New Ideas. New Materials.

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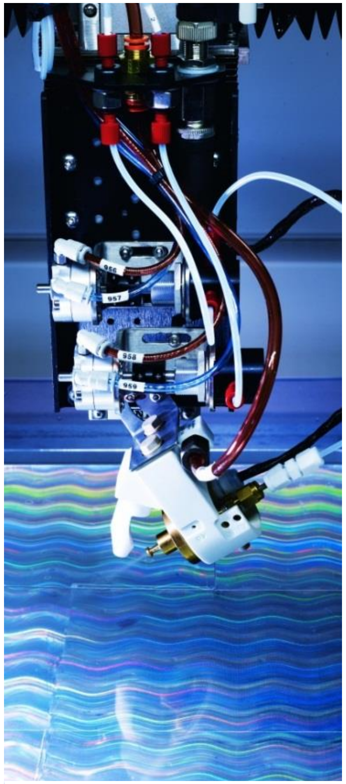

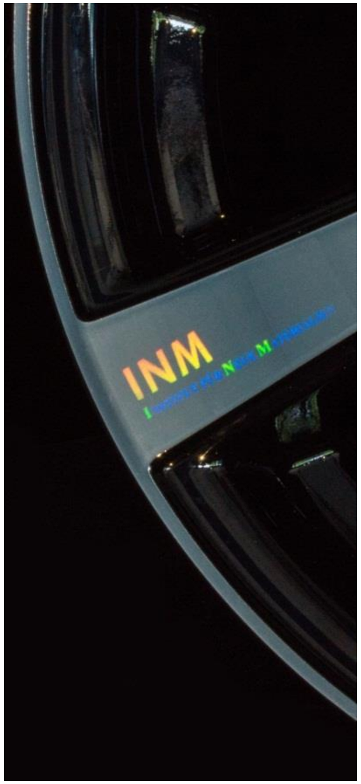

OPTICAL MATERIALS

Dr. Peter Rogin, Dr. Peter W. de Oliveira
Saarbrücken, 2017

New Ideas. New Materials.

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1.1 Significance of light

How we perceive the world

Vision – our most important tool for perceiving our surroundings

- evolved several hundred million years ago
- vital not only for humans

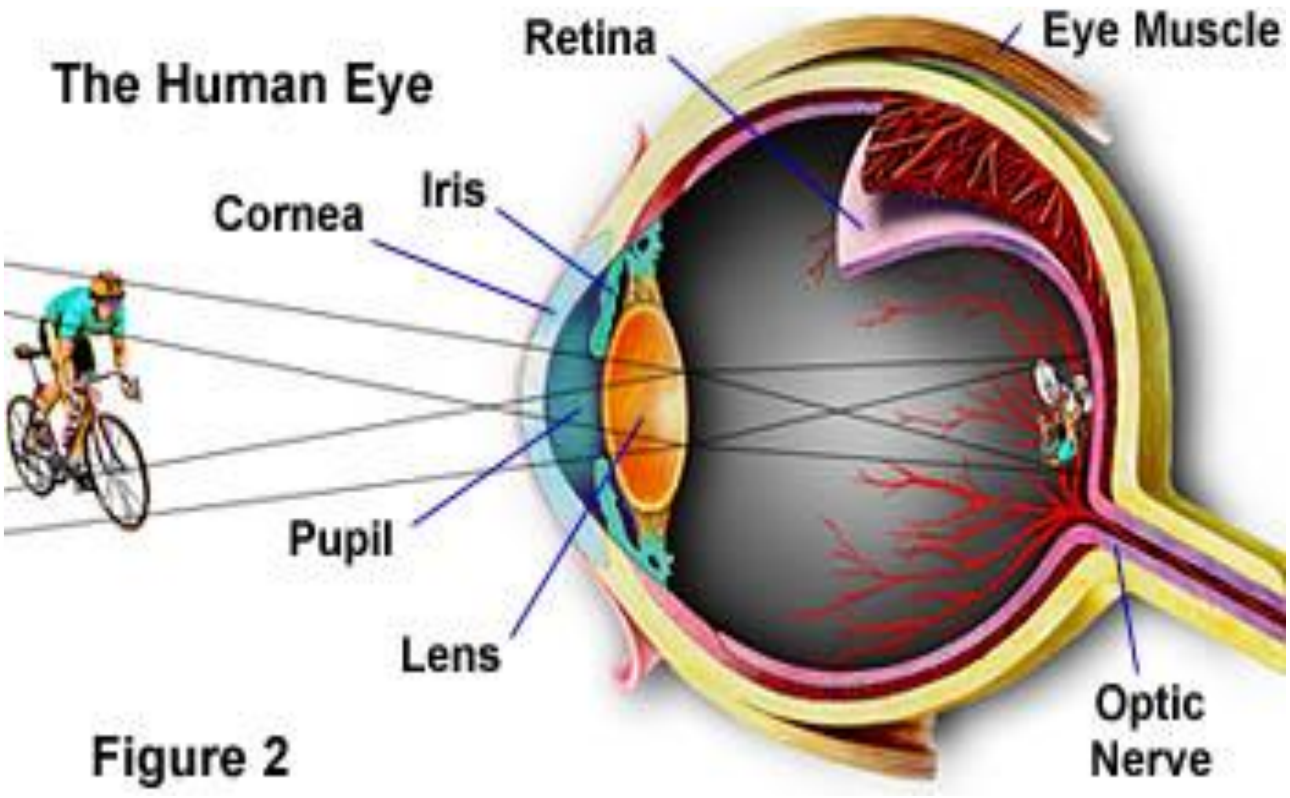
- high resolution imaging perception
  - Far field resolution: ca. 1 arc minute
  - Near field resolution: ca. 100 µm

- long range (millions of light years)

Phrases (german and english):

- “Sich ein Bild machen”
- “Ein Bild sagt mehr als tausend Worte”
- “Seeing is believing”

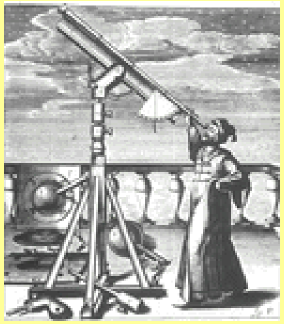
1.1 Significance of light
The eye – a biological optical system

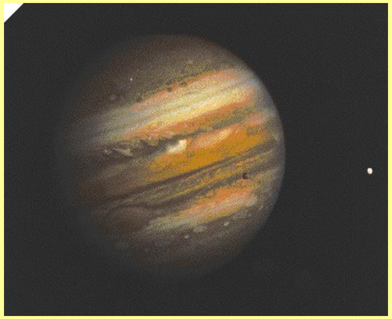


1.1 Significance of light

Expanding our capabilities of perception

Optical instruments for a better understanding of the world we live in



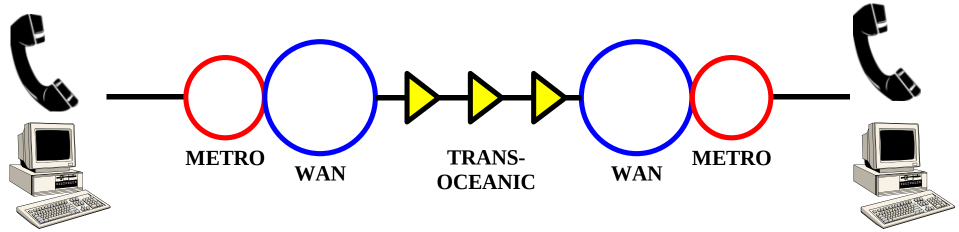


Telescopes help us to understand our universe

Microscopes let us see a microscale world

1.1 Significance of light
Technical applications of optics

telecommunication

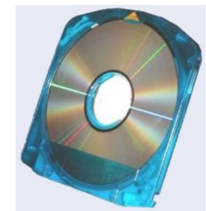


telephone
data
internet

optical storage media

CD/DVD

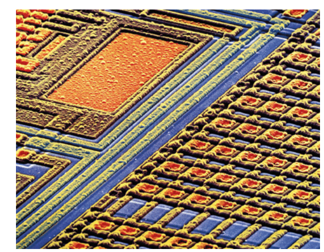
Blu-ray disc (25GB)



Precision laser machining

Laser cutting

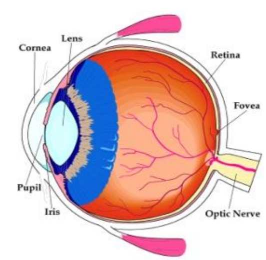
Laser writing on human hair

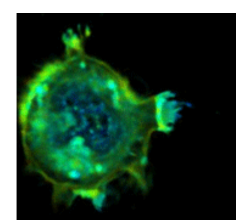


Photolithography

biomedical imaging and therapy

Corrective laser eye surgery

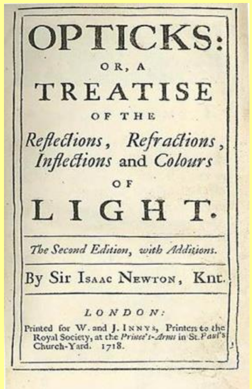




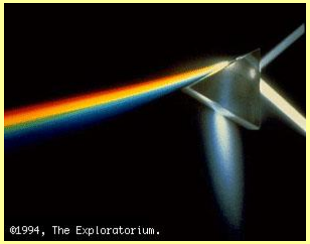
3-D laser imaging of cell

1.2 What is light?
Historical Controversy

Particles

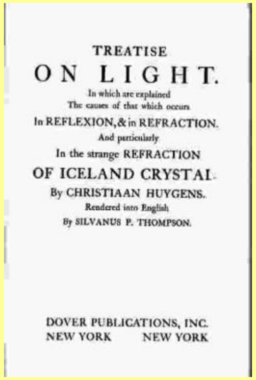

OPTICKS: OR, A TREATISE OF THE Reflections, Refractions, Inflections and Colours OF LIGHT.
The Second Edition, with Additions.
By Sir Isaac Newton, Knt.
LONDON: Printed for W. and J. Innys, Printers to the Royal Society, at the Prince's-Arms in St. Paul's Church-Yard. 1718.

