Engineering visual appearance with nanostructures

Kevin Vynck

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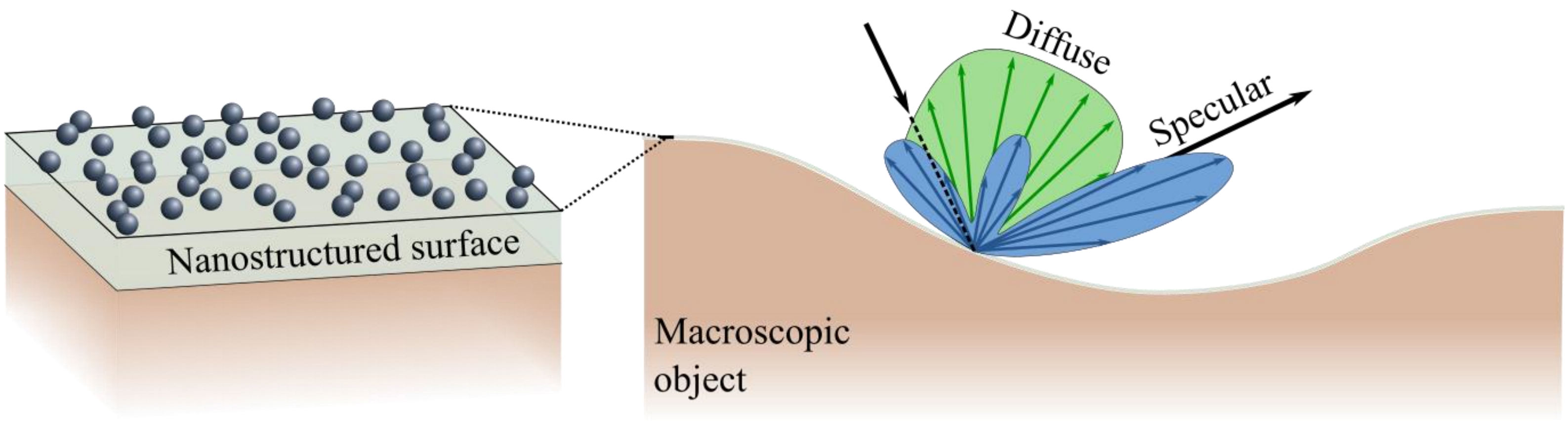

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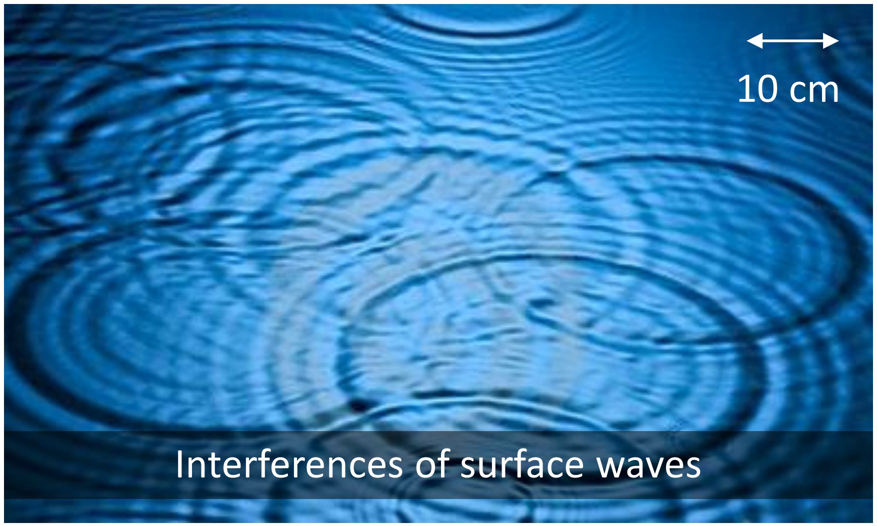
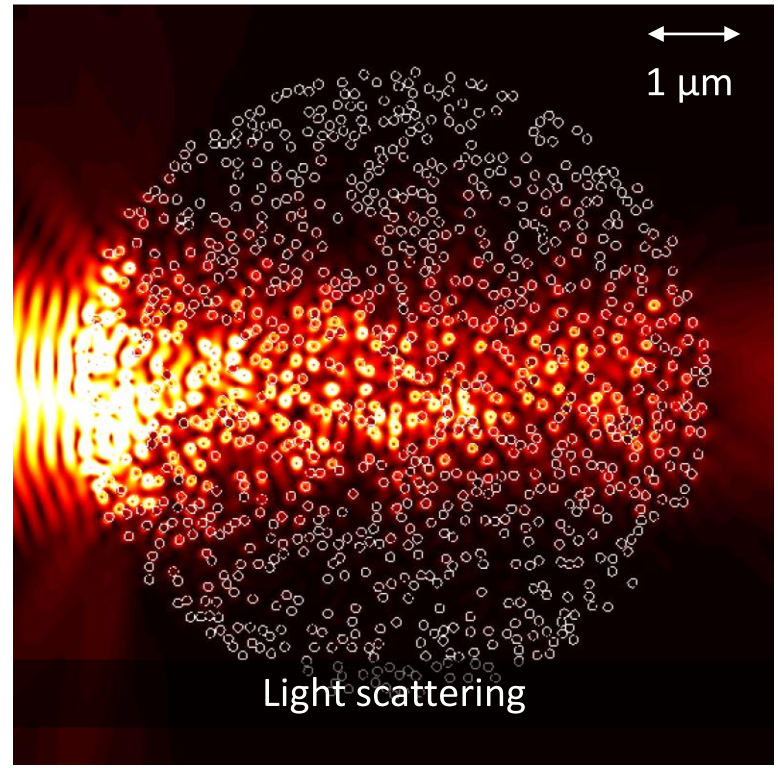
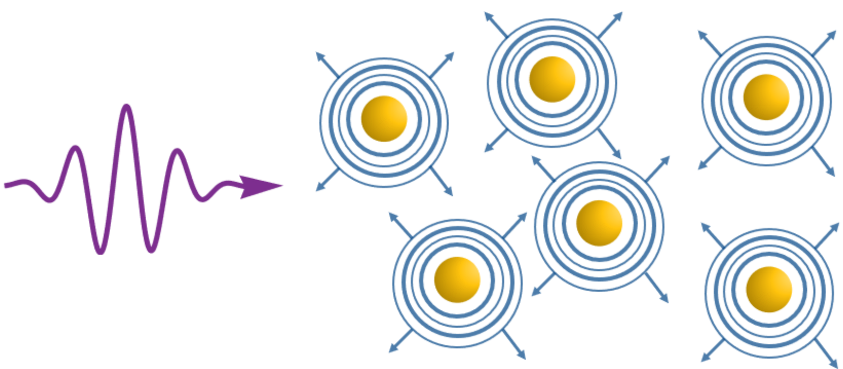
Light propagation and interferences

