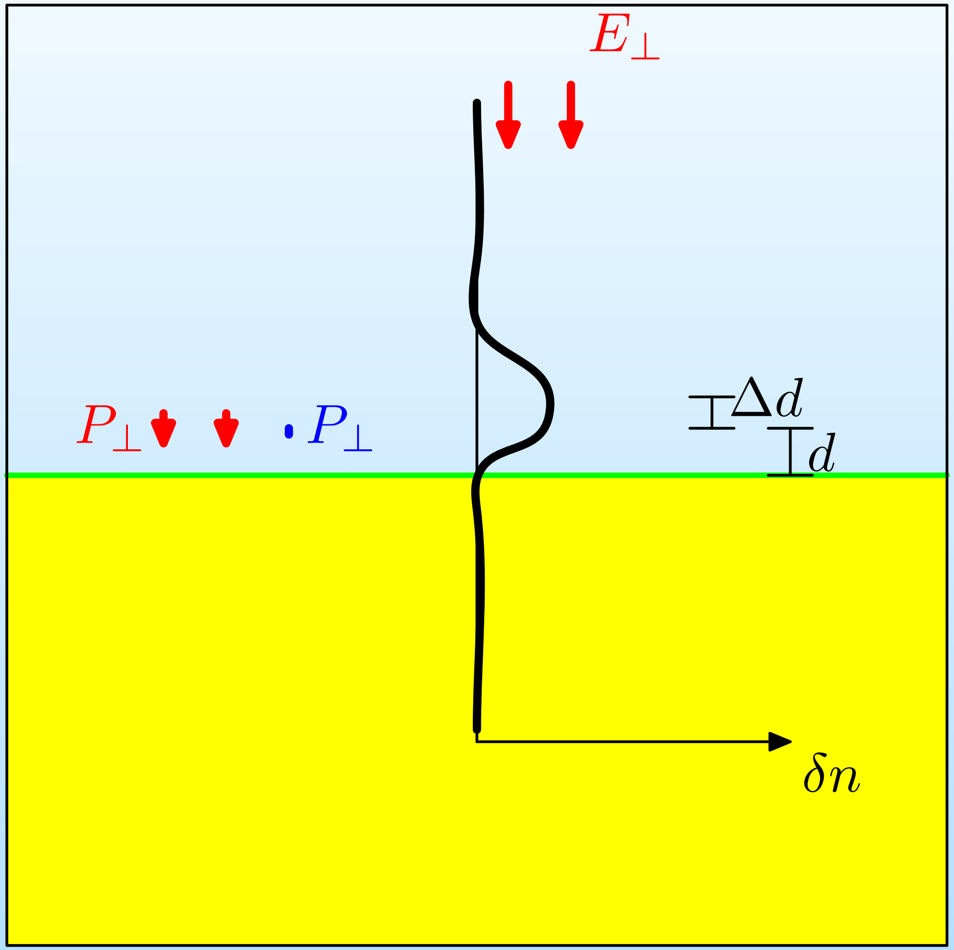

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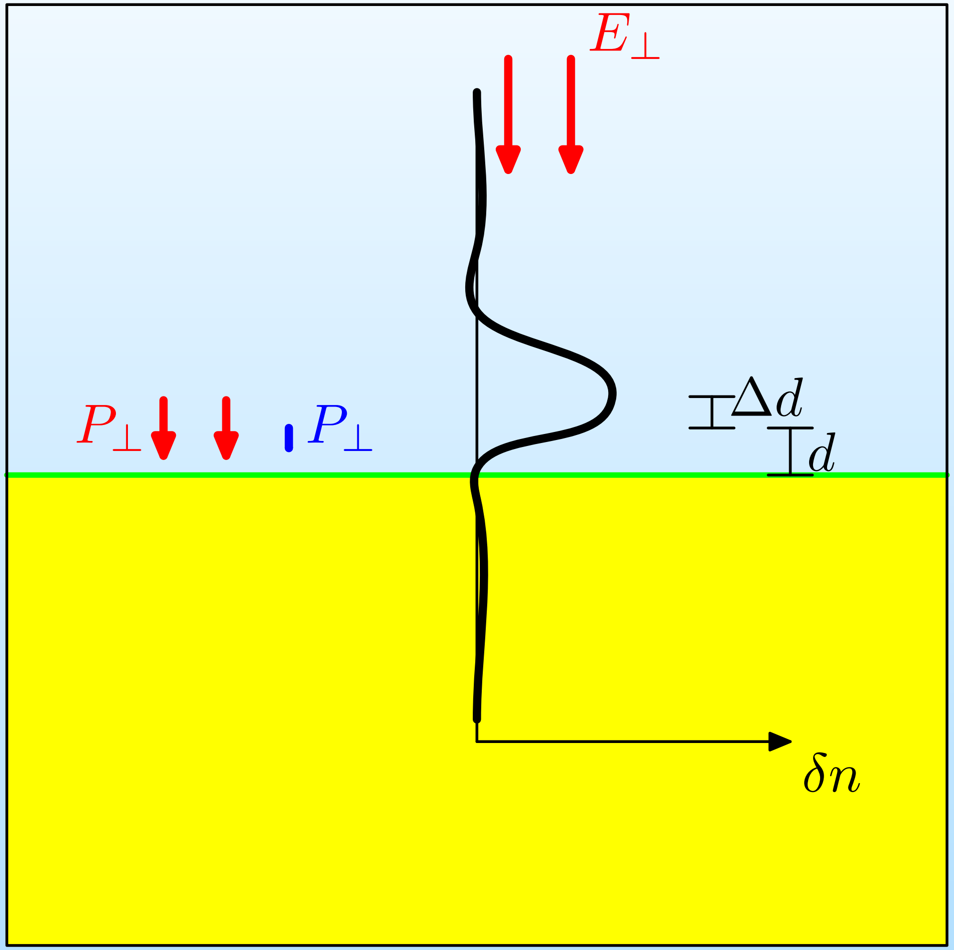

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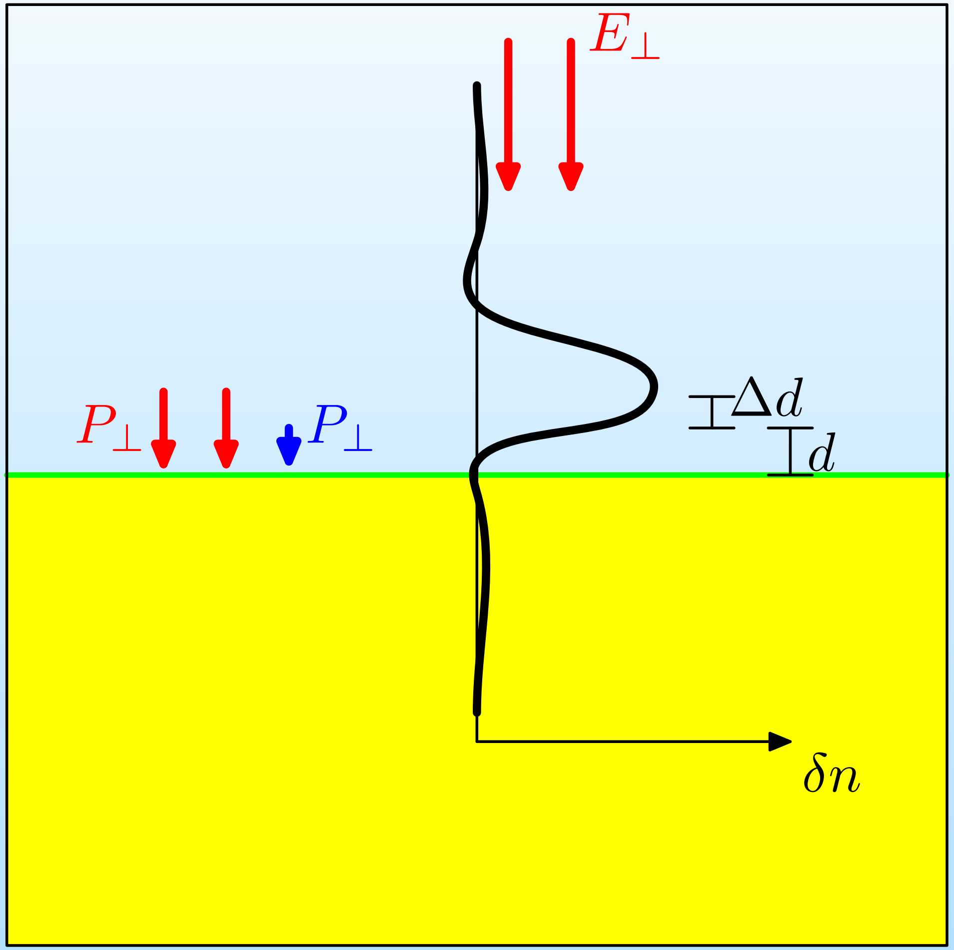

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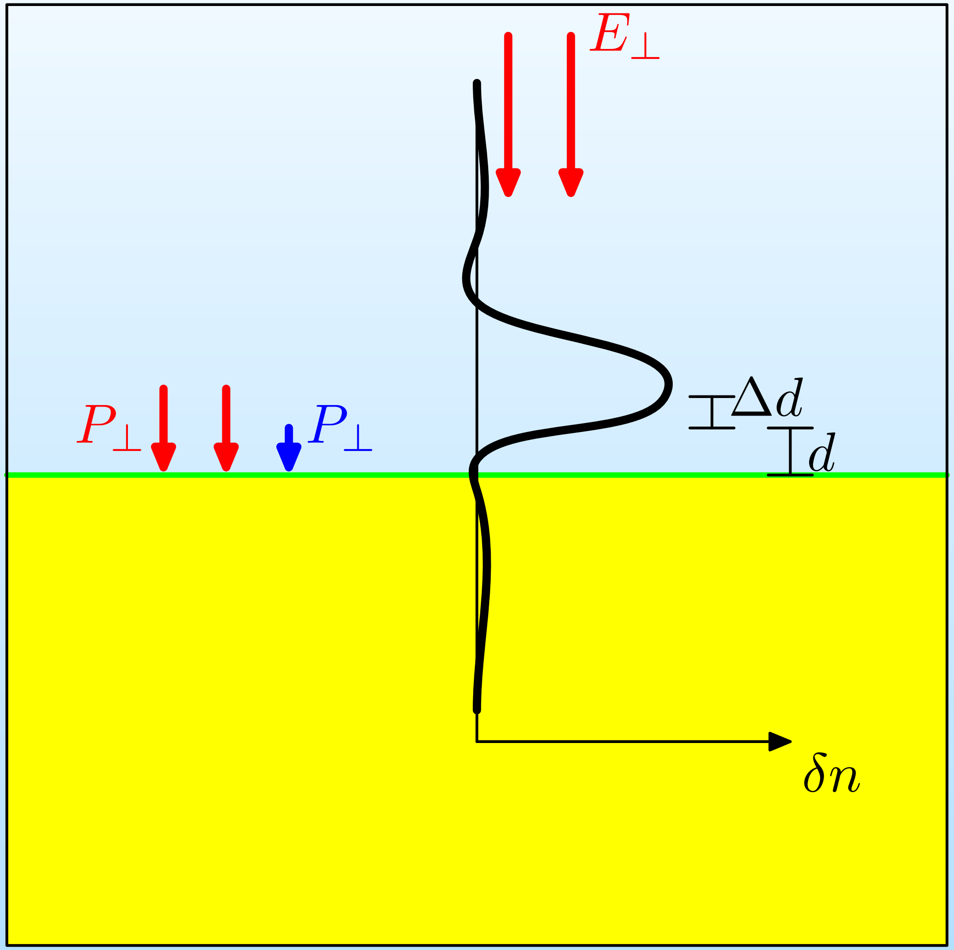

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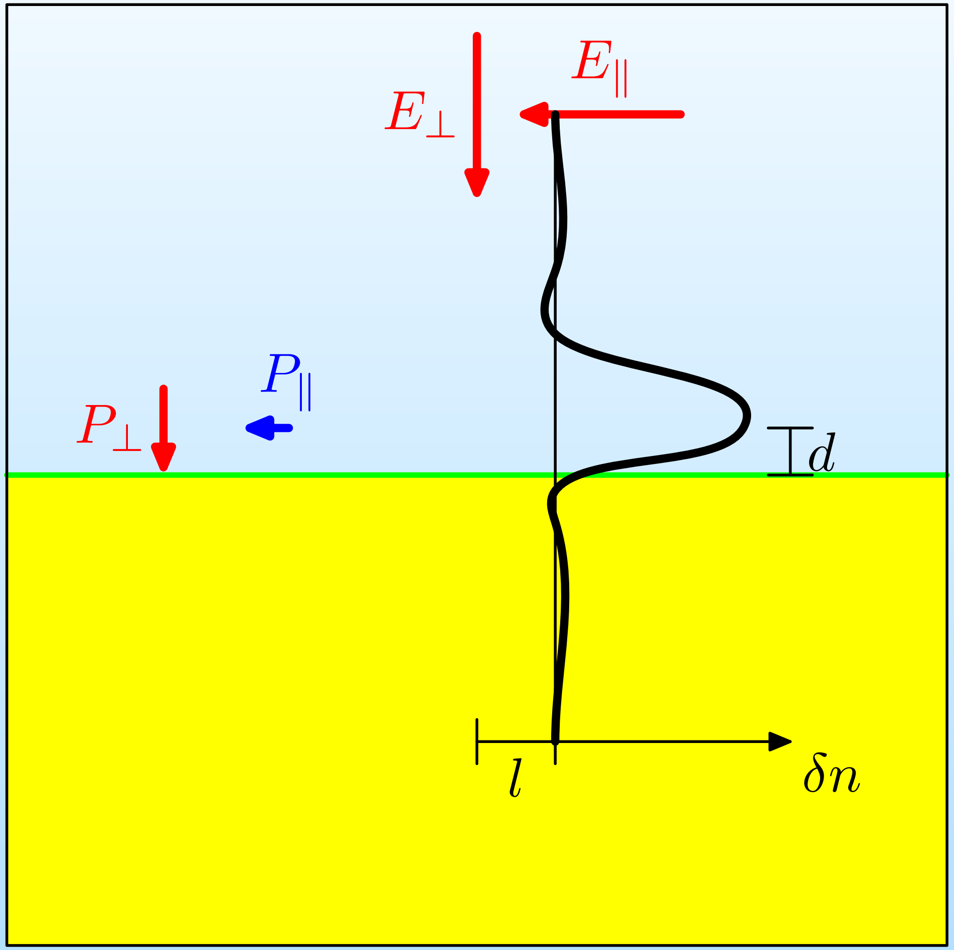