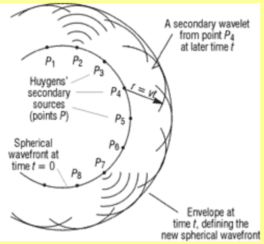

Sir Isaac Newton (1642-1727)



Waves


Christaan Huygens (1629-1695)


TREATISE ON LIGHT. In which are explained The causes of that which occurs In REFLEXION, & in REFRACTION. And particularly In the strange REFRACTION OF ICELAND CRYSTAL. By CHRISTIAAN HUYGENS. Rendered into English By SILVANUS P. THOMPSON.
DOVER PUBLICATIONS, INC. NEW YORK NEW YORK



1.2 What is light?

Comparison of theories

Particles (classical):

- explains straight line propagation
- explains reflection (elastic bouncing)
- has difficulties with refraction
- does not explain diffraction & related phenomena

Waves (classical):

- less intuitive
- successfully explains all phenomena of classical optics

Quantum mechanics:

- answer depends on how the question is asked
- unambiguously particle-like (photons):

  quantization of energy hf and momentum $\frac{h}{2\pi}k$

1.3 Wave theory

The wave equation (1)

Wave propagation

= specific mode of evolution of a quantity depending on position and time ("**field**", "**amplitude**")

Examples:

- Height of water surface on the sea
- Pressure (sound = acoustic waves)
- Electric field $\vec{E}$ and magnetic field $\vec{H}$ (light)

Wave equation

Description of wave propagation for a generalized field A:

$$\frac{\partial^2 A}{\partial x^2} + \frac{\partial^2 A}{\partial y^2} + \frac{\partial^2 A}{\partial z^2} = \frac{1}{v^2}\frac{\partial^2 A}{\partial t^2}$$

For electromagnetic waves: a consequence of Maxwell's equations

1.3 Wave theory

The wave equation (2)

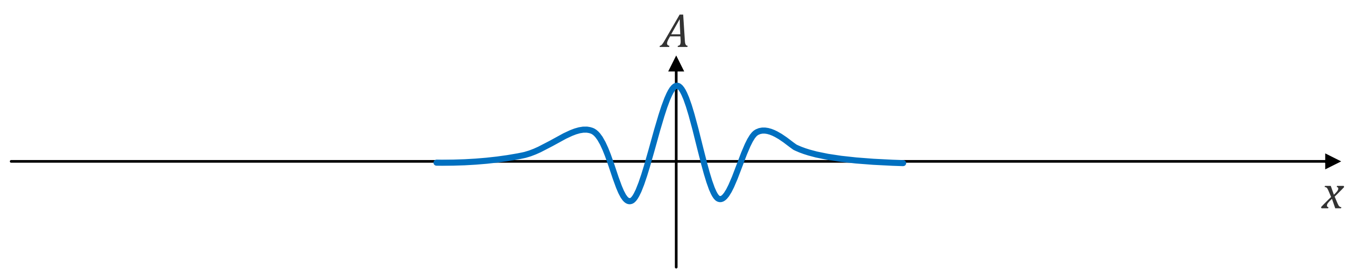
Simplest case – only one spatial dimension :

$$\frac{\partial^2 A}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 A}{\partial t^2}$$

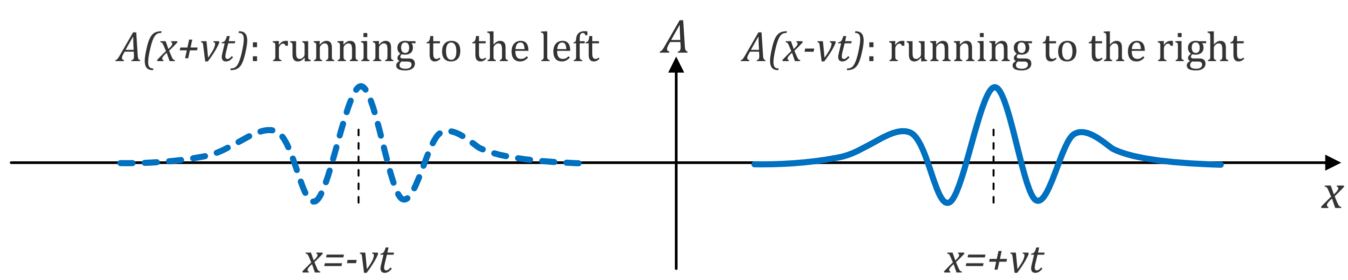
General solutions: $A(x,t) = A(x - v \cdot t)$ or $A(x,t) = A(x + v \cdot t)$

(v = velocity of propagation)

at t = 0:



later time t>0:



1.3 Wave theory

Harmonic waves (one-dimensional)

Harmonic (sine/cosine) dependency on position and time:

Amplitude of a harmonic wave propagating in +x direction:

$$A(x,t) = A_0 \cdot cos\left[\frac{2\pi}{\lambda}(x - v \cdot t)\right] = A_0 \cdot cos(k \cdot x - \omega \cdot t) = A_0 \cdot \cos(\varphi)$$

Where

- λ = **wavelength** (distance between two repeat units)
- $\omega = 2\pi f = \frac{2\pi v}{\lambda}$ = **angular frequency** (2π times the oscillation **frequency** f)
- $k = \frac{2\pi}{\lambda}$ = **wave number** = number of repeat units on 2π length units
- $\varphi = k \cdot x - \omega \cdot t$ = **phase** of the harmonic function

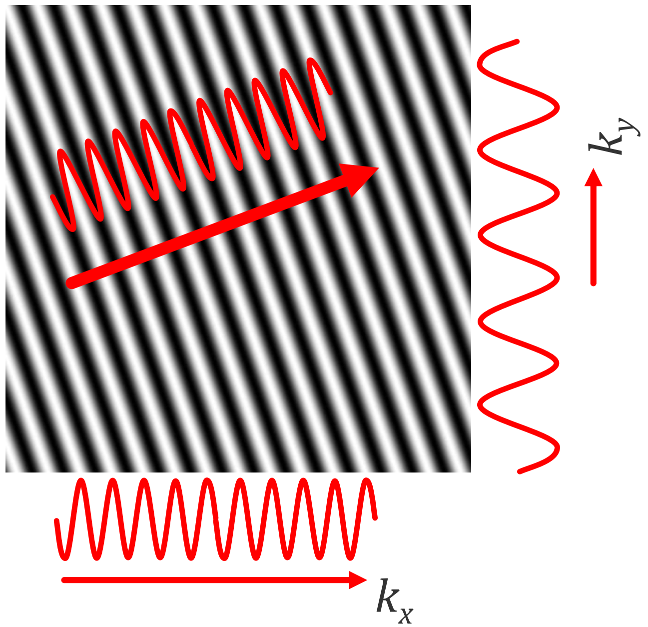
1.3 Wave theory
Generalizations

Plane waves in 3D space:

Wave number $k \rightarrow$ wave vector $\vec{k}$

- Points along direction of propagation
- Length = 2π/wavelength*
- Wave fronts (planes of constant phase) are perpendicular to $\vec{k}$

*true for individual vector components as well



Using complex numbers: $\exp(i \cdot \varphi) = \cos(\varphi) + i \cdot \sin(\varphi)$

$$A(x,t) = Re\left[A_0 \cdot \exp\left\{i \cdot (\vec{k} \cdot \vec{x} - \omega \cdot t)\right\}\right] = Re[A_0 \cdot \exp(i \cdot \varphi)]$$

Why: Adding phases is simpler, generalized formalism covers more cases

1.4 Light as an electromagnetic wave
Electric and magnetic fields

Electric field $\vec{E}$

- Defined as the force $\vec{F}$ acting on a test charge q, scaled by the magnitude of that test charge:

$$\vec{F} = q \cdot \vec{E}$$

- The electric field has a strength and a direction → **vector**
- It depends on the location in space (coordinate vector $\vec{x}$) → **field** (and, generally, on time t as well):

$$\vec{E} = \vec{E}(\vec{x}, t)$$

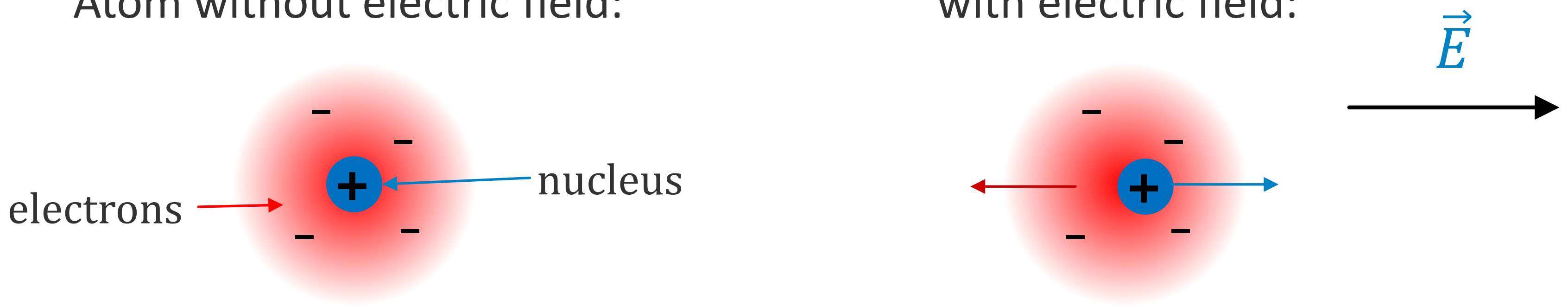
Magnetic field $\vec{H}$ (or $\vec{B} = \mu \cdot \mu_0 \cdot \vec{H}$)

- Can be defined similarly (difficulty: there are no “magnetic charges”)
- Usually not interesting for optics: magnetic permeability μ is 1 for almost all materials at optical frequencies