Like surface waves on water, **light** is a wave that **propagates** and **interferes**



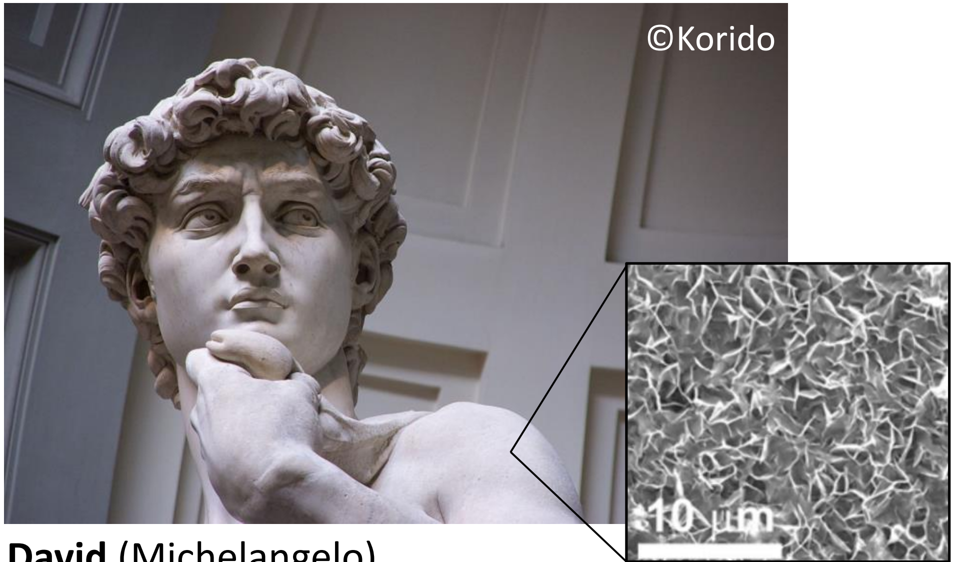




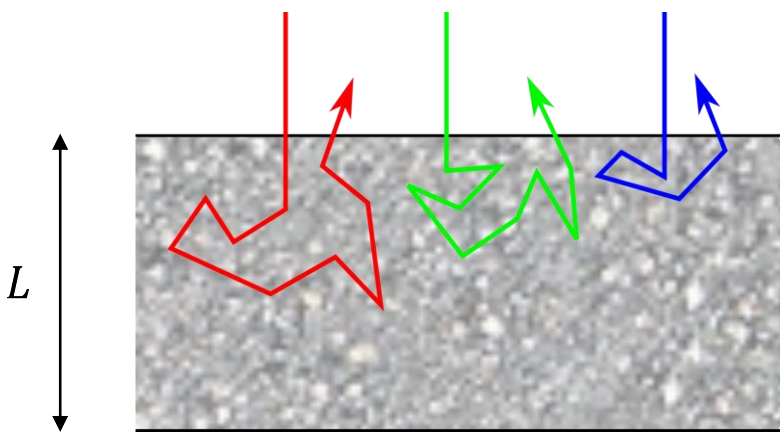
Heterogeneities in matter **scatter light** in new directions

Visual appearance of disordered materials

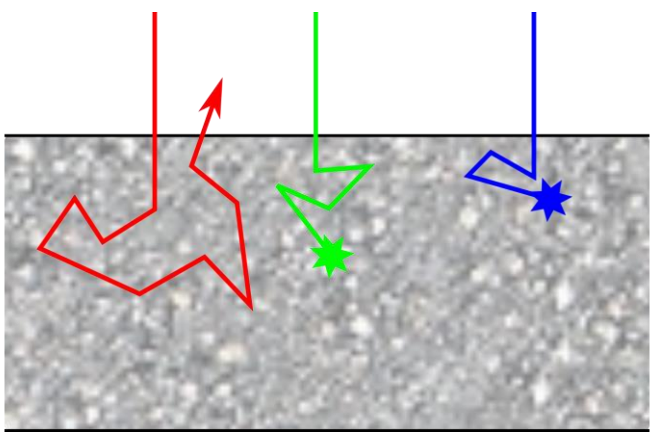
Opaque, white, matte



David (Michelangelo)