$$\chi_{\perp\|\|} \propto b \propto l$$

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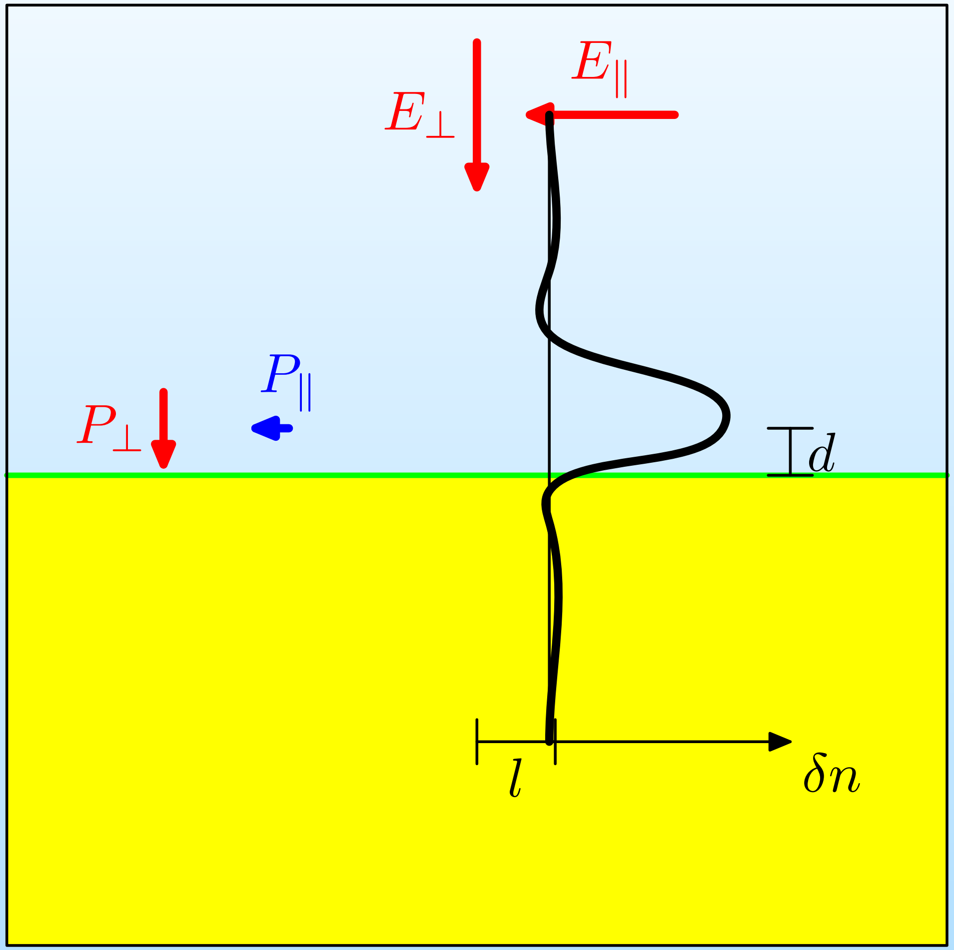

$$\chi_{\perp\parallel\parallel} \propto b \propto l$$

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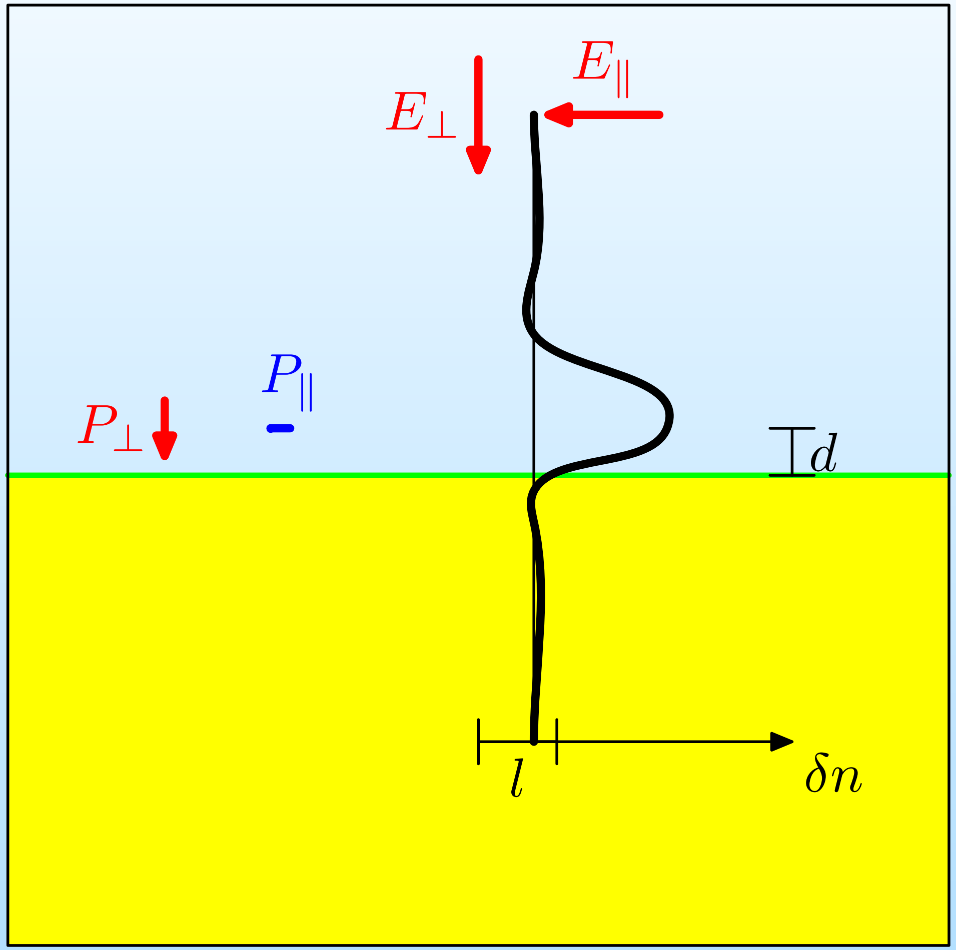

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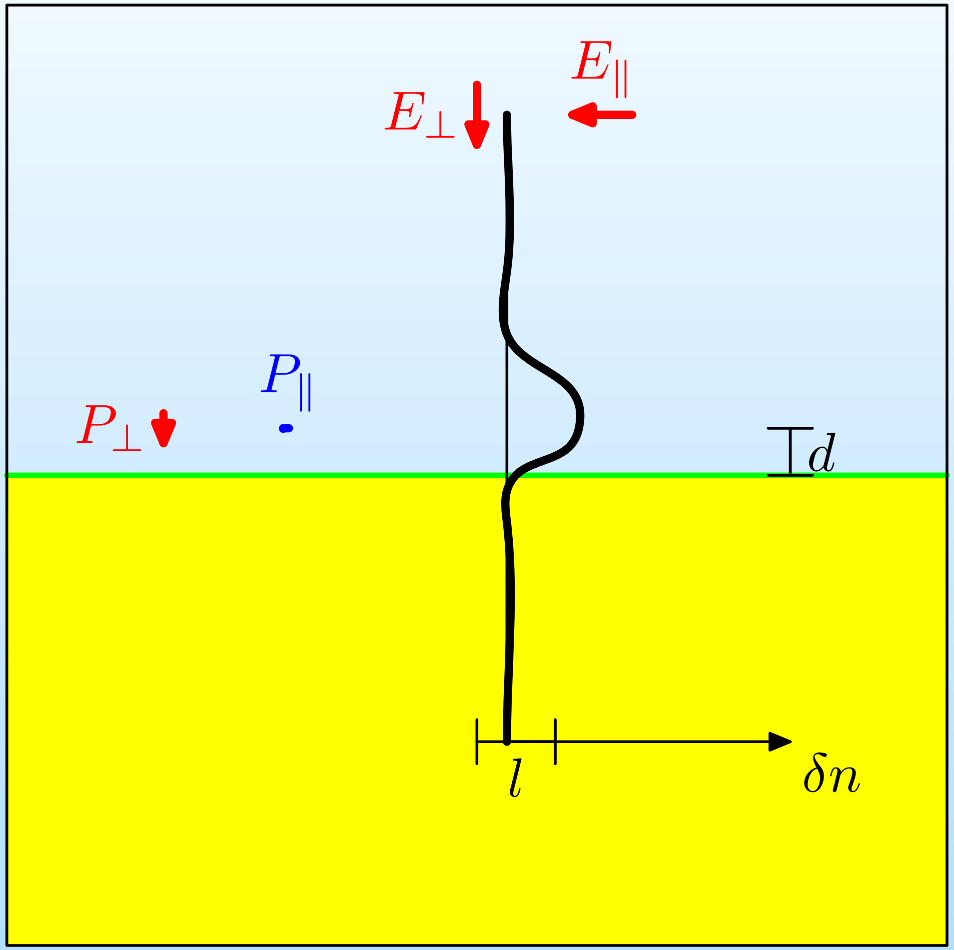

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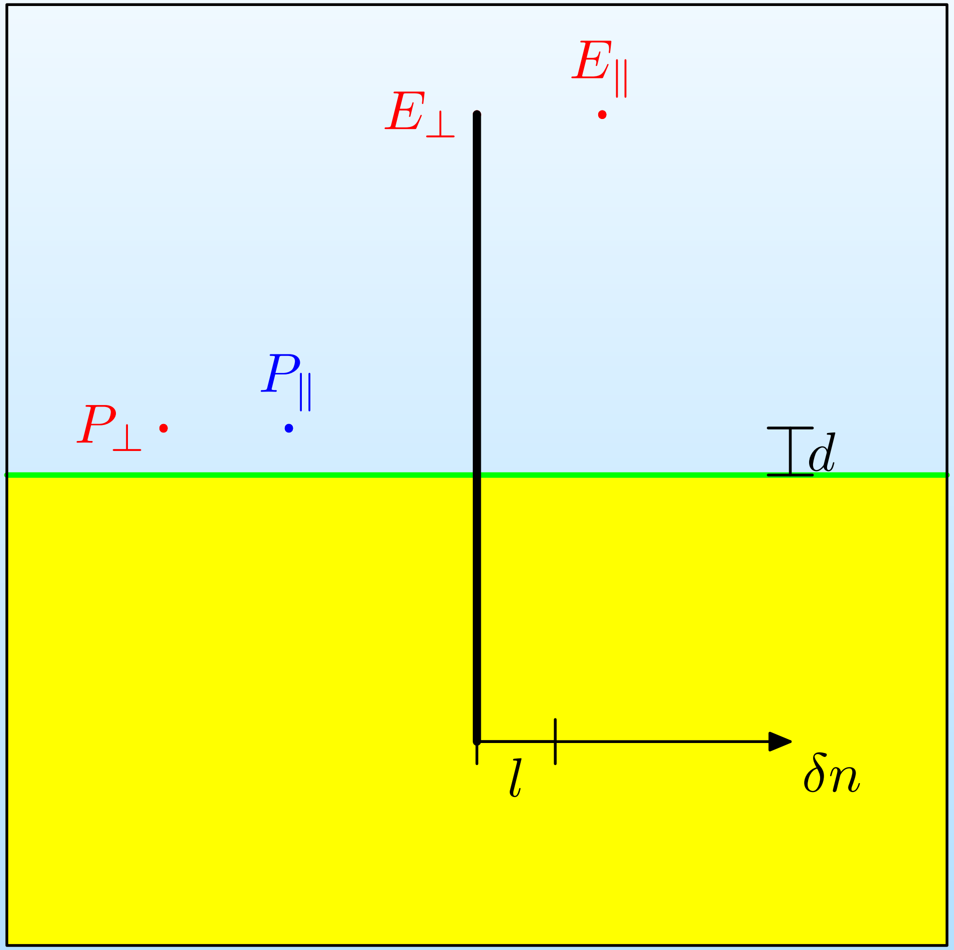