1.4 Light as an electromagnetic wave

Electric field and matter

Atom without electric field: with electric field:



symmetric charge distribution induced dipole

- Density $\overrightarrow{P}$ of induced dipoles (dielectric polarization) is proportional to the electric field: $\vec{P} = \chi \cdot \vec{E}$
- χ (the dielectric susceptibility) is a real number if the material's reaction to the electric field is instantaneous
- χ has a (frequency dependent) imaginary component if the reaction lags behind ($\rightarrow$ absorption)
- Important quantity: (relative) dielectric permittivity $\varepsilon = \chi + 1$

1.4 Light as an electromagnetic wave

Electromagnetic waves

Wave equation for electric field (from Maxwell‘s equations):

$$\frac{\partial^2 \vec{E}}{\partial x^2} + \frac{\partial^2 \vec{E}}{\partial y^2} + \frac{\partial^2 \vec{E}}{\partial z^2} = \varepsilon \varepsilon_0 \mu \mu_0 \frac{\partial^2 \vec{E}}{\partial t^2} = \frac{n^2}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2}$$

where

- $\boldsymbol{c} = \sqrt{\frac{1}{\varepsilon_0 \cdot \mu_0}}$ (= 299 792 458 m/s)
  speed of light (in vacuum)
  (ε_0, μ_0 = vacuum permittivity / permeability)

- $\boldsymbol{n} = \sqrt{\boldsymbol{\varepsilon} \cdot \boldsymbol{\mu}}$ = refractive index (of a material)
  (ε, μ = relative permittivity / permeability for a given material)

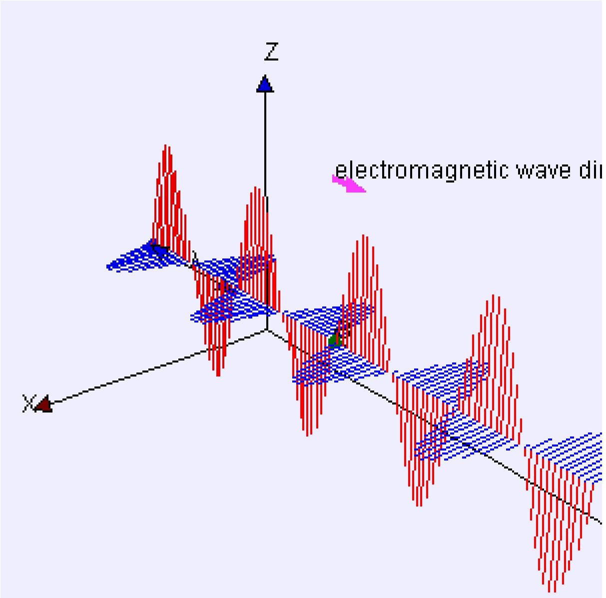
→ A material slows down light by a factor of n

Harmonic waves: λ and $\vec{k}$ depend on the material: $\lambda \rightarrow \frac{\lambda}{n}, \quad \vec{k} \rightarrow n \cdot \vec{k}$

1.4 Light as an electromagnetic wave
Harmonic electromagnetic waves in isotropic media

Relation between wave vector and field vectors

- Electric field $\vec{E}$ and magnetic field $\vec{H}$ are perpendicular to each other and to $\vec{k}$
- Amplitudes are linked: $\|\vec{E}\| = \sqrt{\frac{\mu\mu_0}{\varepsilon\varepsilon_0}} \cdot \|\vec{H}\|$



Loo Kang Wee (via Wikipedia)

Polarization:

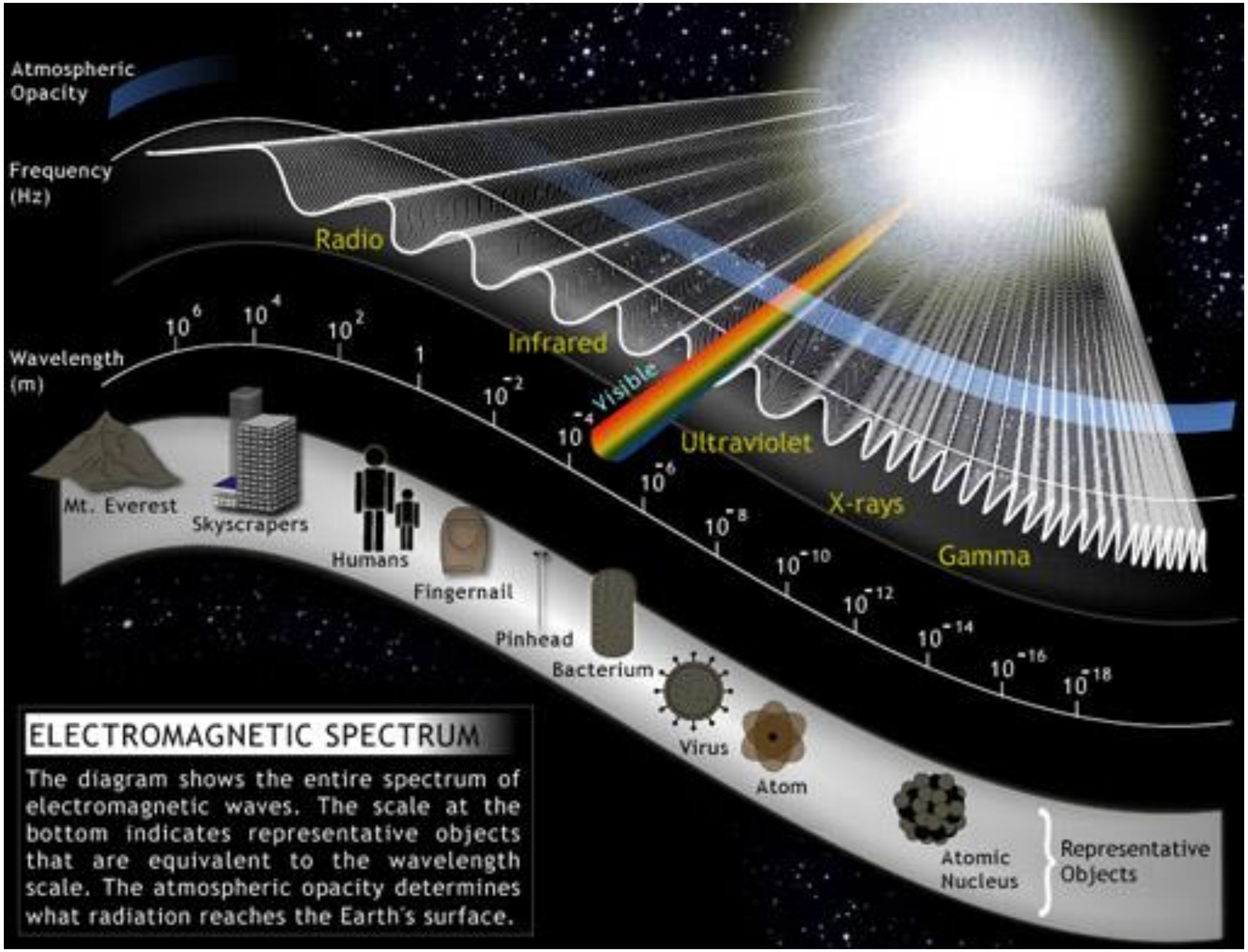
- Linear polarization: $\vec{E}$ and $\vec{H}$ oscillate in orthogonal planes
- Circular / elliptical polarization is also possible

Intensity:

- Intensity I = power per unit area perpendicular to $\vec{k}$
- $I = \|\vec{E} \times \vec{H}\|$: proportional to the squared amplitude

1.4 Light as an electromagnetic wave

Light in the electromagnetic spectrum



Visible light: ~ 380 – 780 nm

1.4 Light as an electromagnetic wave
Interfaces between different materials

Continuity conditions (required by Maxwell's equations)

- Tangential components of $\vec{E}$ and $\vec{H}$ are continuous, i.e., the same on both sides of the interface
- Perpendicular components of $\vec{D} = \varepsilon\varepsilon_0\vec{E}$ and $\vec{B} = \mu\mu_0\vec{H}$ are continuous

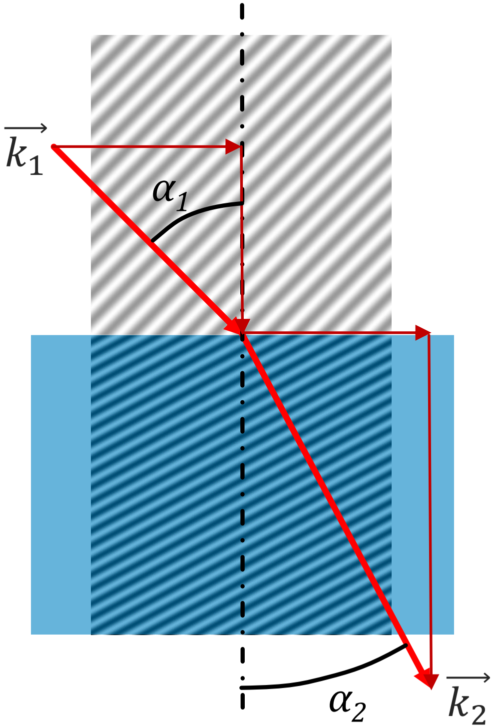
Consequence (a): Snell's law of refraction

- Continuity conditions are true at every point of the interface

  $\rightarrow$ tangential component of $\vec{k}$ is continuous

Length of $\vec{k}$ changes according to different refractive index

$\rightarrow$ perpendicular component must adapt



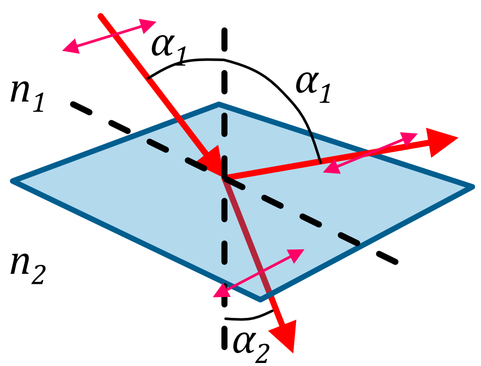
(some trigonometry) $\rightarrow n_1 \sin\alpha_1 = n_2 \sin\alpha_2$