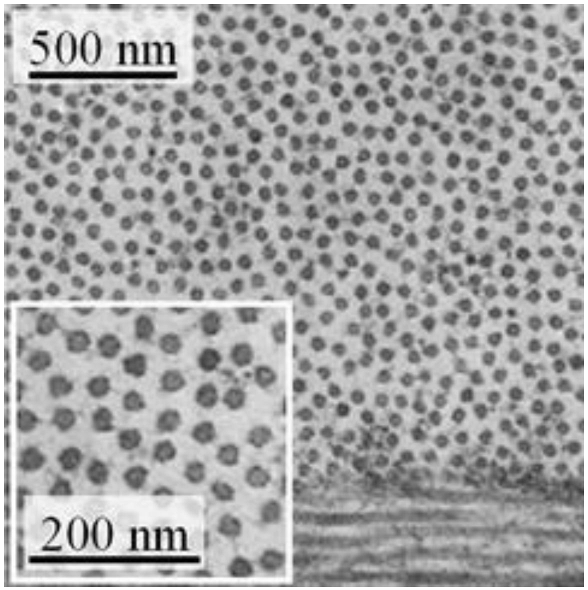
Colors created by absorption

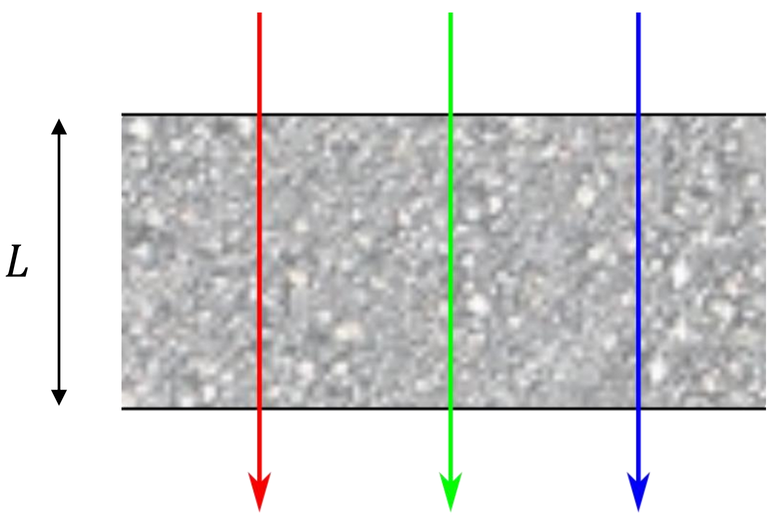


Visual effects created by *interference* in disordered materials

Transparency of the cornea

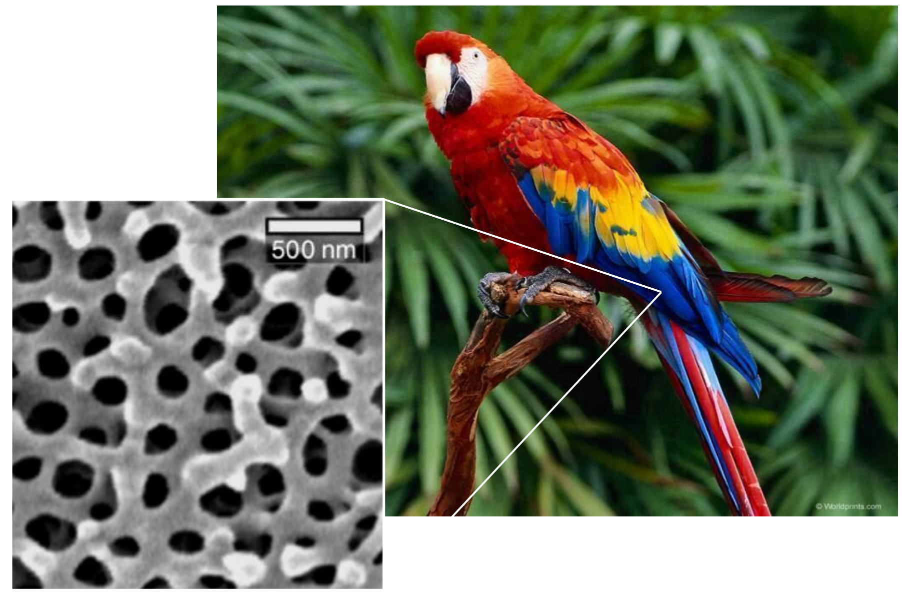
D. M. Maurice, J. Physiol. **136**, 263 (1957)

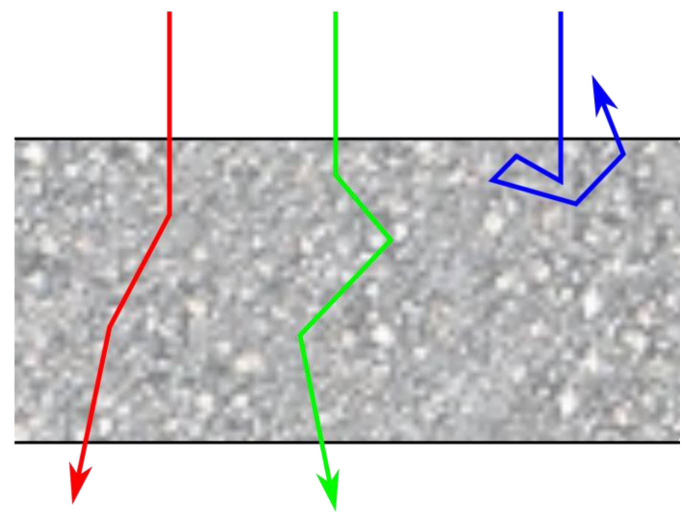




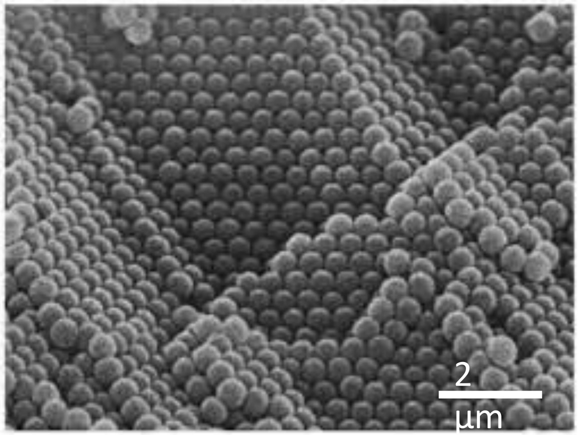
Structural colors in the living world

for instance, H. Yin *et al.,* PNAS **109**, 10798 (2012)