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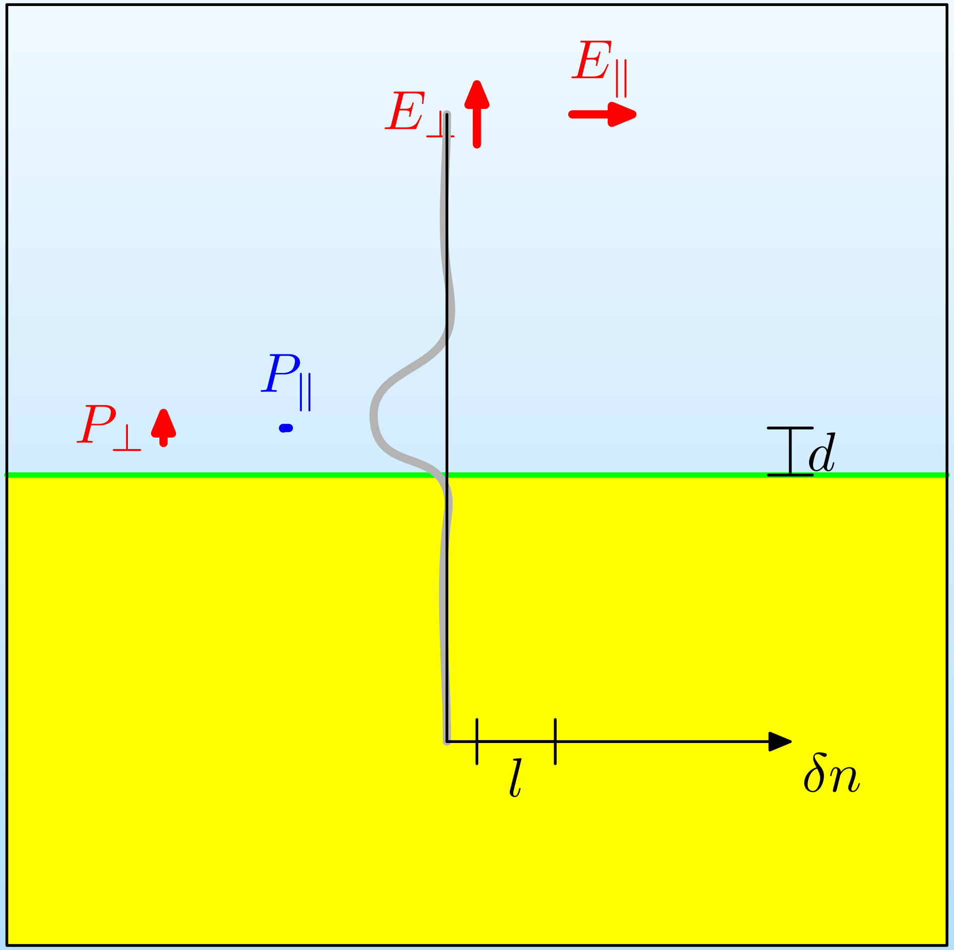

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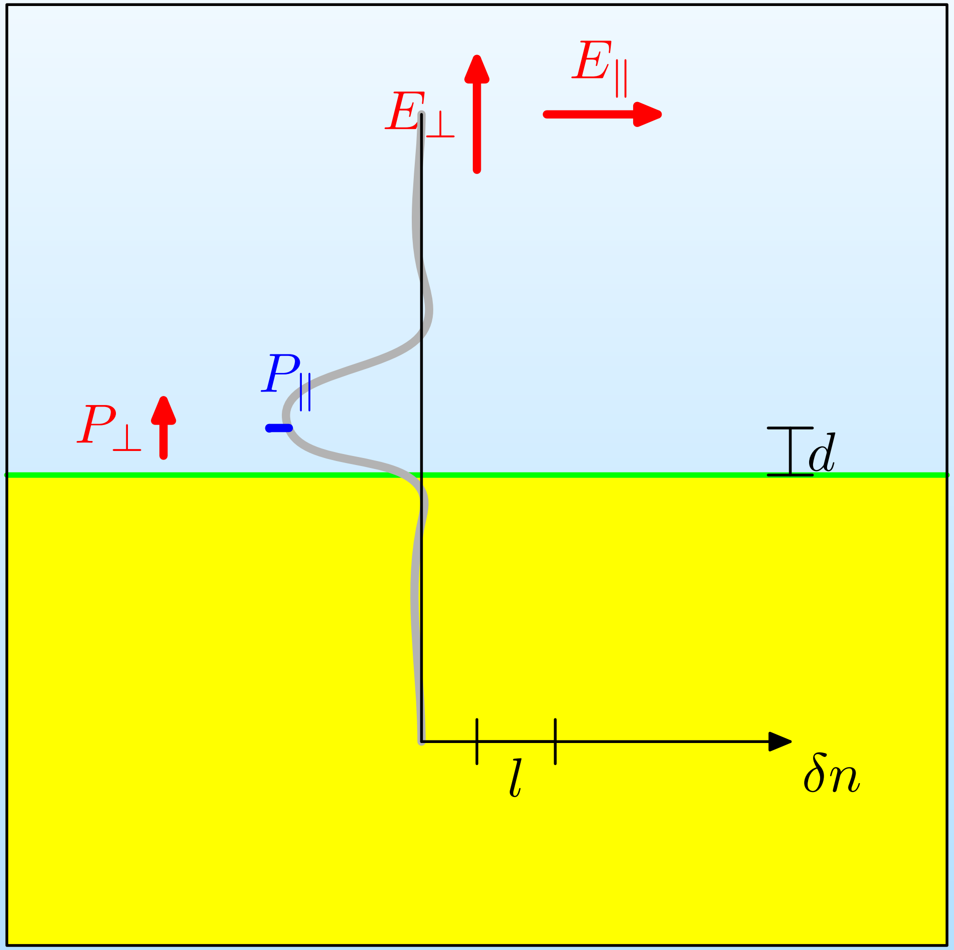

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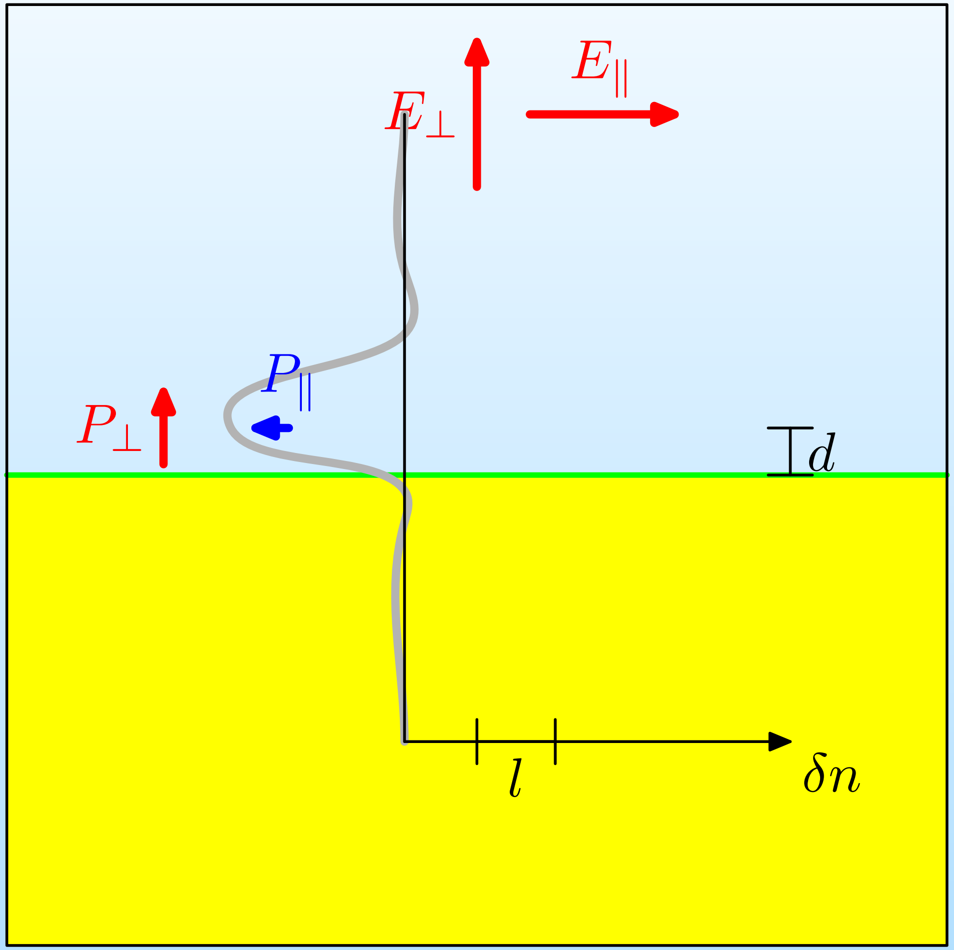

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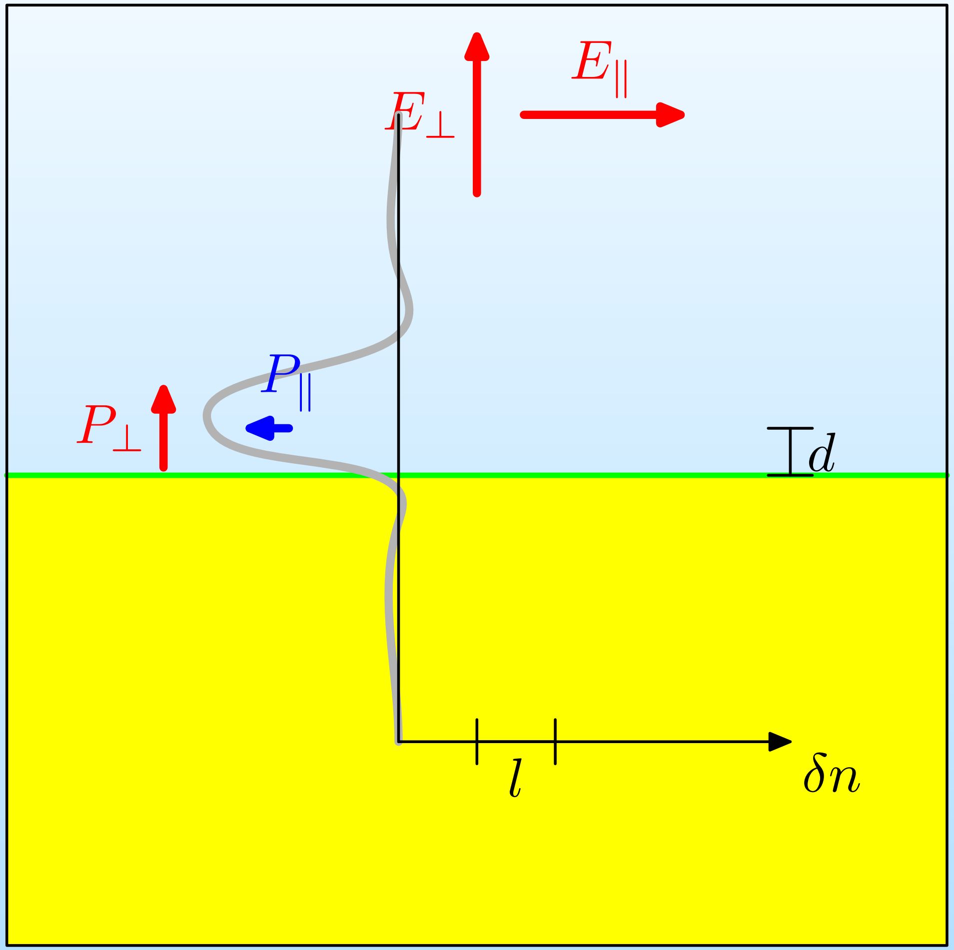

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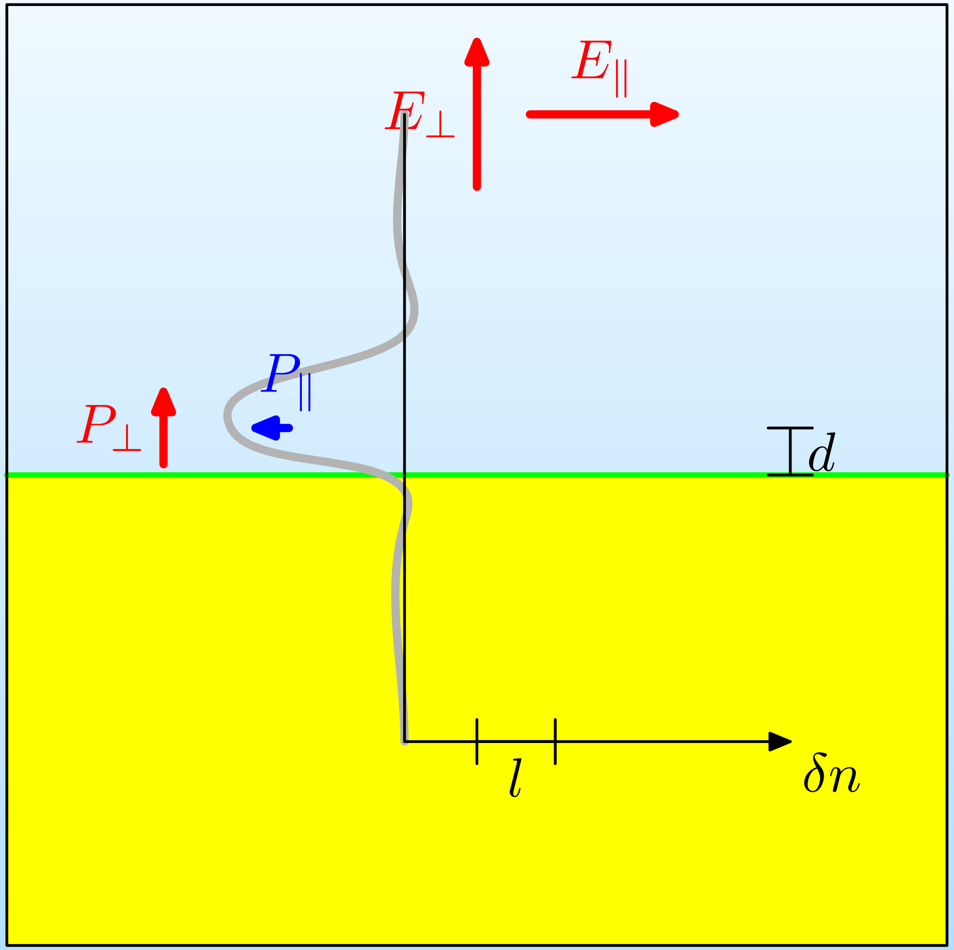