1.4 Light as an electromagnetic wave

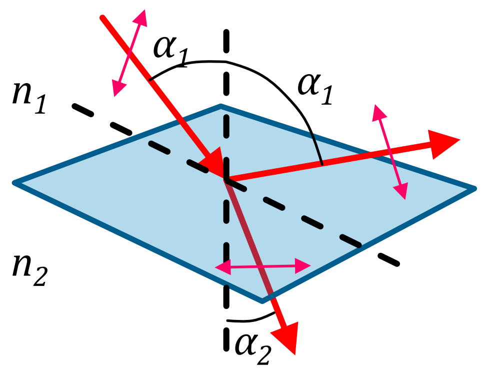
Interfaces between different materials

Consequence of continuity conditions (b): Fresnel coefficients

- Three waves to match all conditions : incident, transmitted, reflected
- Matching conditions depend on polarization



s polarization („senkrecht“)



p polarization („parallel“)

plane of incidence is spanned by 3 wave vectors

polarization is defined by $\vec{E}$ field with respect to the plane of incidence

- Amplitude reflection and transmission coefficients:

$$r_s = \frac{n_1 \cos\alpha_1 - n_2 \cos\alpha_2}{n_1 \cos\alpha_1 + n_2 \cos\alpha_2} \qquad r_p = \frac{n_1 \cos\alpha_2 - n_2 \cos\alpha_1}{n_1 \cos\alpha_2 + n_2 \cos\alpha_1}$$

$$t_s = \frac{2n_1 \cos\alpha_1}{n_1 \cos\alpha_1 + n_2 \cos\alpha_2} \qquad t_p = \frac{2n_1 \cos\alpha_1}{n_1 \cos\alpha_2 + n_2 \cos\alpha_1}$$

reflected:

$$E_r = r \cdot E_i$$

transmitted:

$$E_t = t \cdot E_i$$

1.4 Light as an electromagnetic wave

Interference

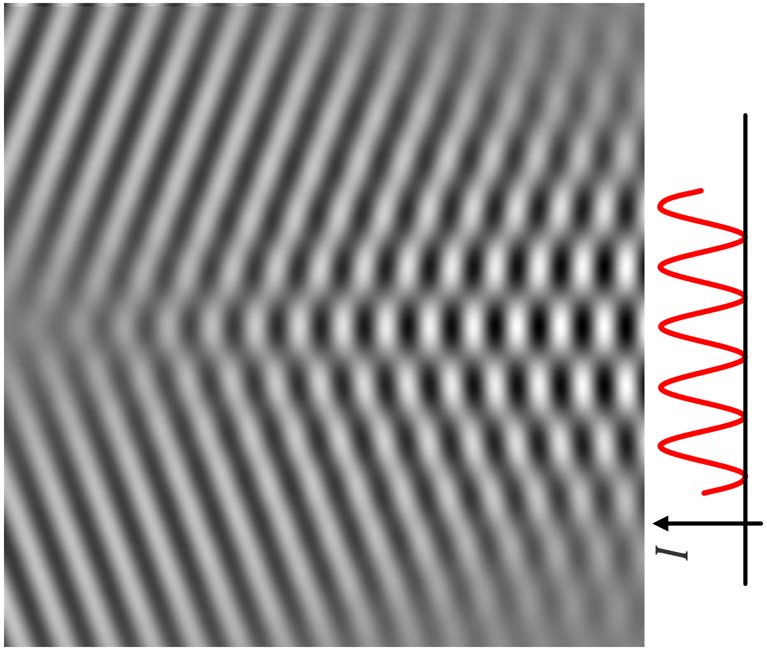
Superposition of waves → amplitudes add up

Constructive interference:

- same direction / sign
- $I \propto (E_1 + E_2)^2 = E_1^2 + E_2^2 + 2E_1E_2$
- Intensity > sum of separate intensities

Destructive interference:

- opposite direction / sign
- $I \propto (E_1 - E_2)^2 = E_1^2 + E_2^2 - 2E_1E_2$
- Intensity < sum of separate intensities



Required: coherence = constant phase relationship

- spatial: different points of a light source are correlated
- temporal: sufficiently stable frequency for paths of different length

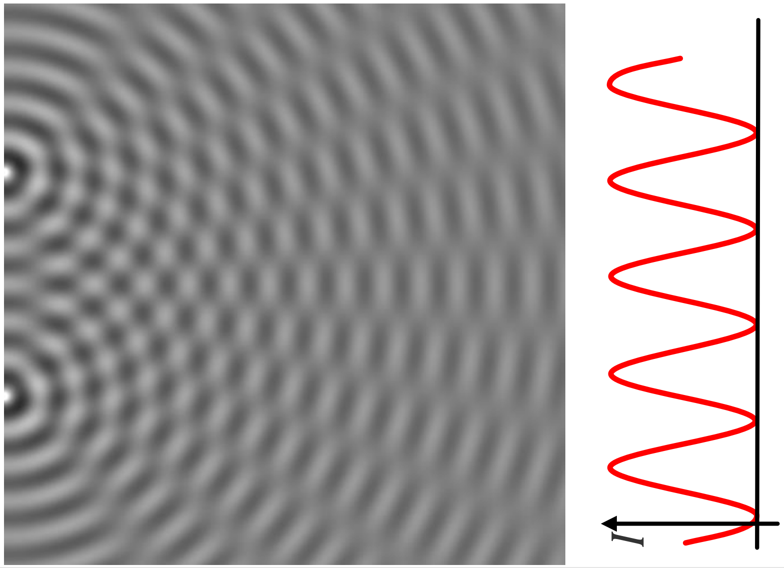
1.4 Light as an electromagnetic wave
Huygens' principle

Not everything is a plane wave

Basic idea: Each point in space is the origin of a spherical wave correlated with the wave field. All spherical waves interfere with each other.

- Undisturbed case: The result is the wave field as it was
- Disturbed case: Basis for **scalar diffraction theory** (Perturbation: any inhomogeneity in the material, i.e. the spatial distribution of ε)

- Example: Young's double-slit experiment → ultimate proof for wave character of light



2.1 Optical effects of periodic microstructures
Gratings and lattices

Description of periodic structures in space

Grating: 2D (sheet-like) structure, periodic within the sheet plane

Lattice: 3D (volume) structure, periodic in all three dimensions

Simplest case: grating of parallel lines

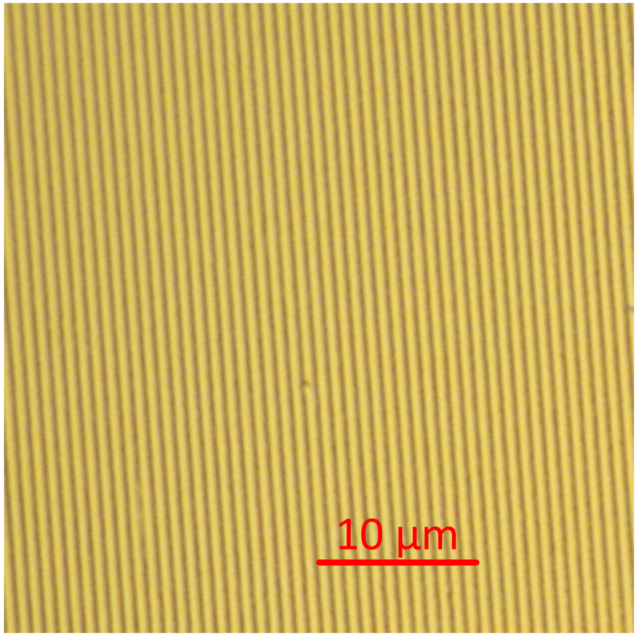
Just like an optical wave, but static:

$$F(\boldsymbol{x}) = A \cdot \cos(\vec{K} \cdot \vec{x})$$

$\vec{K}$ = grating vector (or lattice vector)

F can be any quantity relevant to optics:

- refractive index
- absorption
- height of a surface (2D gratings only)



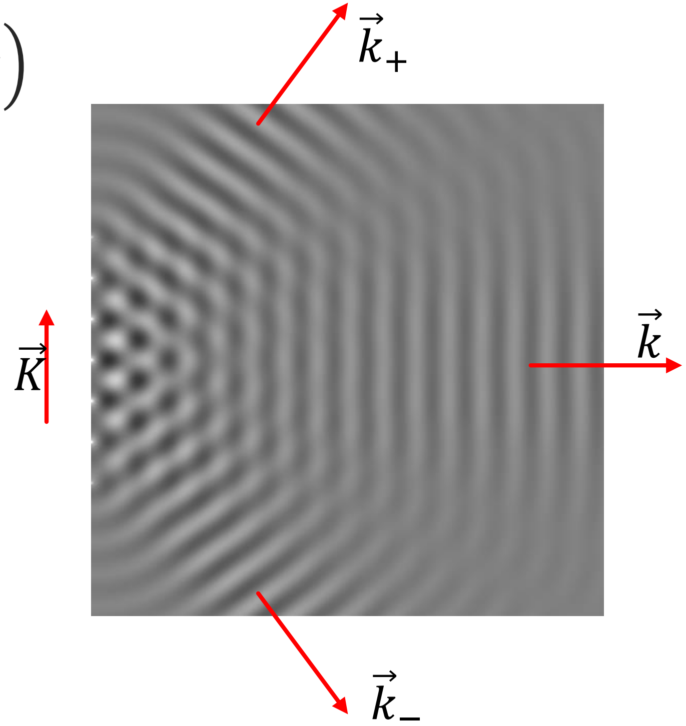
Diffraction grating of a monochromator (microscope image)