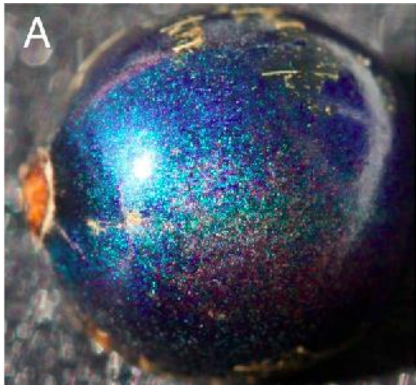


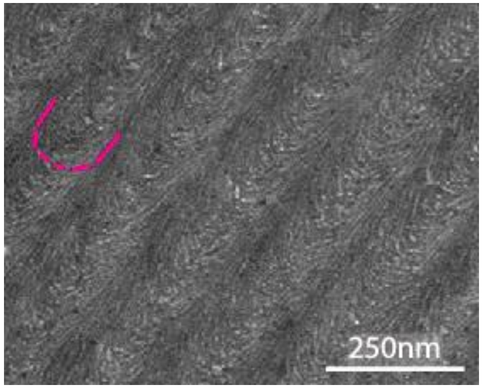
Other splendid visual appearances in nature



Opal (gemstone)

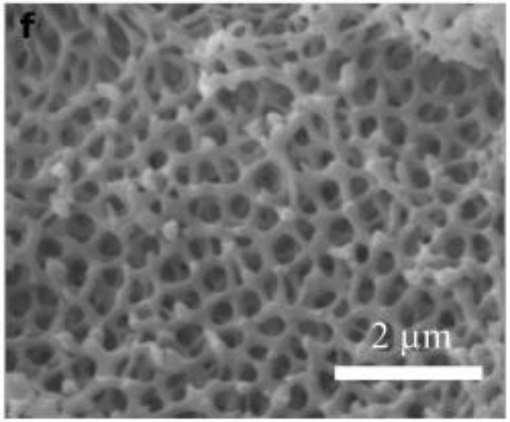
H. Miguez *et al.*, Appl. Phys. Lett. **71**, 1148 (1997)





Pollia condensata (plant)

Vignolini *et al.*, PNAS **109**, 15712 (2012)



Kingfisher (bird)

Stavenga *et al.*, J. Exp. Biol. **214**, 3960 (2011)

By the way, what is visual appearance?

845-22-019 Appearance,
International Electronical Commission IEC

Aspect of visual perception through which an object is perceived to have attributes such as size, shape, colour, texture, gloss, transparency, and opacity

A critical issue for many fields of activity

Vehicle design

Cosmetics

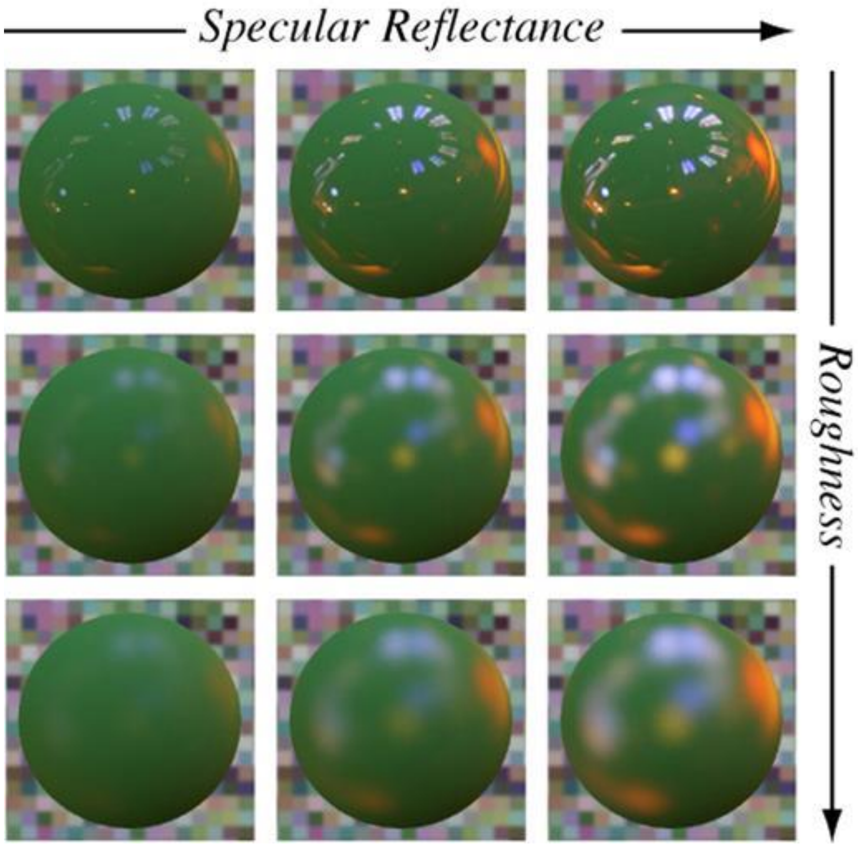
Architecture

Visual appearance is much more than just color

Visual appearance depends on

- the **lighting environment** (directions, spectrum)
- the **shape** of the object (concave/convex shapes, multiple reflections, ...)
- the weight between **specular** and **diffuse** components (glossiness, ...)

The subtle relation between the **scattering properties** of a material and its **visual appearance** has been studied in great details by the **computer graphics community**



Fleming *et al.*, "Real-world illumination and the perception of surface reflectance properties", J. Vis. **3**, 347 (2003)

Predictive rendering in Computer Graphics

Highly-optimized **ray tracing** techniques in **complex lighting environments**, wherein the **optical properties** of materials are determined on **physical grounds**