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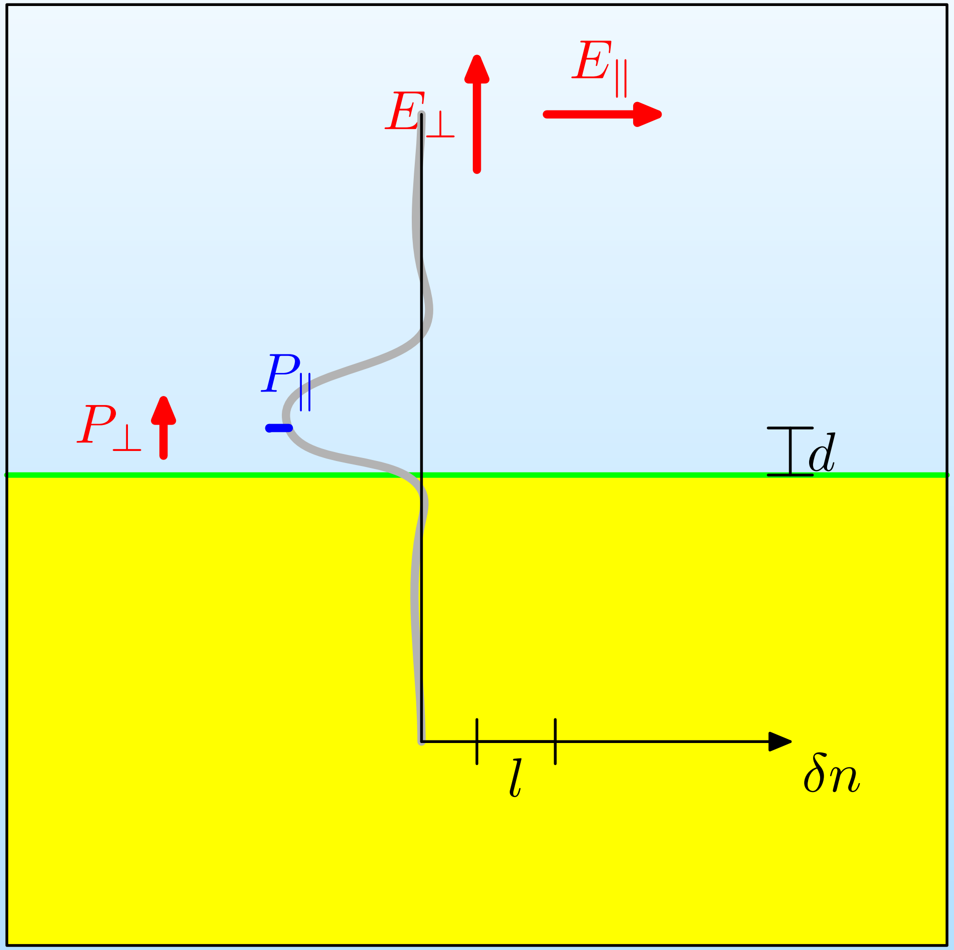

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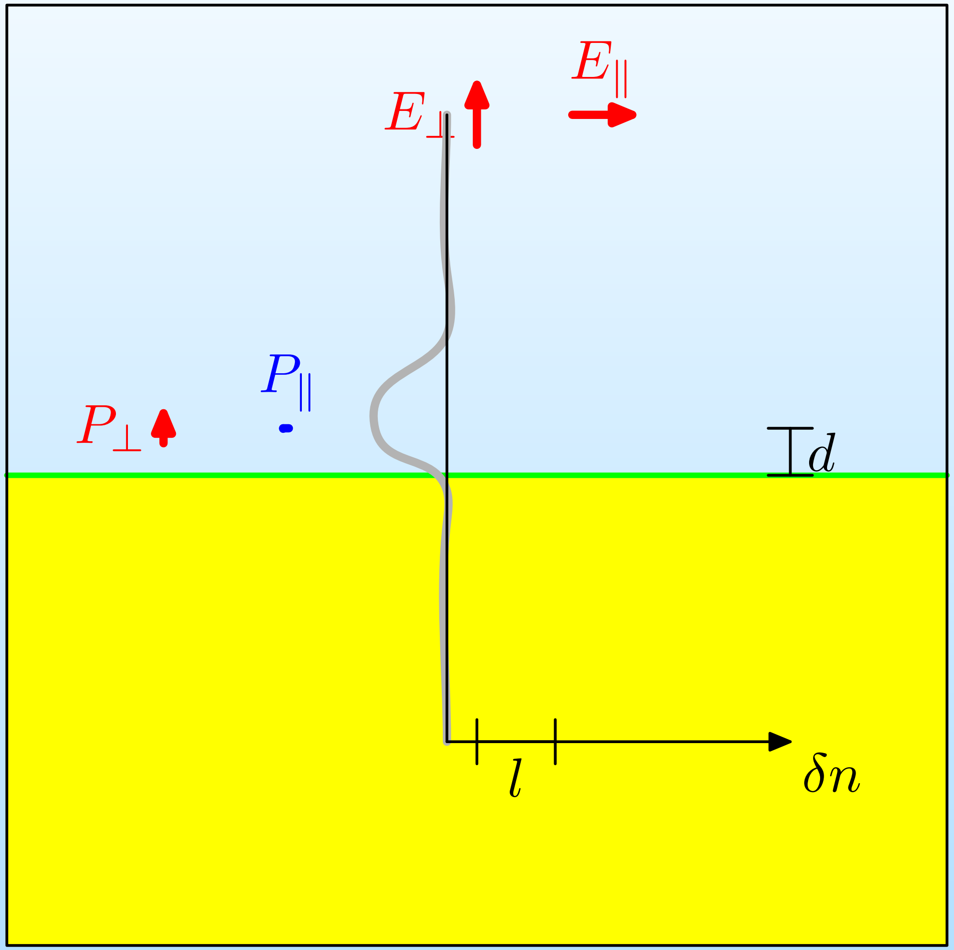

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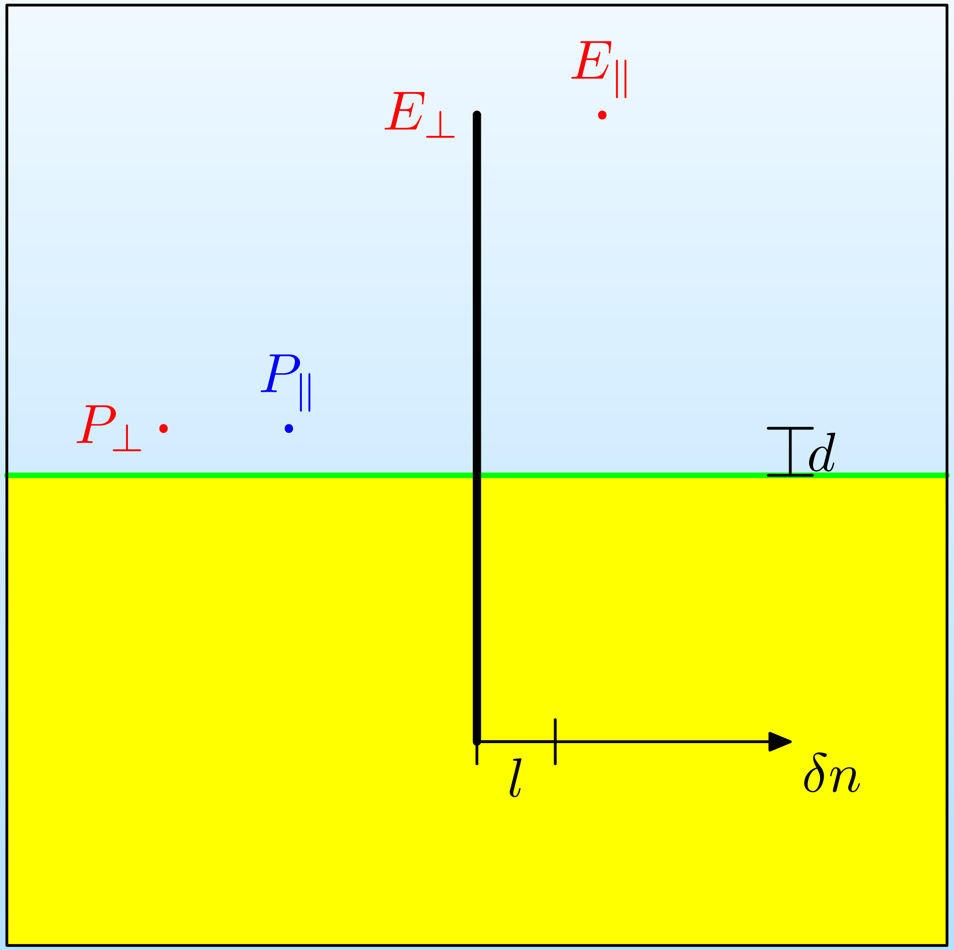

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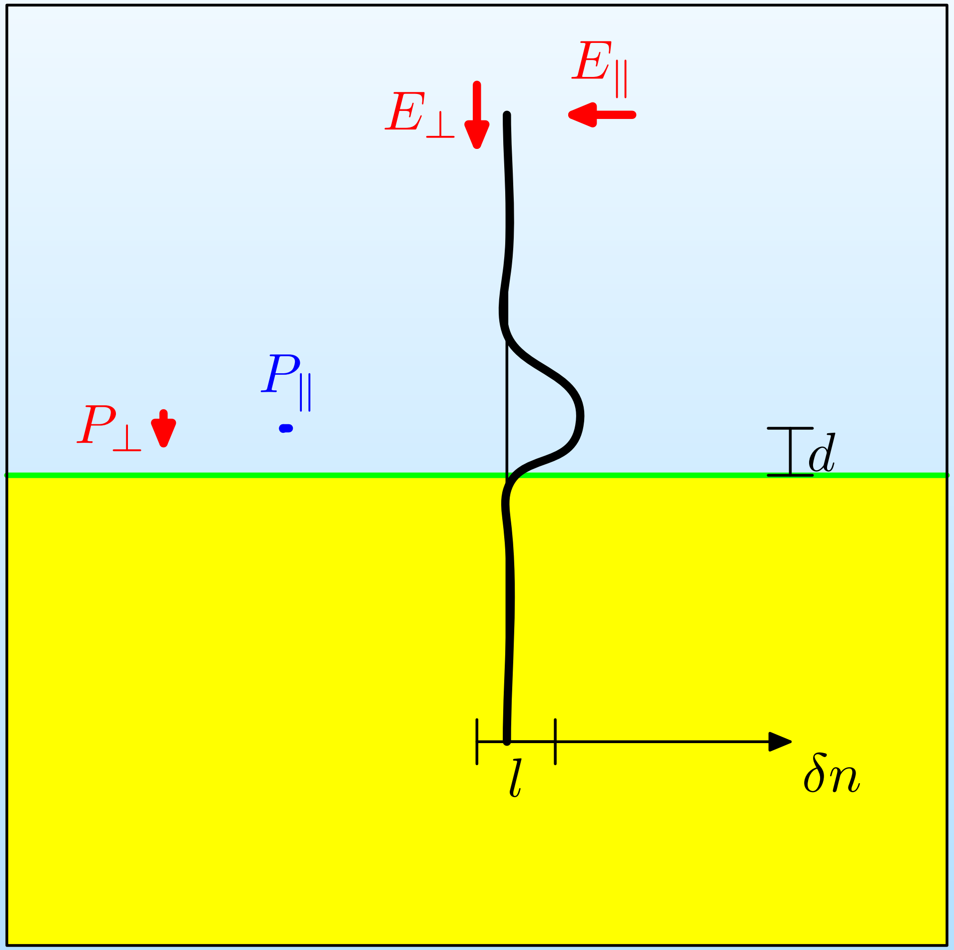

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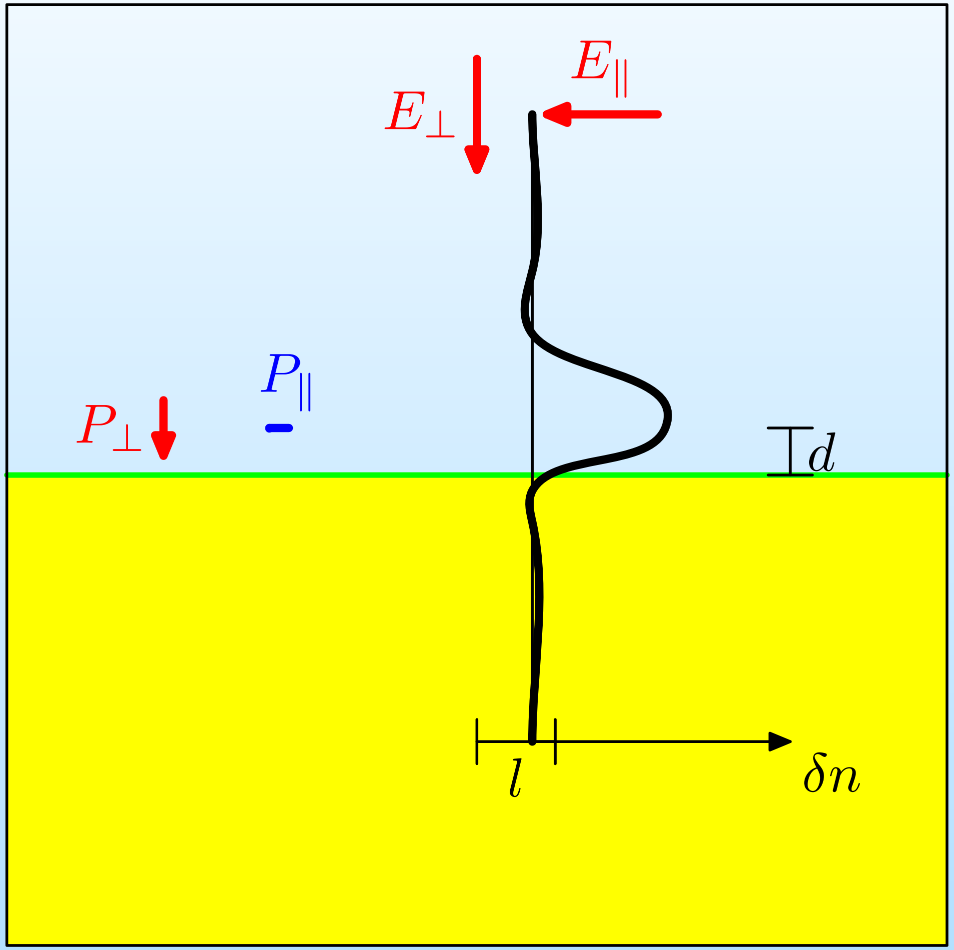