Interaction of a light wave with a grating

Incident light:

$$\vec{E}_{incident}(\vec{x},t) = \vec{E}^{0}_{incident} cos\left(\vec{k}\cdot\vec{x} - \omega t\right)$$

$\vec{k}$ is not parallel to the grating plane



Result:

- Attenuation of incident wave
- Additional plane waves:

$$\vec{E}_{\pm}(x,t) = \vec{E}^{0}_{\pm} \cos\left(\vec{k}_{\pm}\cdot\vec{x} + \delta_{\pm} - \omega t\right)$$

- tangential component of $\vec{k}_{\pm}$ is obtained by adding / subtracting $\vec{K}$
- perpendicular component of $\vec{k}_{\pm}$ adjusts to maintain correct length

2.1 Optical effects of periodic microstructures
Diffraction – general case

General description of a periodic structure:

Superposition of harmonic modulations with different K (Fourier representation)

Condition for diffraction: There must be a lattice vector $\vec{K}$ present with

$$\vec{k}_{diffracted} = \vec{k}_{incident} \pm \vec{K} \qquad \text{(Bragg condition)}$$

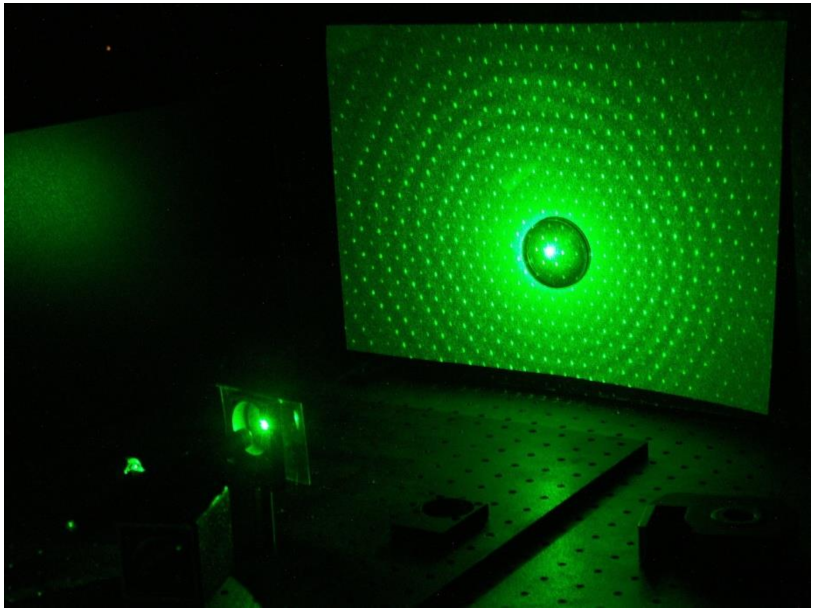
Additionally, the length of $\vec{k}$ must remain constant (conservation of energy).

- Diffraction only for special combinations of incident and diffracted wave vectors
- Basis for crystal structure analysis by X-ray diffraction

Special case for thin gratings: perpendicular component of $\vec{k}_{\pm}$ adjusts to maintain correct length

2.1 Optical effects of periodic microstructures

Examples



hexagonal array of holes in a metal film

CD / DVD

natural opal

2.2 Non-periodic microstructures
From diffraction to scattering

Loss of strict periodicity in the structure

→ Fourier representation turns into a continuous spectrum

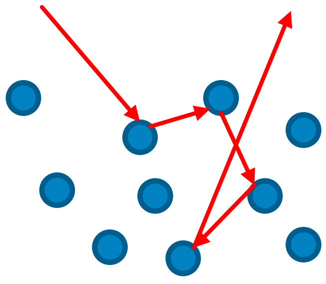
→ Loss of selectivity in the diffraction condition

Partial loss of periodicity:

- Still some selectivity
- Preferences for some wavelengths: structural colors
- Preferences for some angles

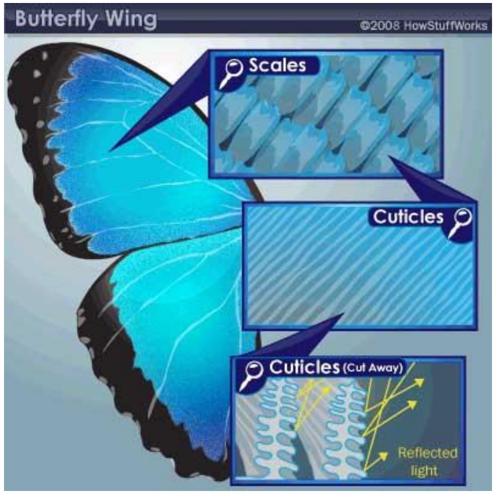
Complete loss of periodicity / complete randomness:

- Uniform scattering
- Can be interpreted as a “random walk” of photons



2.2 Non-periodic microstructures
Examples

Partially periodic



Completely random

2.3 Periodic nanostructures
Metamaterials

Transition from “micro” to “nano”:

- Semi-official: feature size < 100 nm
- Convenient for optics: periodicity < $\lambda/2$ (roughly equivalent for visible light)

Why?

- Periodicity < $\lambda/2$ means $K > 2 \cdot k$
- No chance to maintain correct length of the diffracted wave vector, even with a full reversal of the direction of propagation
- Result: periodic structure becomes invisible!

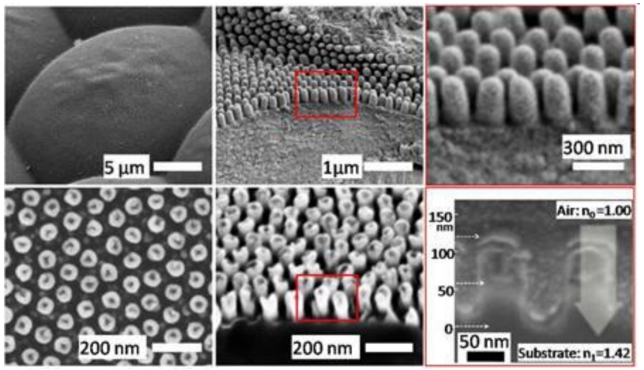
But: Properties of the structural units still remain active

- Anisotropy & polarization
- Unusual dispersion relations (wavelength dependence of refractive index)

2.3 Periodic nanostructures

Metamaterials - Examples

Moth eye: one of few examples for optical wavelengths

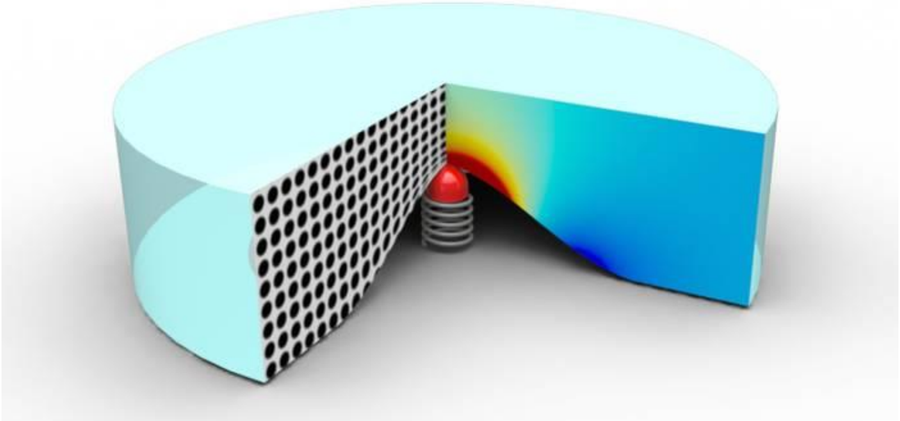


Many proof of principle demonstrations with microwaves

Cloaking devices

Negative refractive index

…



Metamaterial cloak (Source: K. Kim, Yonsei University; via Welt der Physik)

3.1 Vertically structured surfaces

Modifying reflectivity

Surface reflection from transparent materials

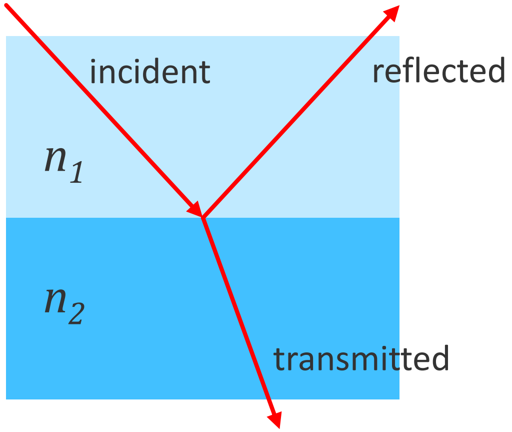
- Reason: Matching electromagnetic field amplitudes on both sides of the surface (Fresnel reflection)

- Amplitude reflection coefficient:

$$r = \frac{n_1 - n_2}{n_1 + n_2}$$

@ normal incidence (angle dependent)

(Intensity reflection coefficient is r^2!)



Task: Either decrease or increase reflectivity

3.1 Vertically structured surfaces

Why antireflective surfaces?