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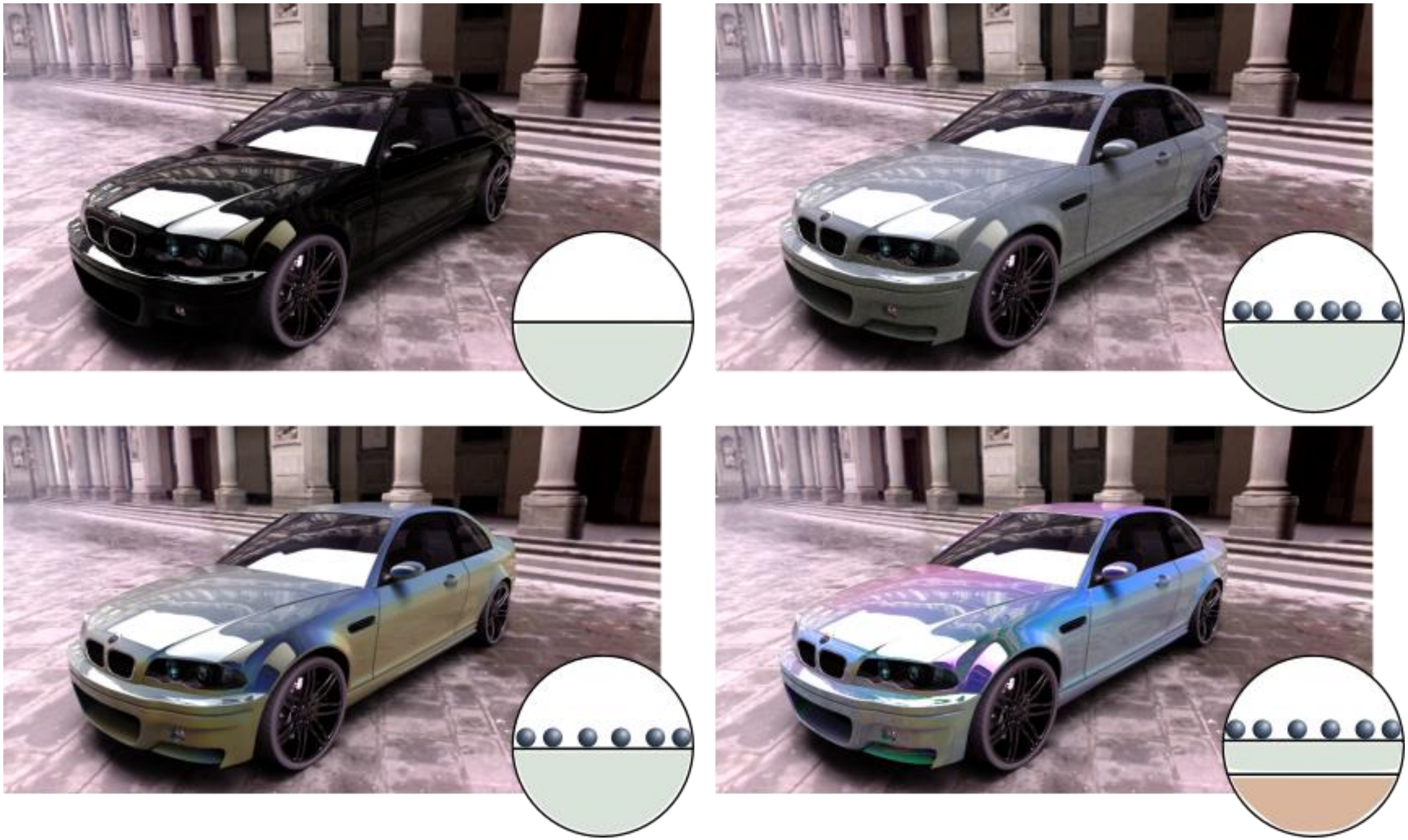
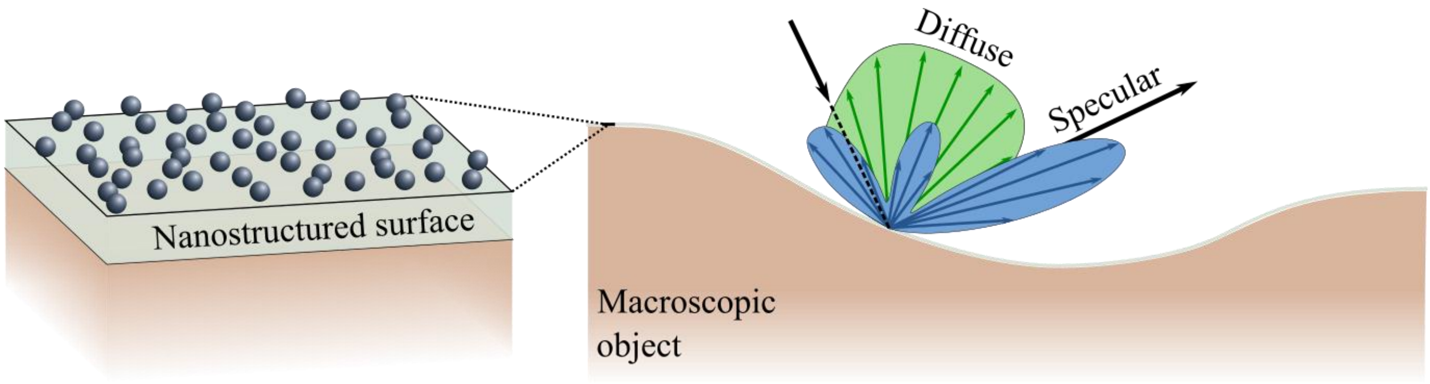
Predictive rendering of nanostructured objects

Numerical platform merging **electromagnetic modelling** and **computer graphics** to predict the **visual appearance of macroscopic objects covered by complex nanostructured surfaces**

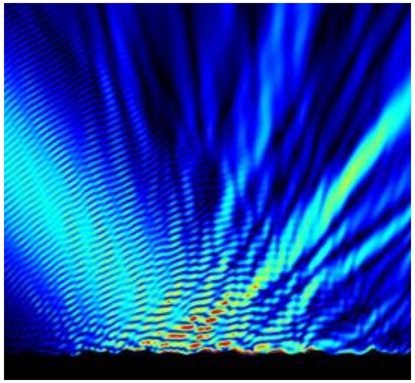


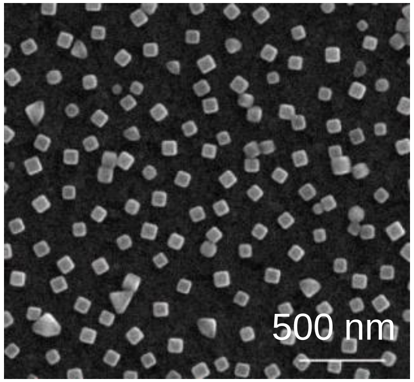
K. Vynck, R. Pacanowski *et al.*, Nature Materials **21**, 1035-1041 (2022)