$\chi_{\perp\parallel\parallel} \propto b \propto l$

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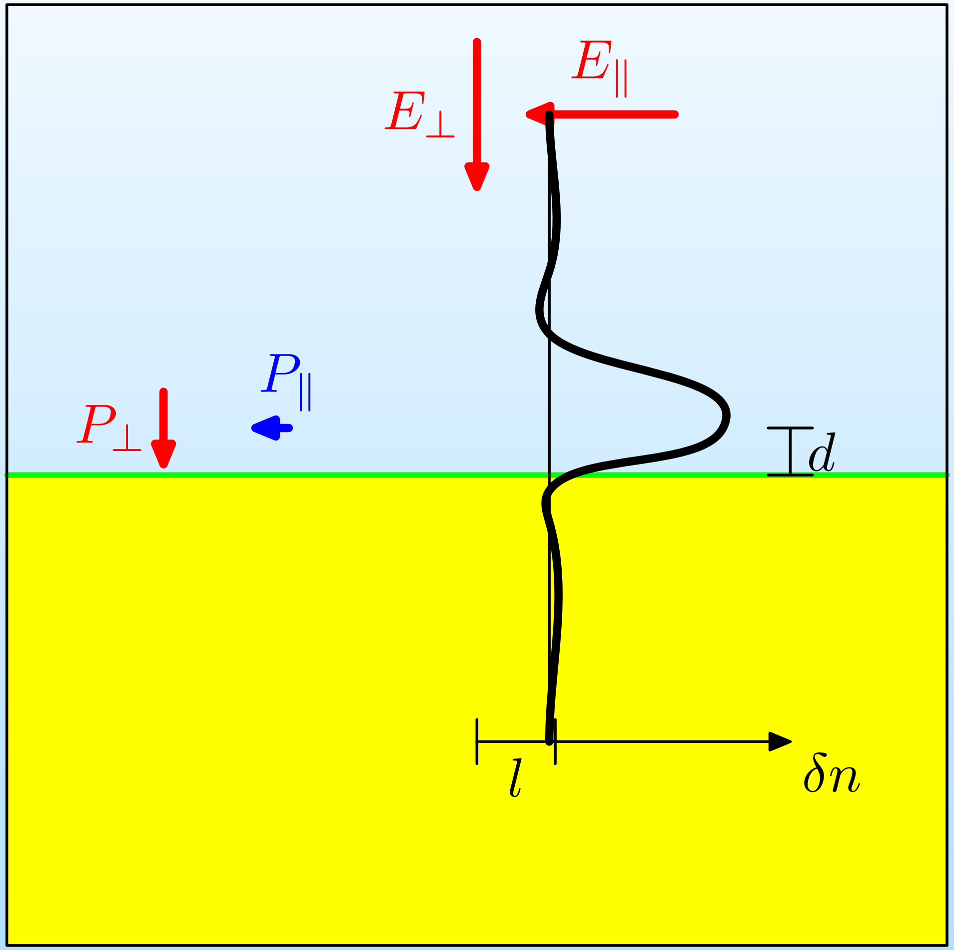

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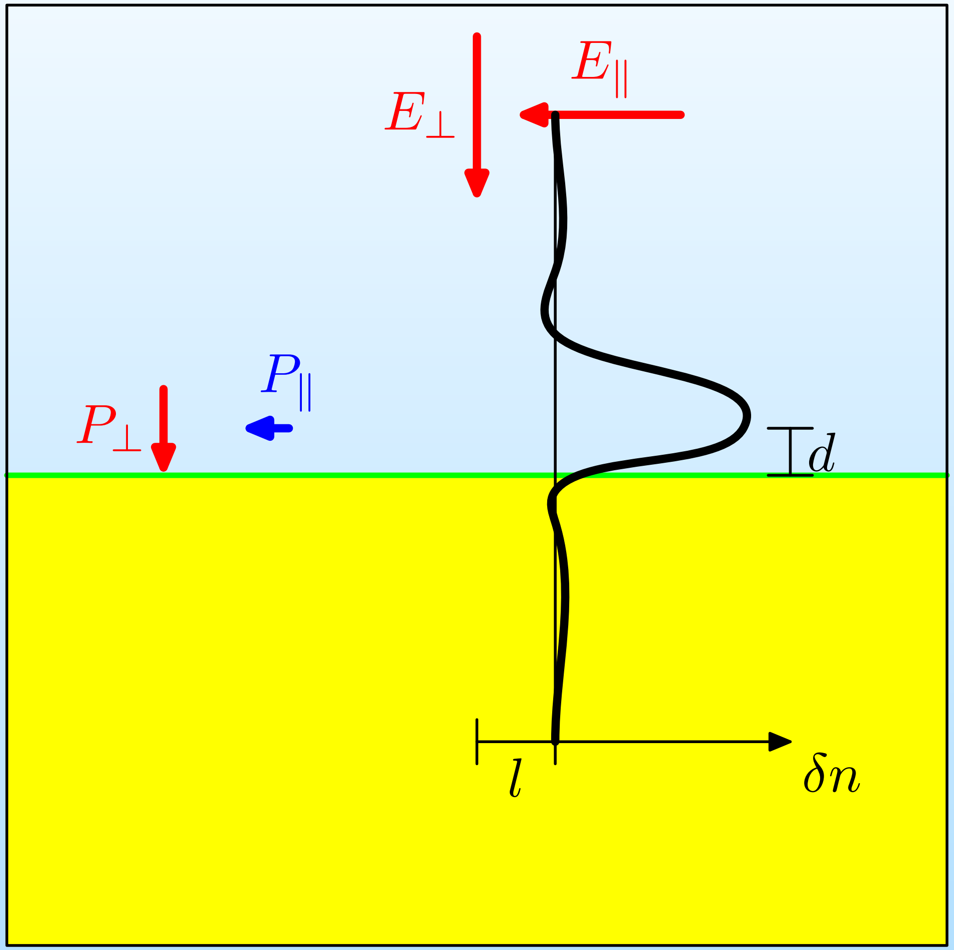
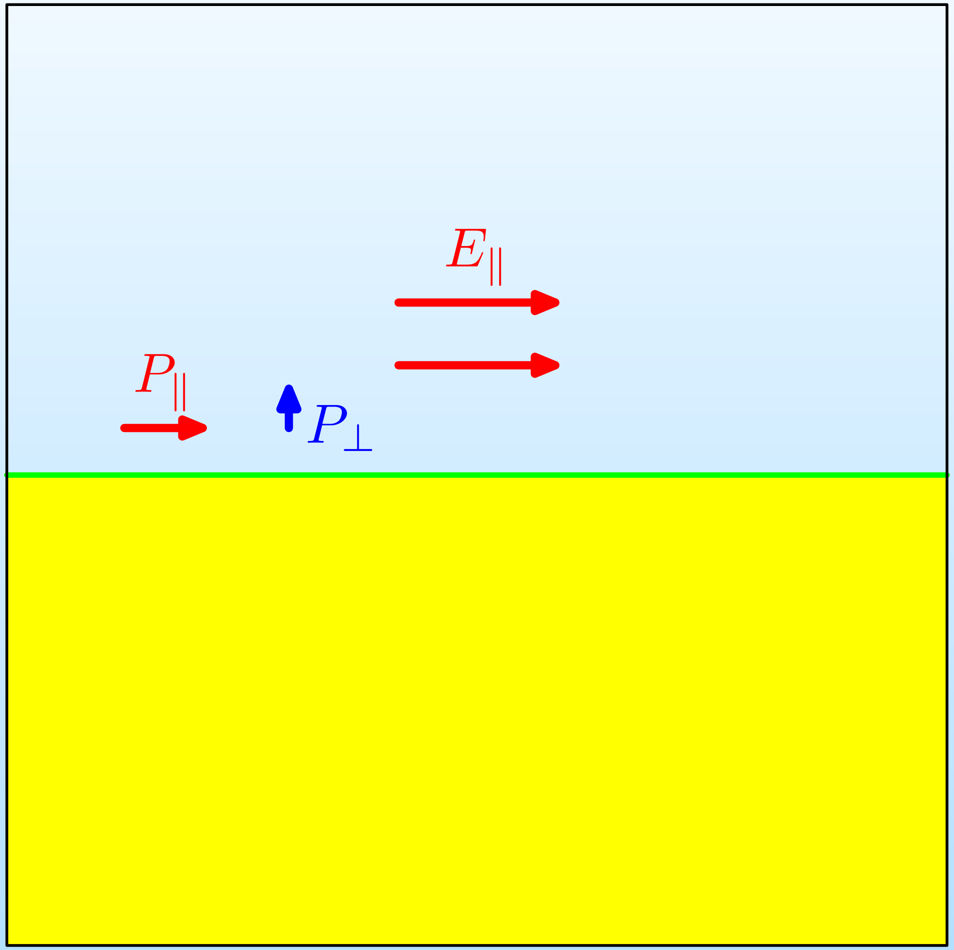


$$\chi_{\perp\parallel\parallel} \propto b \propto l$$

Nonlinear Surface Response: f



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

Harmonic Dipolium: a

$$a(\omega) \equiv -64\pi^2 n_B e \left(\frac{\epsilon_B(\omega)}{\epsilon_B(\omega)-1}\right)^2 \chi^s_{zzz}(\omega).$$

$$\begin{aligned} a(\omega) = \quad 2 & \quad \big([\epsilon_B(2\omega)-\epsilon_B(\omega)][2\epsilon_B(\omega)-\epsilon_B(2\omega)-\epsilon_B(\omega)\epsilon_B(2\omega)] \\ & \quad +[\epsilon_B(\omega)]^2[1-\epsilon_B(2\omega)]\log[\epsilon_B(\omega)/\epsilon_B(2\omega)]\big) \\ / & \quad [\epsilon_B(2\omega)-\epsilon_B(\omega)]^2. \end{aligned}$$

a depends only on the bulk dielectric functions $\epsilon_B(\omega)$ and $\epsilon_B(2\omega)$, analytically.

Approximate expression for *arbitrary* ϵ_B (?). Accounts for strong field variation at surfaces. Ignores surface states, surface modified polarizability, surface local field corrections . . .

Harmonic dipolium: b, f

$$\chi_{\|\|z}(\omega) = \chi_{\|z\|}(\omega) = \frac{1}{4e}\frac{n_B \alpha^2(\omega)}{\epsilon_B(\omega)}.$$

Parametrize:

$$b(\omega) \equiv -64\pi^2 n_B e \frac{\epsilon_B(\omega)}{(\epsilon_B(\omega)-1)^2}\chi^s_{\|\|z}(\omega) = -1$$

Finally: $f \propto \chi_{z\|\|} = 0$.

Bulk response: d

$$\vec{P}^{(2)} = -\frac{n_B}{e}\alpha(\omega)\alpha(2\omega)\left(2\vec{E}\cdot\nabla\vec{E} - \frac{1}{2}\nabla E^2\right) - \frac{n_B}{2e}\alpha^2(\omega)\nabla\cdot(\vec{E}\vec{E}).$$

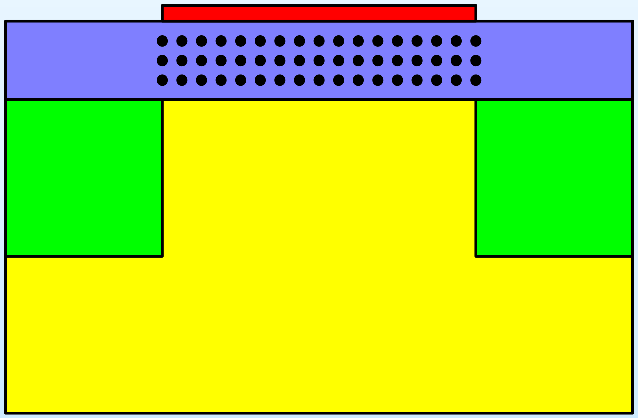
Plane wave: ∇ *perpendicular* to $\vec{E}$. Then,

$$P^{(2)} \equiv \frac{1}{32\pi^2 ne}(\epsilon_B(\omega)-1)(\epsilon_B(2\omega)-1)d(\omega)\nabla E^2$$

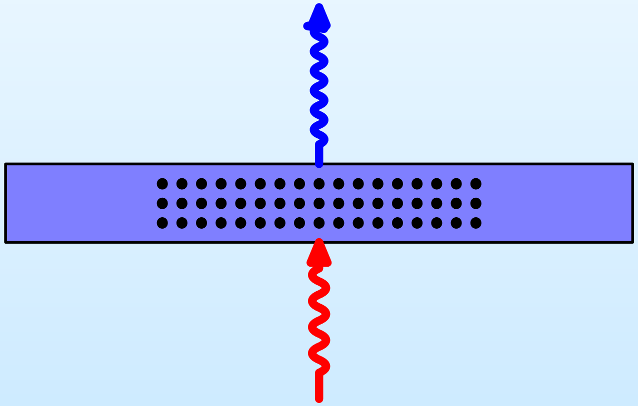
where: $d = 1$.