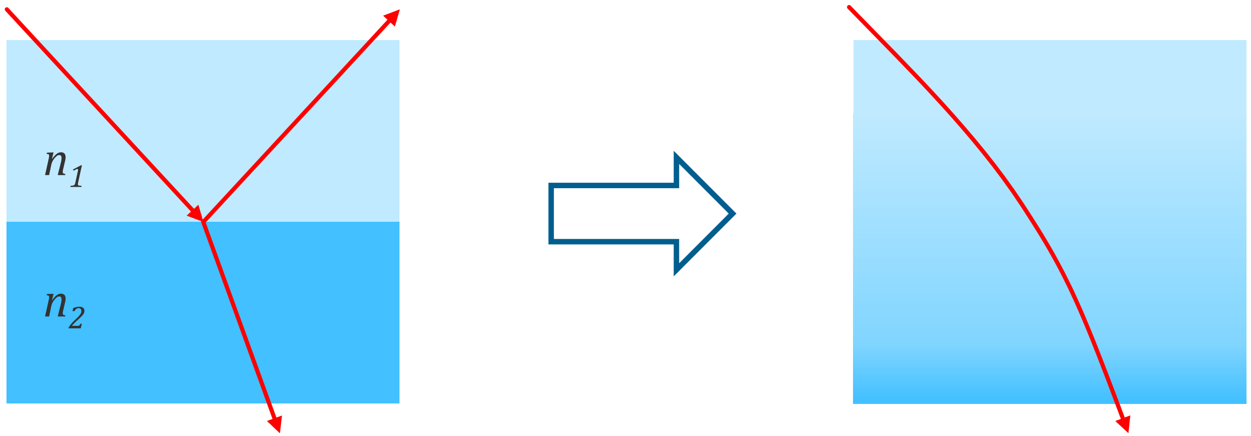
Maximize light throughput:

Maximize contrast:

3.1 Vertically structured surfaces

Approaches for antireflective surfaces (2)

Gradient index (GRIN) surfaces



True GRIN is difficult, approximation by a series of layers with small refractive index differences is possible.

Additional difficulty: Refractive index of air is 1.0, but the lowest refractive index of a solid material is 1.38 (MgF_2); porous silica can go down to 1.22, but has other issues.

Not competitive in practice

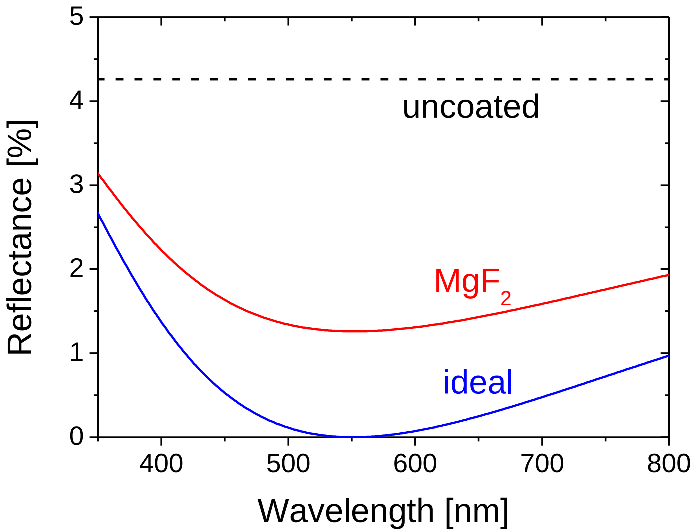
3.1 Vertically structured surfaces
Approaches for antireflective surfaces (2)

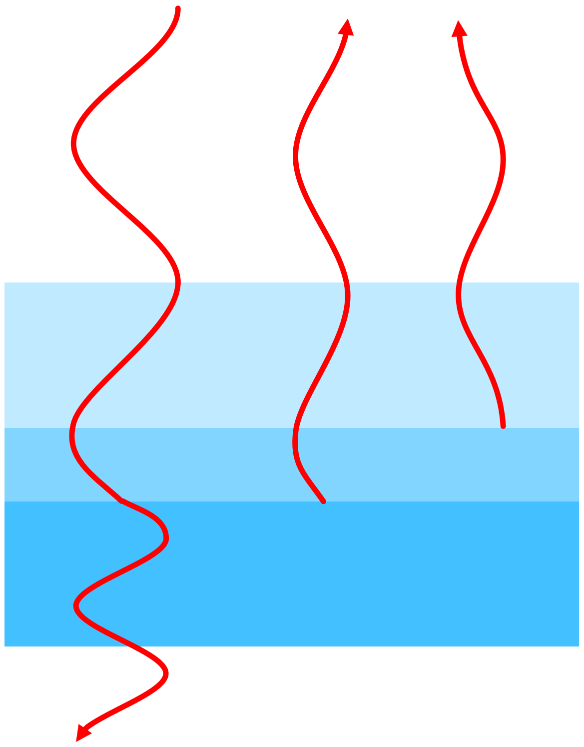
Single interference layer

Destructive interference of reflected partial waves

Layer parameters for optimum antireflective effect:

- refractive index = $\sqrt{n_1 n_2}$
- thickness = $\lambda/4$





Technically used for low cost applications

3.1 Vertically structured surfaces

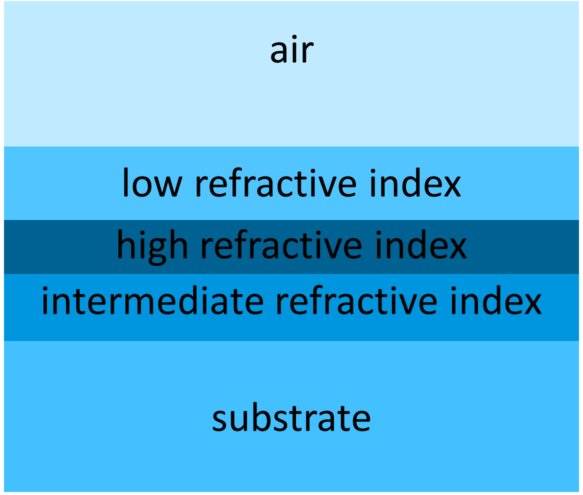
Approaches for antireflective surfaces (3)

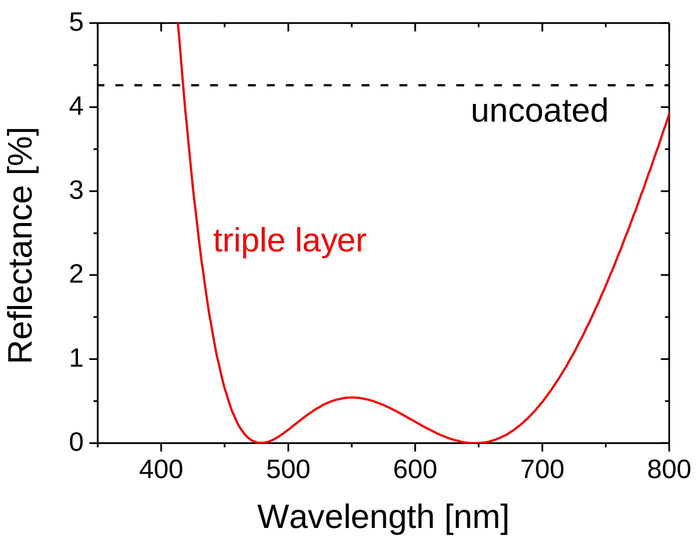
Multiple interference layers

Increased bandwidth

Various designs possible (example: 3 layers)

Still, generally: thickness of each layer = $\lambda/4$



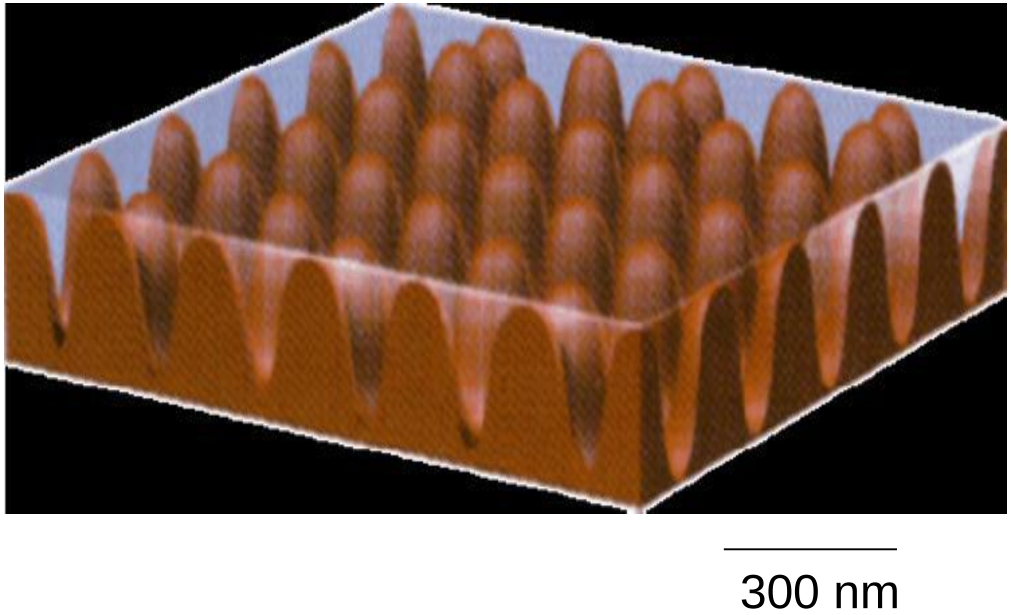


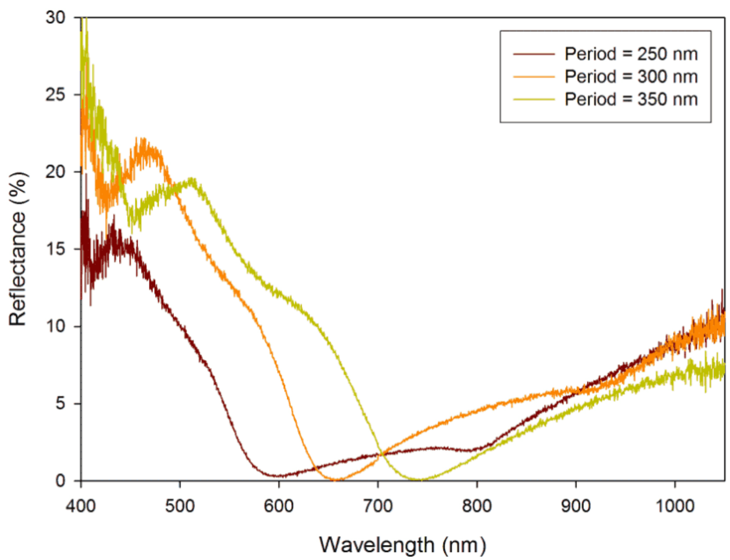
3.1 Vertically structured surfaces
Approaches for antireflective surfaces (4)