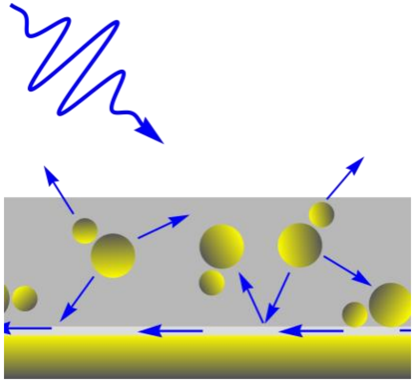
Content of this talk



I.	**II.**	**III.**	**IV.**
Wave scattering by rough surfaces	Complex resonant nanostructures	Modelling of complex nanostructures	Application to visual appearance design







I. Simonsen, Eur. Phys. J. Special Topics **181**, 1-103 (2010)

A. Moreau *et al.*, Nature **492**, 86 (2012)

K. Vynck, R. Pacanowski *et al.*, Nature Materials **21**, 1035 (2022)

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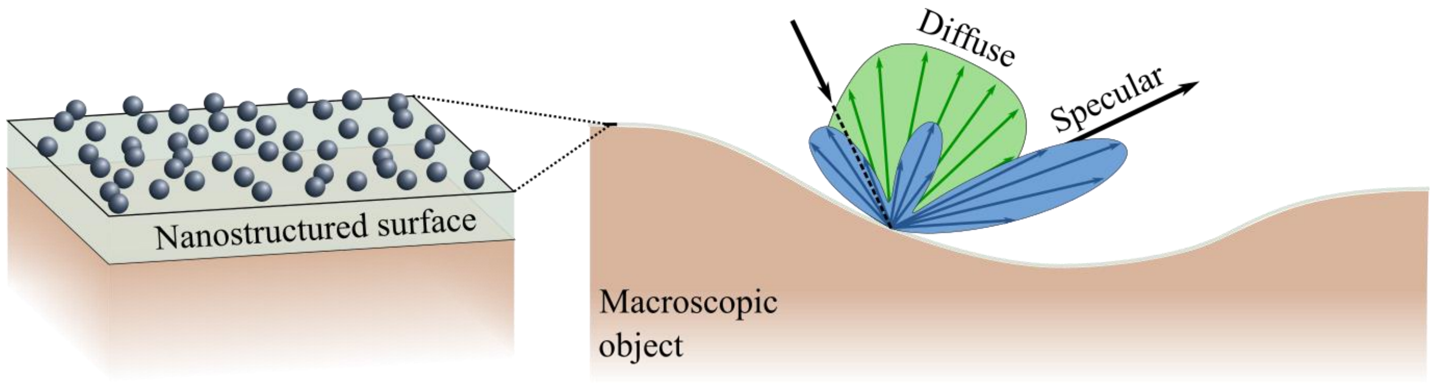

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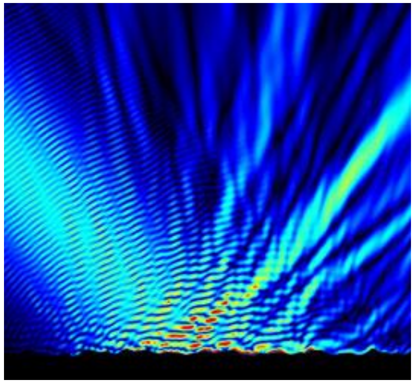
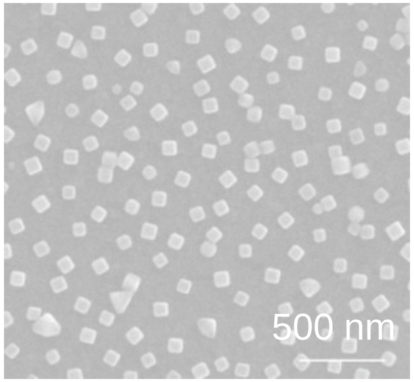
Wave scattering by rough surfaces



II.
Complex resonant nanostructures



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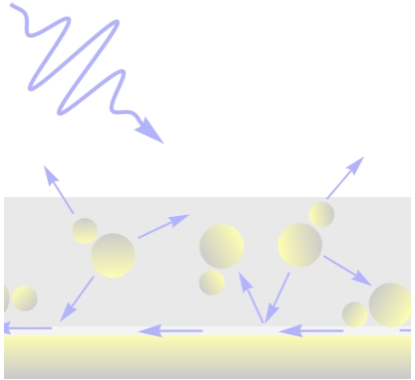
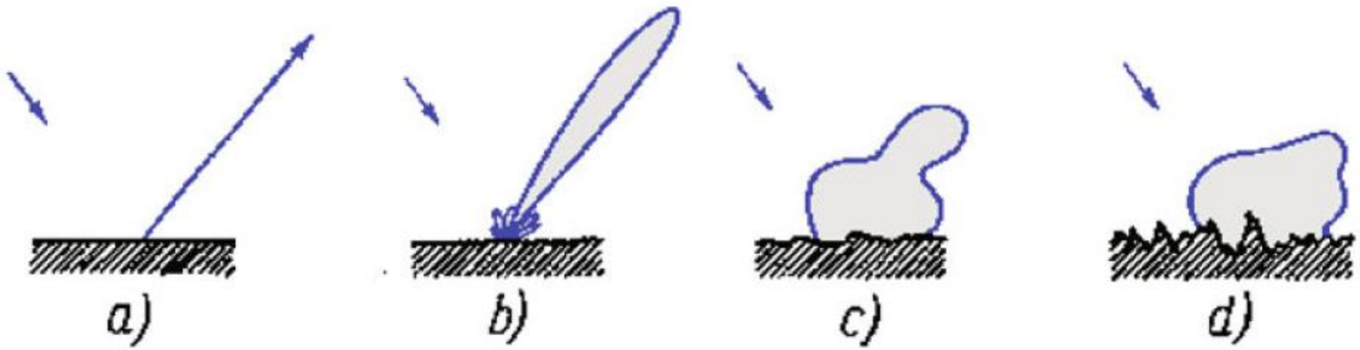
Modelling of complex nanostructures