Buried interfaces: nanoparticles

Flash memories



Observe interfaces with SHG



Experiment

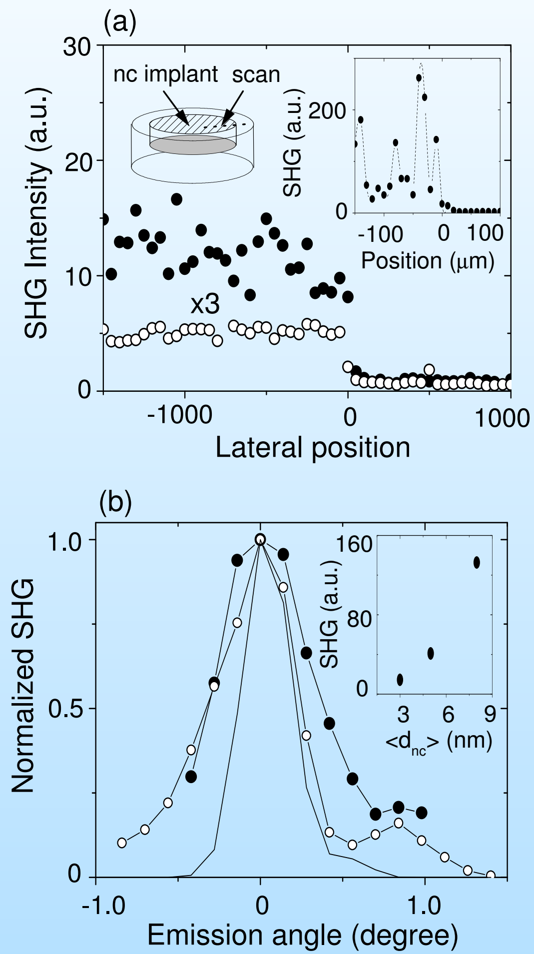


FIG. 3

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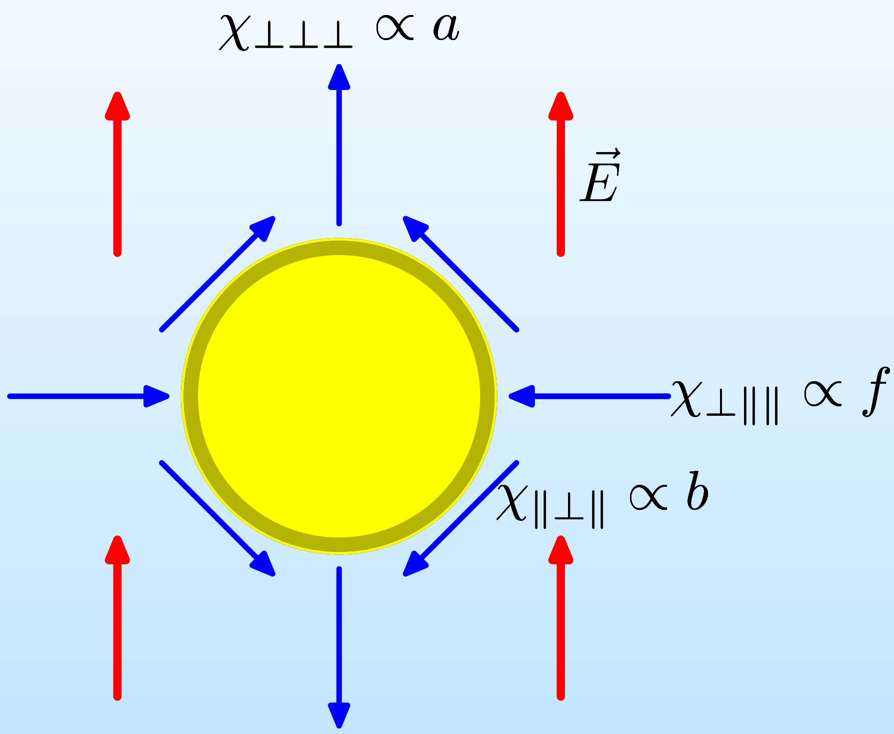
Y. Jiang, P. T. Wilson, M. C. Downer, C. W. White, and S. P. Withrow, Appl. Phys. Lett. **78**, 766 (2001).

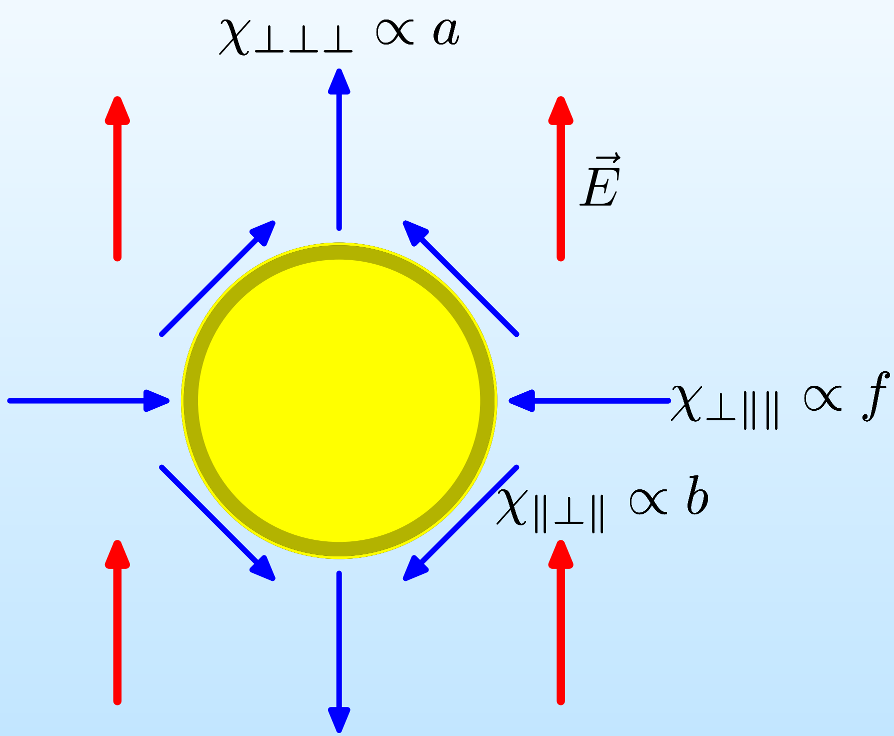
- Signal comes from nanospheres.
- Interface sensitive (annealed in Ar vs. Ar/H_2).
- Forward SHG.
- Edge vs. *bulk*.

Single sphere SHG



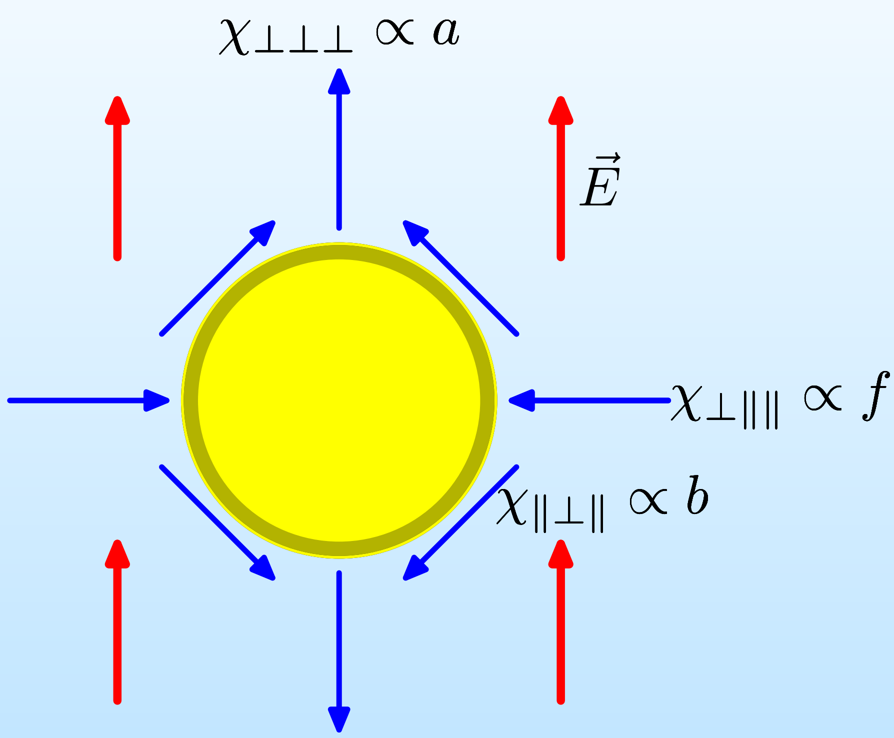
- Centrosymmetry is locally lost. . .

Single sphere SHG



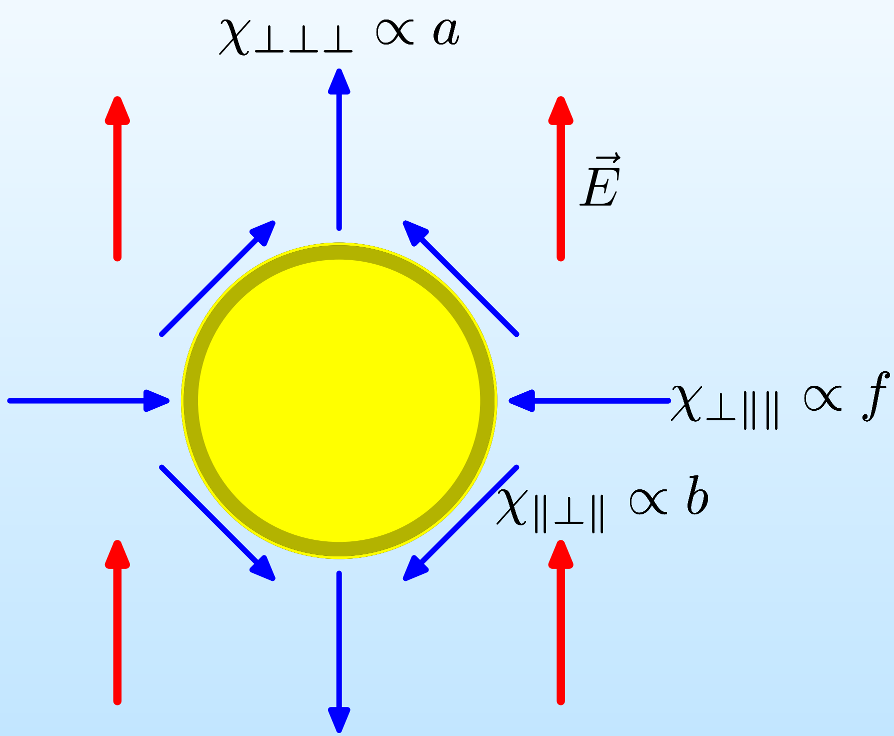
- Centrosymmetry is locally lost...
- but globally recovered.

Single sphere SHG



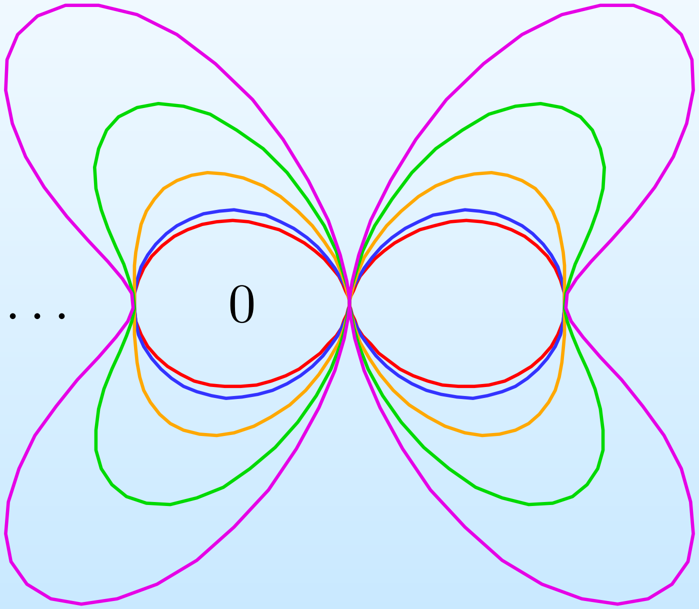
- Centrosymmetry is locally lost. . .
- but globally recovered.
- Total dipole is null. . .

Single sphere SHG



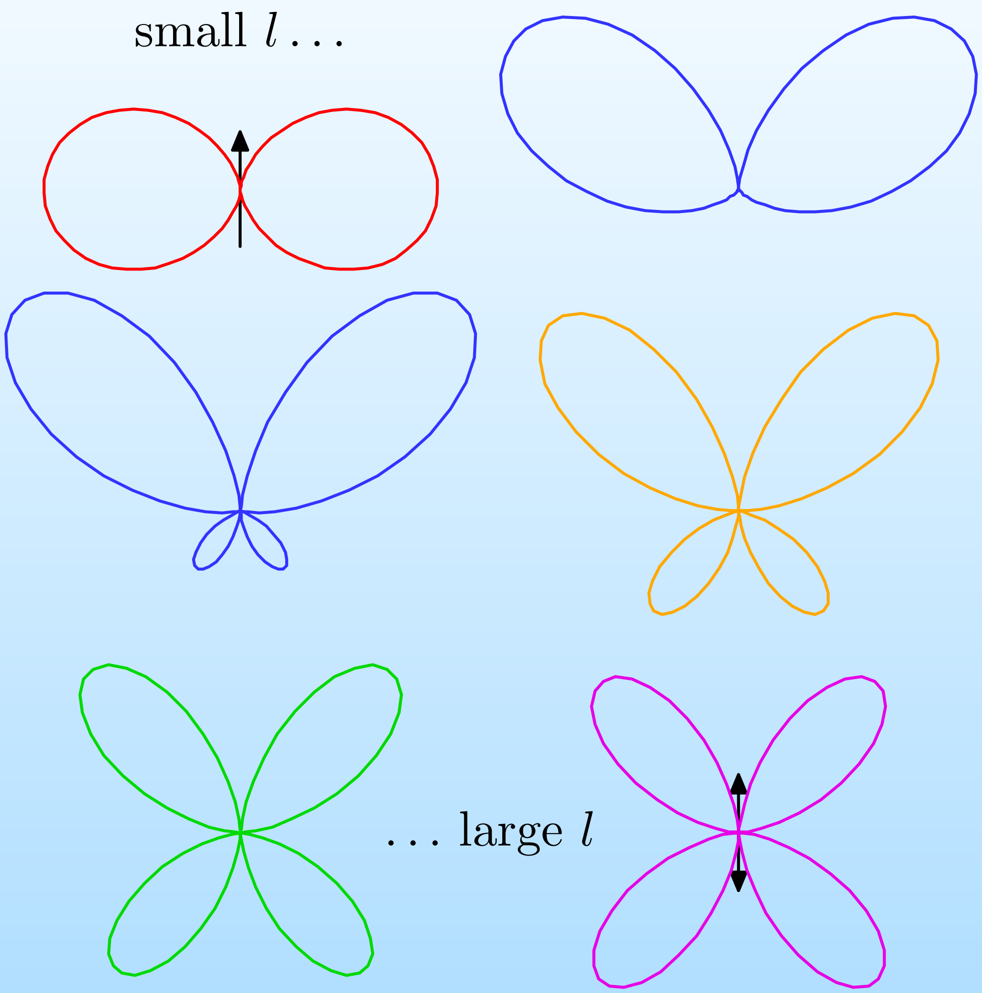
- Centrosymmetry is locally lost. . .
- but globally recovered.
- Total dipole is null. . .
- unless field is inhomogeneous.