Moth eye structures

Metamaterial to achieve

- low average refractive index
- some GRIN effect





Rather limited technical application

sensitive to soiling and wear

3.1 Vertically structured surfaces

Materials for interference layer systems

General requirements for layer materials:

- Refractive index: from very low to very high
- Transmission range may vary depending on the application
- Resistance to environmental conditions depending on the application

Typical materials:

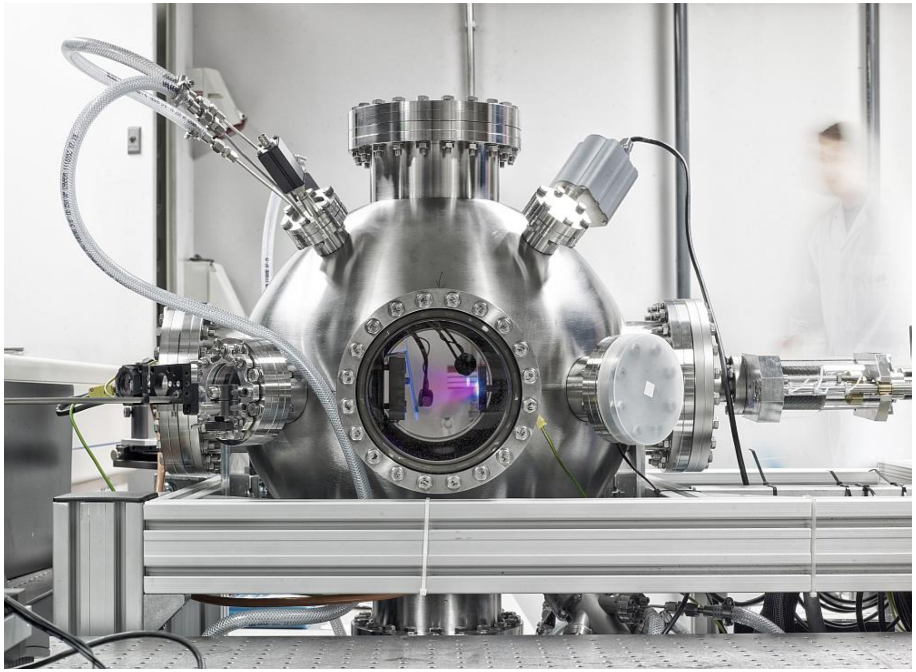
- MgF_2 (n=1.38, soft, broad transmission range)
- Amorphous silica (SiO_2; n= 1.46, hard, UV transparent)
- Porous silica (n down to 1.22, very soft)
- TiO_2 (n = 2.4 to >3 for dense material; hard; UV cutoff below 400 nm)
- ZrO_2 (n = 2.13; hard; transparent for near UV)

3.1 Vertically structured surfaces
How to make interference layer systems

INM

1. Gas phase deposition

- Physical vapor deposition
- Chemical vapor deposition



Features:

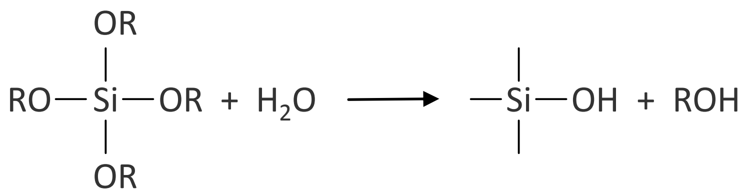
- High quality coatings
- Suitable for small substrates
- High equipment cost

3.1 Vertically structured surfaces

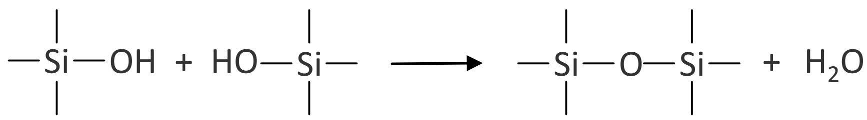
How to make interference layer systems

2. Sol-Gel and related methods

- Wet chemical synthesis based on hydrolysis and condensation reactions starting from suitable precursors



Hydrolysis



Condensation

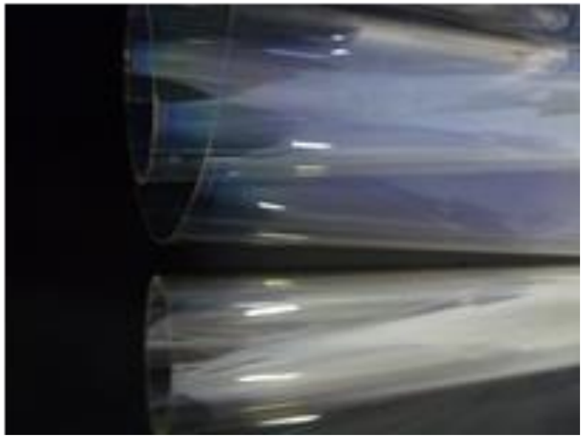
- Depending on synthesis route: nanoparticles or amorphous network dispersed in organic solvent
- May be modified with organic cross-linkers for low-temperature stability
- Various coating methods: Spin coating, dip coating, continuous roll-to-roll processes
- UV and / or thermal curing

3.1 Vertically structured surfaces

Wet coated interference layers

Dip coating for rigid substrates

Roll-to-roll coating line



Coated PET foil

3.2 Horizontally structured surfaces

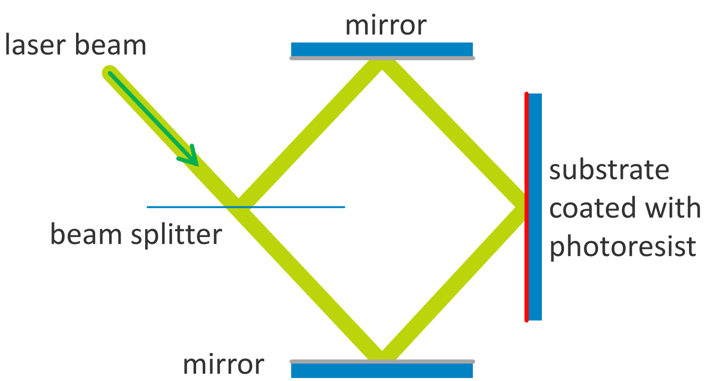
Gratings, holograms and moth eyes

Origination methods for nano-/microstructured surfaces

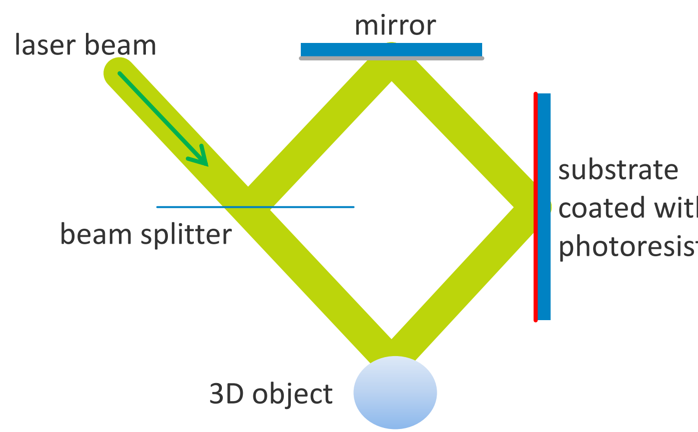
- Self assembly of nano-/microparticles
- Specific etching methods

→ non-deterministic

- Direct writing (laser, electron beam) → high resolution, but very slow
- Holographic writing:



two beam interference
gratings can be stitched (dot matrix)