IV.
Application to visual appearance design

Wave scattering by random rough surfaces

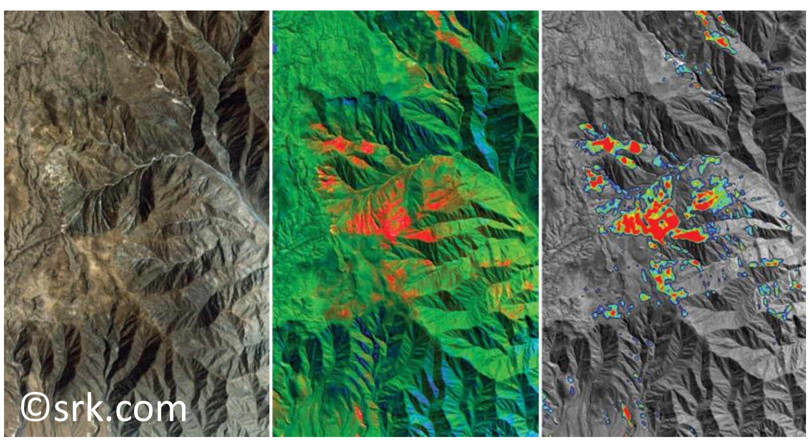
A classical problem for acoustics, optics, microwaves, radio waves, ...



Purely specular → Mostly diffuse

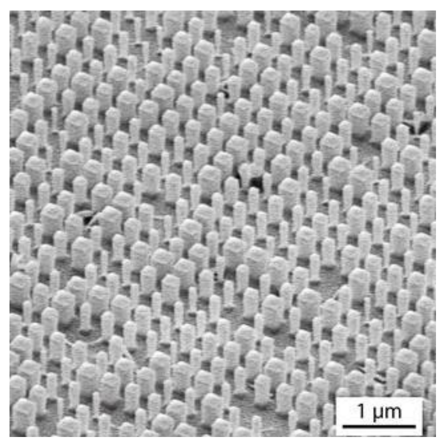
Beckmann & Spizzichino, 1987

... in many fields of application

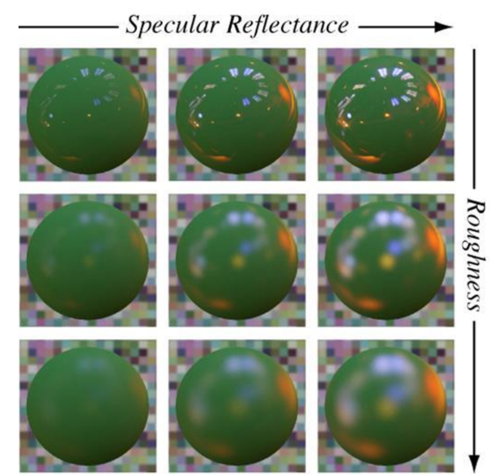


Earth & planetary sciences
(astronomy, geophysics, oceanography, ...)

©caltech.edu



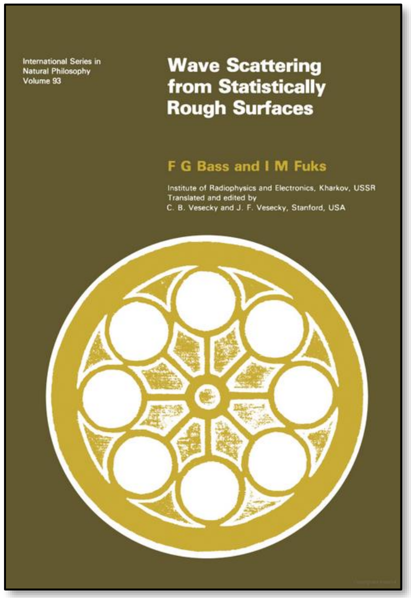
Material spectroscopy
& surface engineering



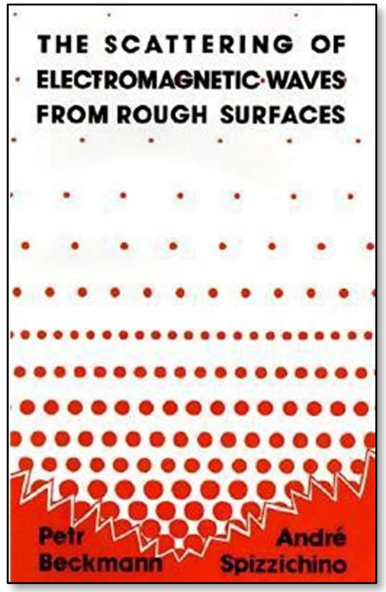
Computer graphics
Fleming *et al.*, 2003