Radiation patterns



$\vec{p}$ y Q_{ij} radiation in phase...

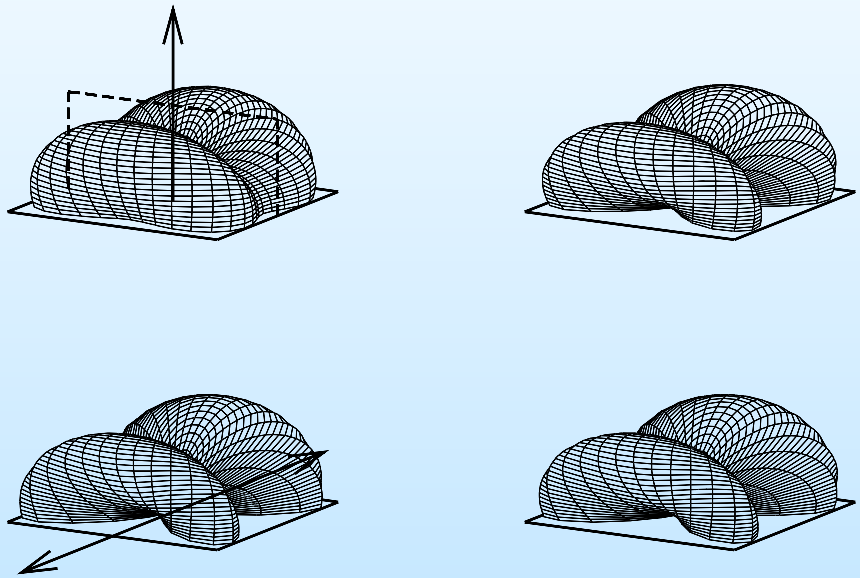
Radiation patterns



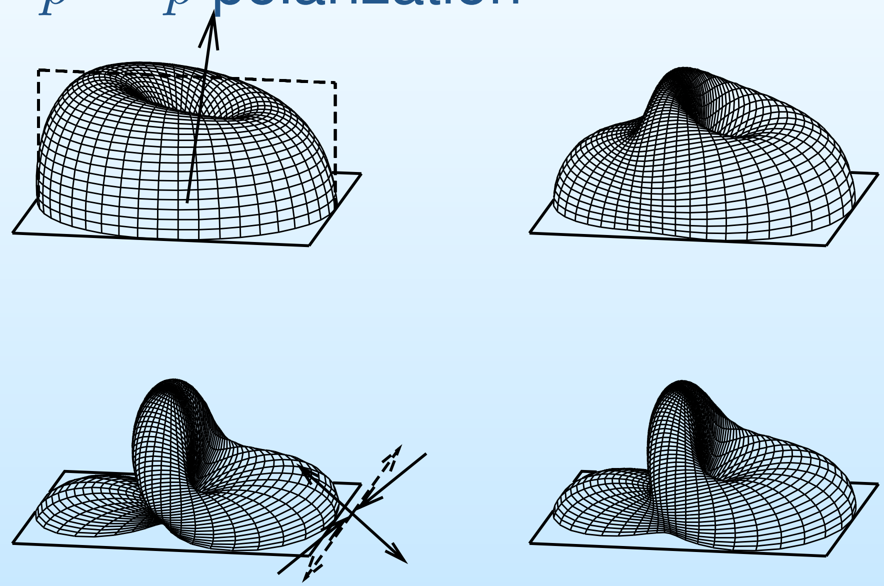
$\vec{p}$ y Q_{ij} radiation in counter-phase. . .

SHG efficiency for nanosphere over substrate

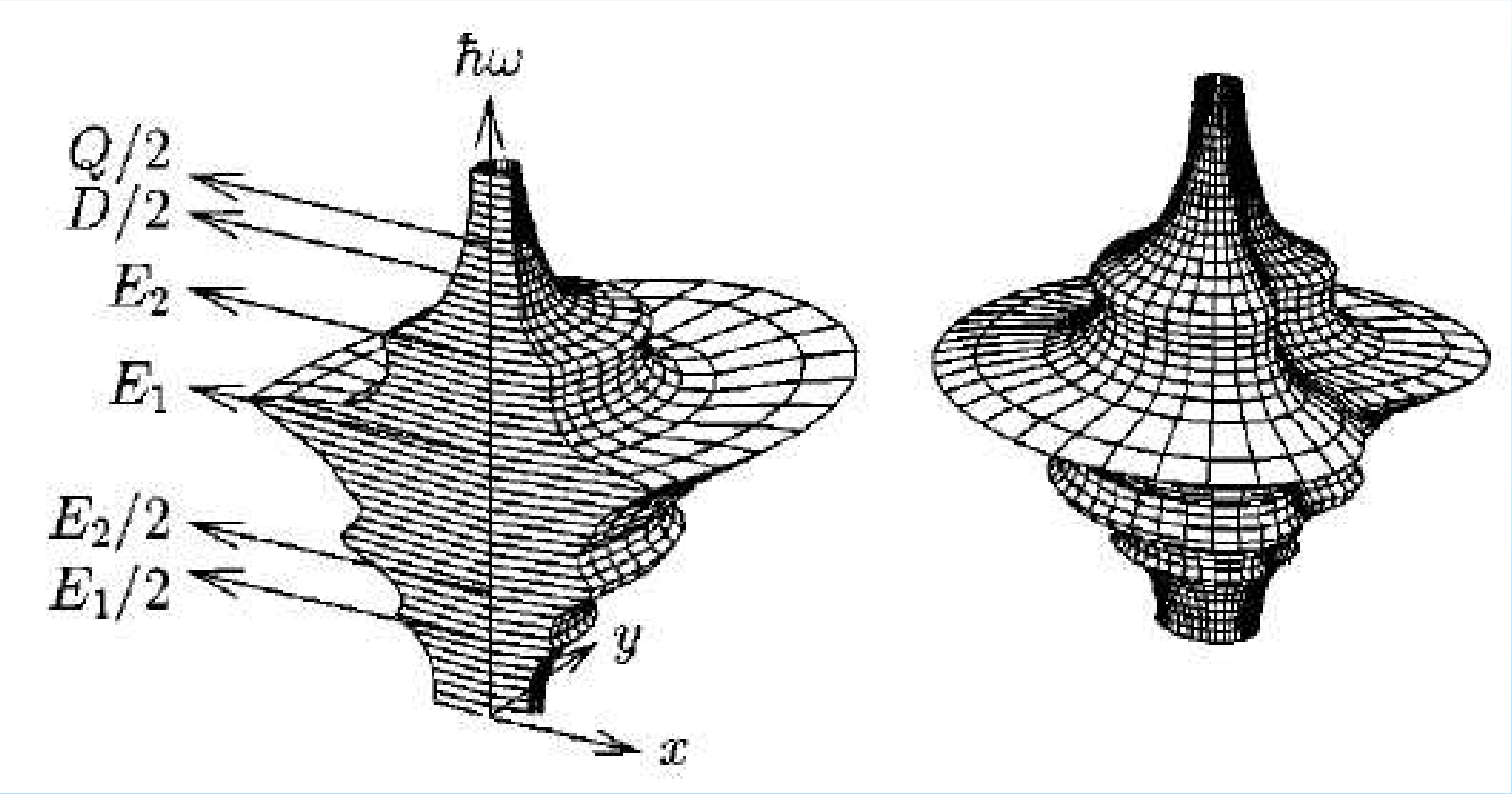
$s \rightarrow p$ polarization



$p \rightarrow p$ polarization



Spectral features: p in, $\theta = \pi/4$



Comparison

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

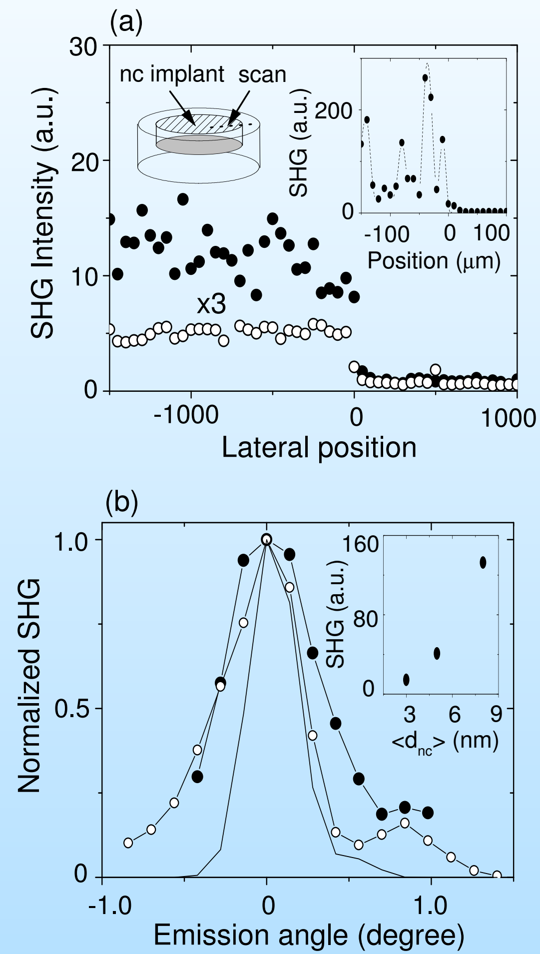


FIG. 3

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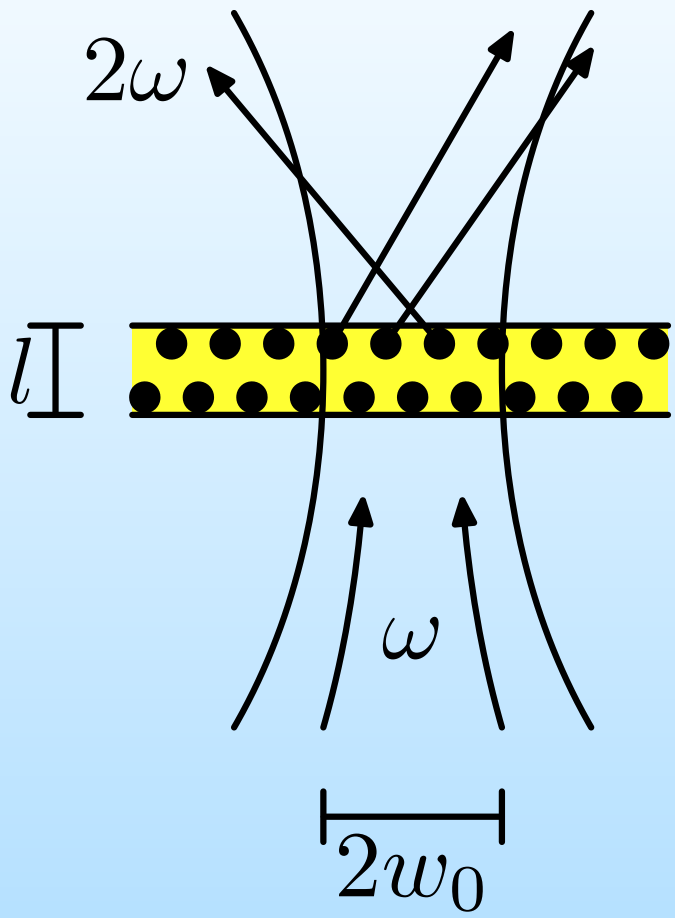
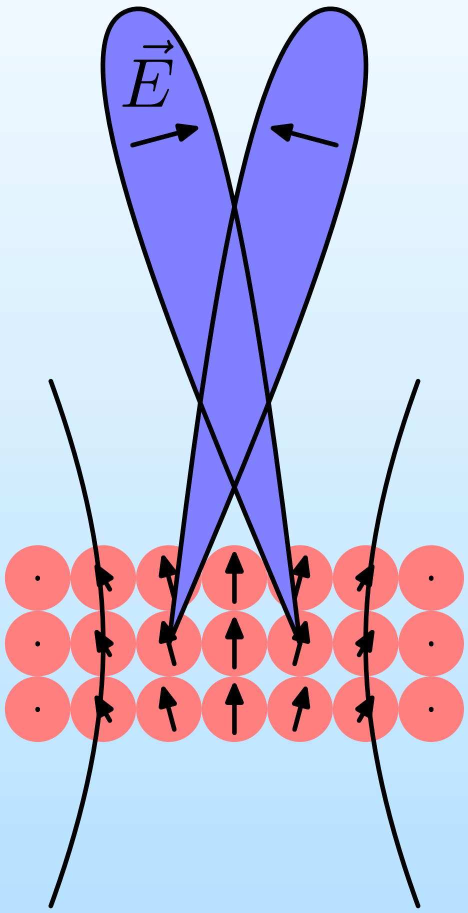
SHG from composite film