classical holography

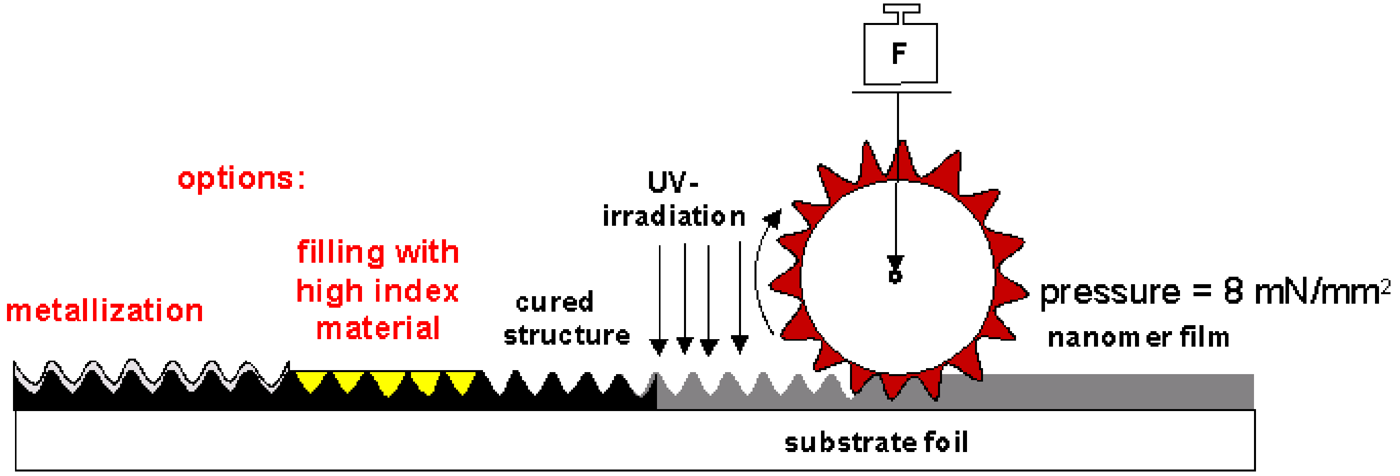
3.2 Horizontally structured surfaces

From master structure to mass production

Origination → Master structure

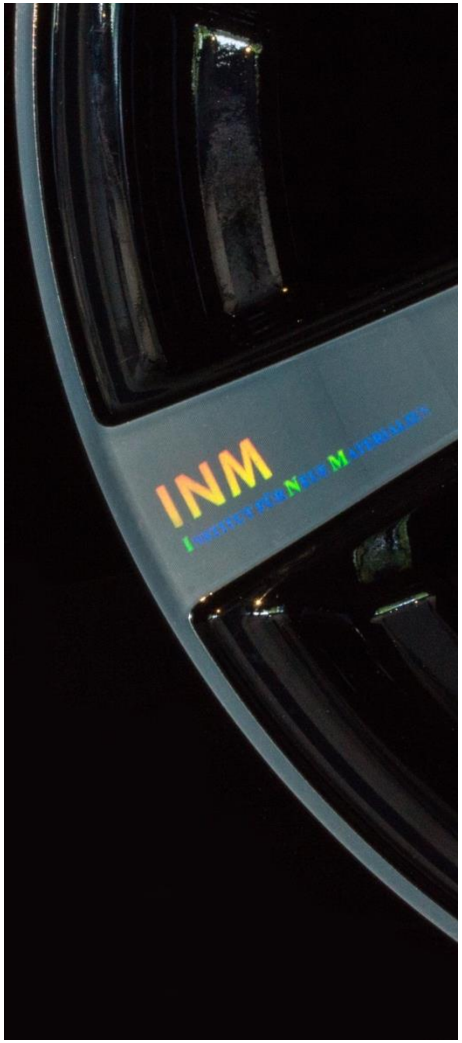
At least one molding step
for mass production typically several
molding and electroforming steps combined

Tool for embossing



3.2 Horizontally structured surfaces
Replication techniques

- Hot embossing
  - limited to thermoplastic polymers
  - needs to cool while in contact with the tool
    → slow process
- Reactive casting
  - UV curing through the substrate foil (needs to be transparent) or through a transparent tool (silicone)
  - well-established process, fast
- Embossing into a thixotropic resin (INM approach)
  - shaping with high shear rate, but no relaxation afterwards
  - curing after removing the tool
  - fast alternative for non-transparent substrates



4. Nanocomposites
Nanoparticles within a matrix

Goal: use nanoparticles to modify the properties of a polymer material …

- Change the refractive index
- Modify the dispersion curve
- Increase hardness / wear resistance
- Add electrical functionalities
- …

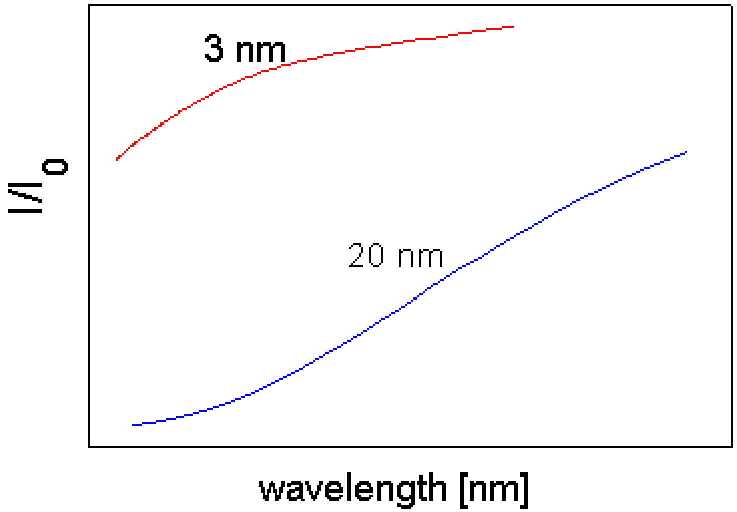
… without sacrificing transparency!

Challenge: Periodic structures may become invisible with feature sizes below $\lambda/4$ (half period), but inhomogeneities in random distributions of particles are much larger than the particles themselves → Particles need to be really small!

4. Nanocomposites
Importance of particle size

Transparency of randomly distributed particles:

$$\frac{I}{I_0} = \exp\left(-4 \cdot \frac{\pi^4}{\lambda^4} \cdot d^3 \cdot \left(\frac{n_p^2 - n_m^2}{n_p^2 + 2 \cdot n_m^2}\right)^2 \cdot c \cdot L\right)$$



I/I_0 = Transmission
λ = Wavelength
d = Particle diameter
n_p = Refractive index particles
n_m = Refractive index matrix
c = Particle concentration
L = Thickness bulk

Notes: 1. Applies also to nanoporous materials

2. Good dispersion (avoiding agglomeration) is equally important

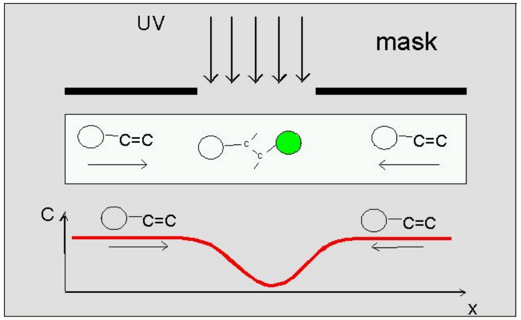
4. Nanocomposites
An example of a nanocomposite for microstructures

Target

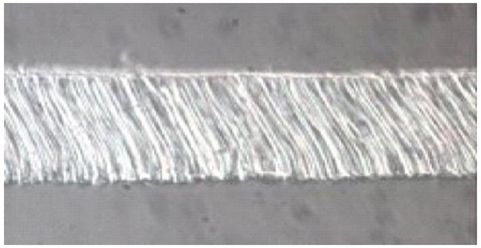
- Development of Light Management Foils (LMF)
- Enhancement of brightness and contrast, reduced viewing angle dependence for LCD
- Better brightness and contrast, lower sensitivity to ambient light for projection screens

Methods

- Photosensitive gradient index material based on cross-linkable nanoparticles in a gel-like matrix
- Irradiation of this material through a mask produces a columnar microstructure with angle-dependent scattering properties
- Continuous roll-to-roll processes for coating, mask lamination and irradiation



Diffusion mechanism of polymerisable nanoparticles



Tilted columnar domains of higher refractive index in cured light management material

4. Nanocomposites
Light management foils

Results

- 50 µm thick films with pronounced angle-dependent scattering
  - High haze (>94 %) for light incident from preferred direction
  - Significantly lower haze for other directions
- LMF as diffuser in LCDs:
  approx. 20 % higher brightness and contrast
- LMF on mirror delivers even greater improvement

Projection screen
LMF on mirror

Applications

- Diffusers for LCD panels
- Projection screens
- Lighting

Summary of most important topics

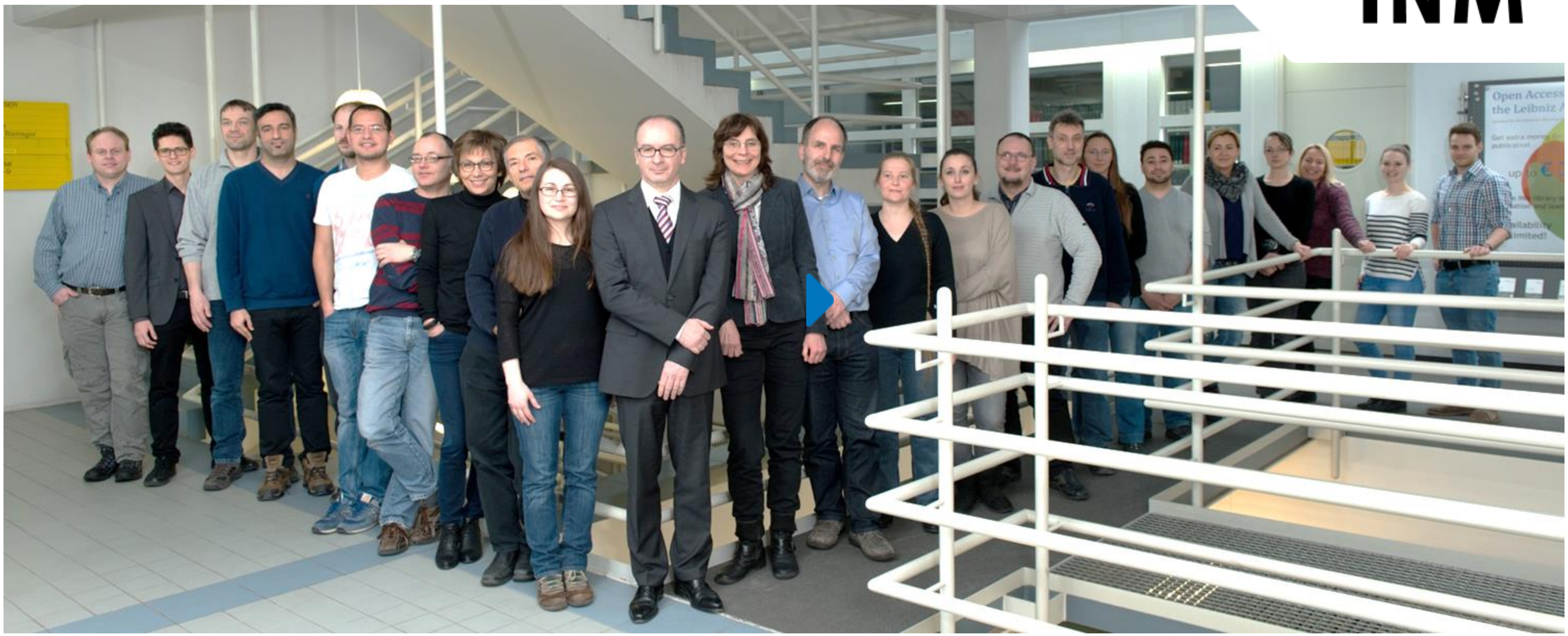
Theory

- What is light
- Formalism for describing electromagnetic waves
- Interaction of light with materials structured on microscopic / submicroscopic scale

Application & technology

- Antireflective surfaces
- Microstructured surfaces
- Nanocomposites

THANK YOU FOR YOUR ATTENTION



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