Theory

$$\begin{aligned}\vec{P}^{nl} &= n_s \vec{p}^{(2)} - \frac{1}{6}\nabla \cdot \overleftrightarrow{Q}^{(2)} \\ &= \Gamma \nabla E^2 + \Delta' \vec{E} \cdot \nabla \vec{E}\end{aligned}$$

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

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

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

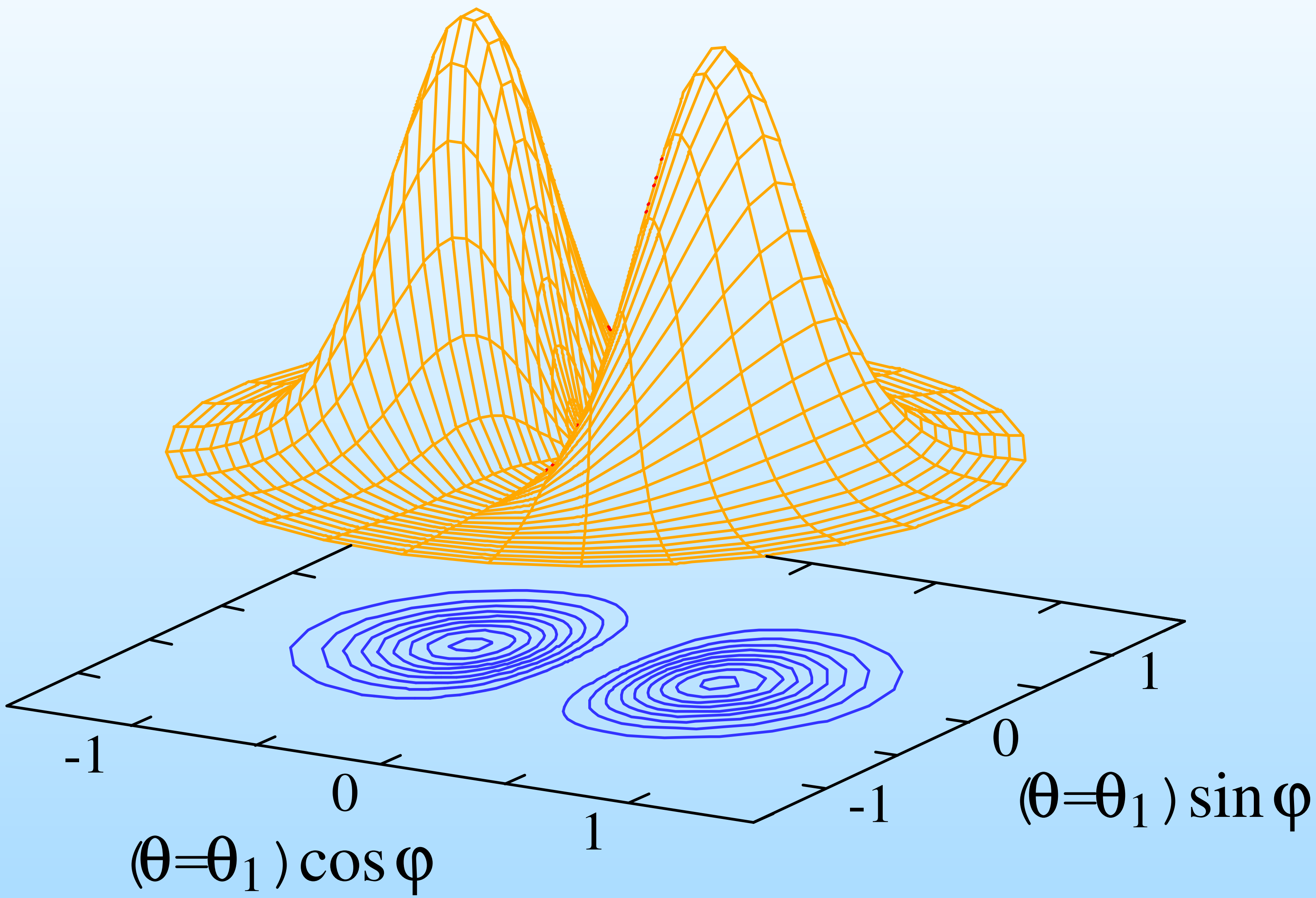
$$\Longrightarrow \vec{A}^{(2)}$$

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

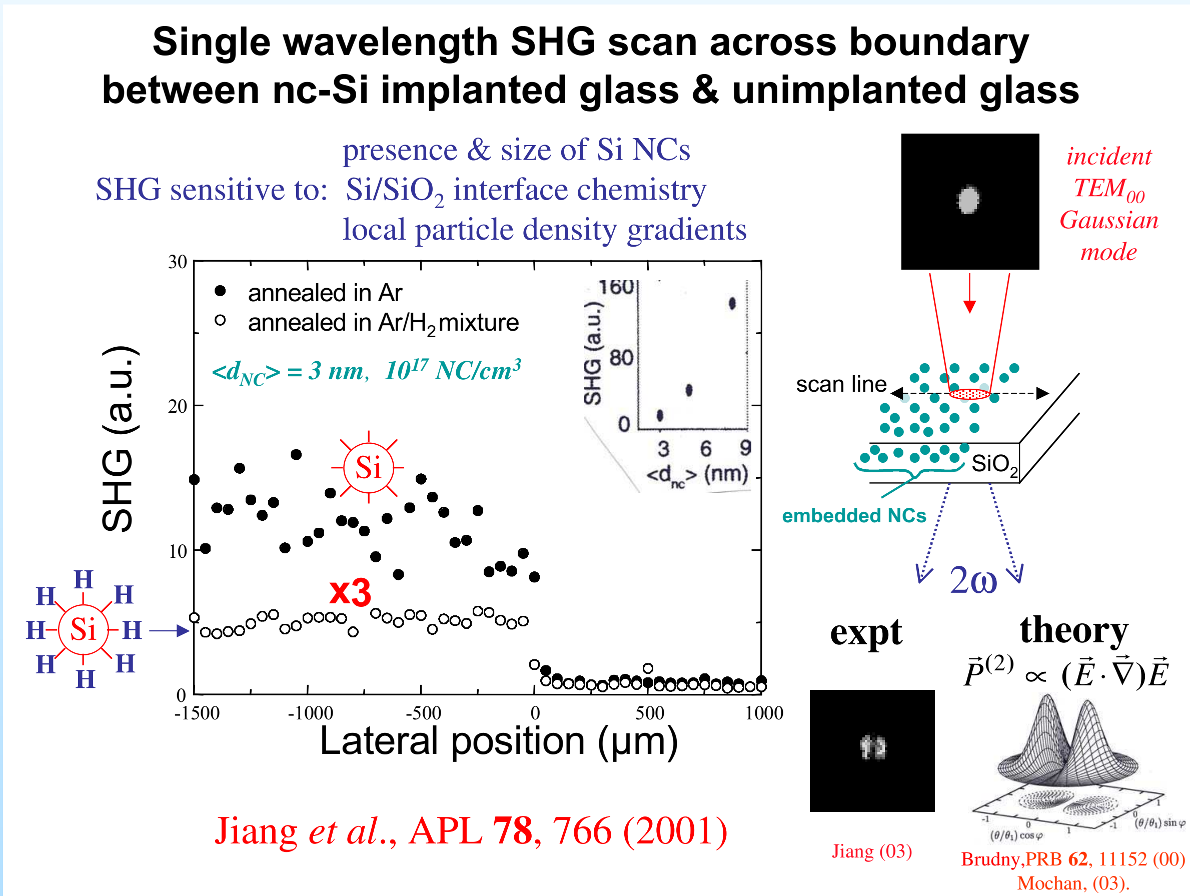
$$\Longrightarrow \vec{S}^{(2)}$$

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

Angular distribution

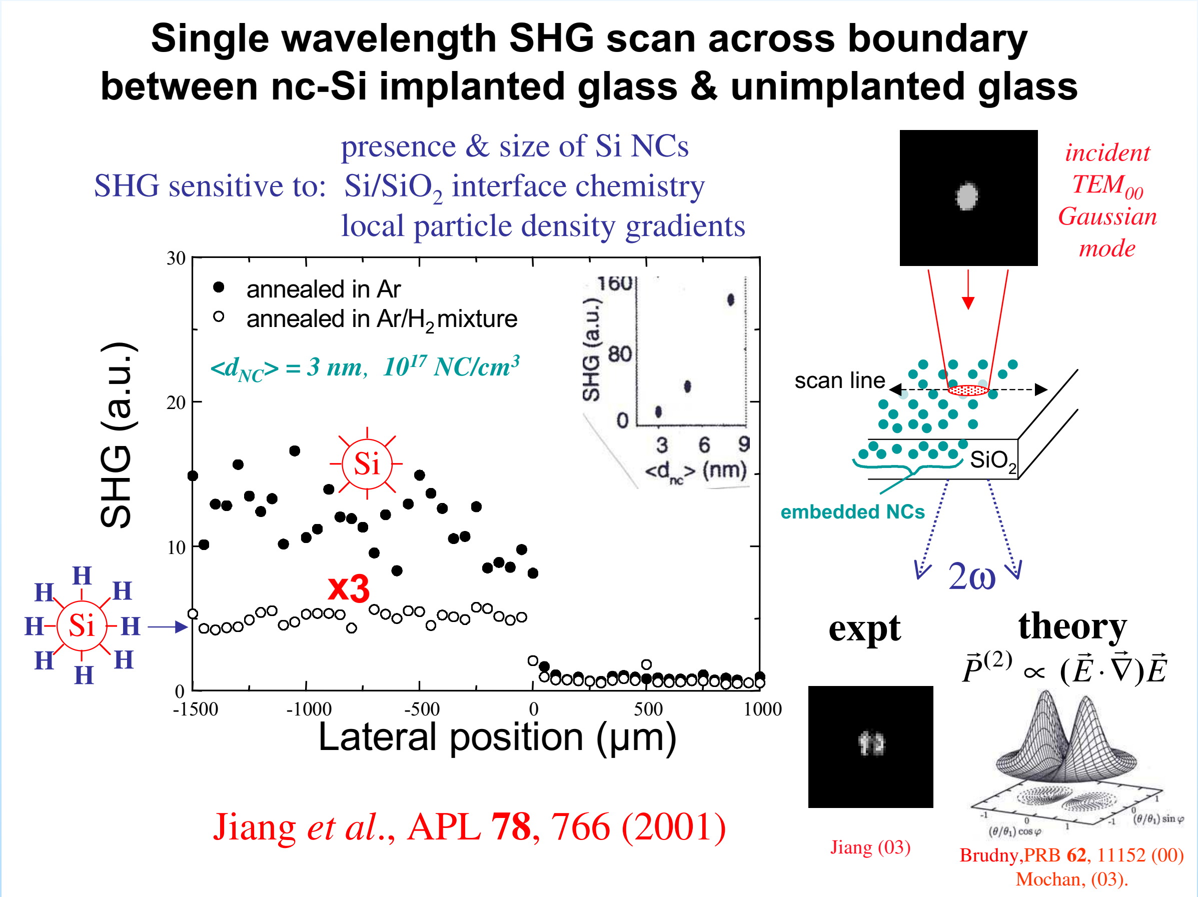


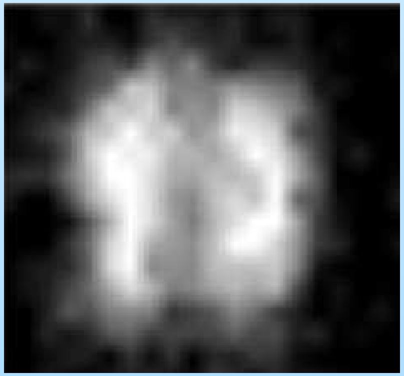
Experiment



$$\vec{P}^{(2)} \propto (\vec{E}\cdot\vec{\nabla})\vec{E}$$

Experiment





Figliozzi et al., submitted to PRL

Efficiency

$$\begin{aligned}\mathcal{E} &= 10^{-2}\zeta(qa_B)^4(ql)^2 f_b^2\theta_1^4 \frac{1}{e^2/a_B}\frac{1}{c/a_B} \\ &\approx 10^{-4}\zeta(qa_B)^4(ql)^2 f_b^2\theta_1^4\,\mathrm{W}^{-1} \\ &\approx 10^{-24}\mathrm{W}^{-1}.\end{aligned}$$

Efficiency

$$
\begin{aligned}
\mathcal{E} &= 10^{-2}\zeta(qa_B)^4(ql)^2 f_b^2\theta_1^4 \frac{1}{e^2/a_B}\frac{1}{c/a_B} \\
&\approx 10^{-4}\zeta(qa_B)^4(ql)^2 f_b^2\theta_1^4\,\mathrm{W}^{-1} \\
&\approx 10^{-24}\mathrm{W}^{-1}.
\end{aligned}
$$

- As $P \propto \vec{E}\nabla\vec{E} \sim E^2/w_0$, efficiency is proportional to incoming intensity, not power!

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$$
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$$

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Efficiency

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- As $P \propto \vec{E}\nabla\vec{E} \sim E^2/w_0$, efficiency is proportional to incoming intensity, not power!
- Larger input power might actually yield less output power!
- Solution: Enhance transverse gradients with two beam SHG.

Conclusions

- The surface of isolated nanoparticles, deposited at surfaces and buried within composites may be observed with SHG.
- Quadrupolar and dipolar contributions may be comparable, giving rise to complex radiation patterns.
- There is no forward radiation, but there is nearly forward radiation from composites.
- Output power cannot be boosted simply by increasing input power.
- SHG may be enhanced orders of magnitude in two-beam geometry.