A long-standing topic covered by many excellent textbooks

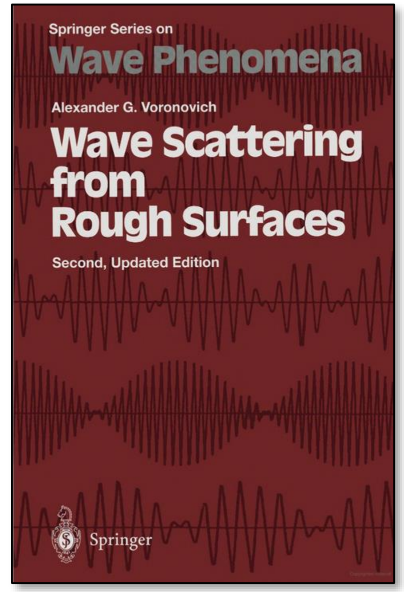
…



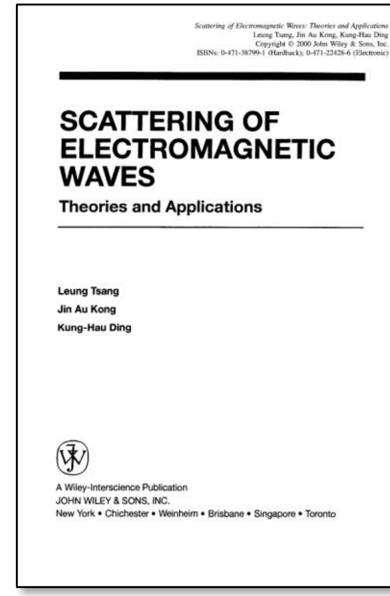
Bass & Fuks, 1979



Beckmann & Spizzichino, 1987



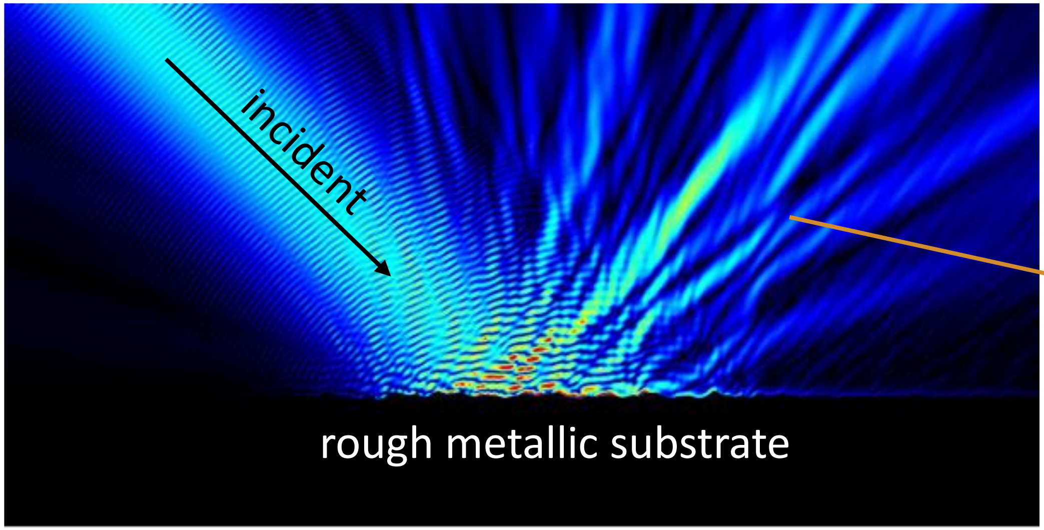
Voronovich, 1994, 1999



Tsang, Kong & Ding, 2000

…

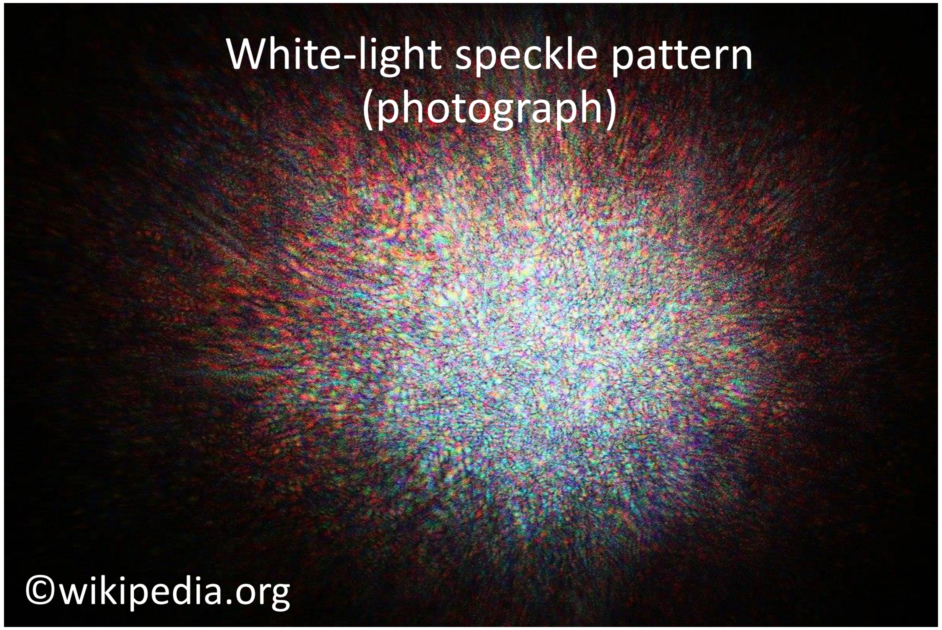
Reflection from a random rough surface



Map of the intensity created by a light beam incident on a rough surface (numerical simulation)

speckle created by
wave interference

I. Simonsen, Eur. Phys. J. Special Topics **181**, 1-103 (2010)



Statistical properties of the **scattered field**

↕

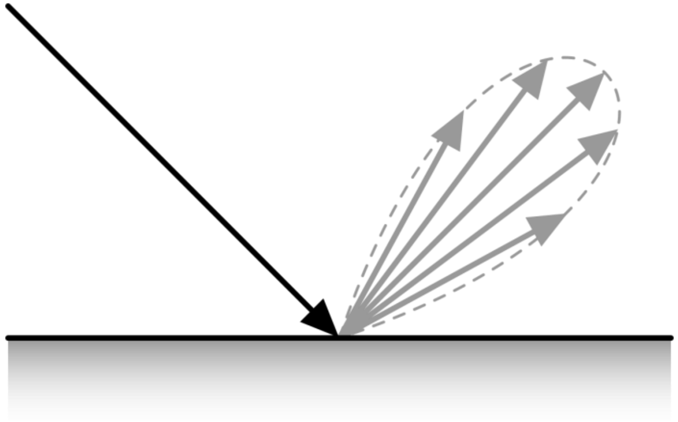
Statistical properties of the **surface topology**

Statistical description of wave scattering

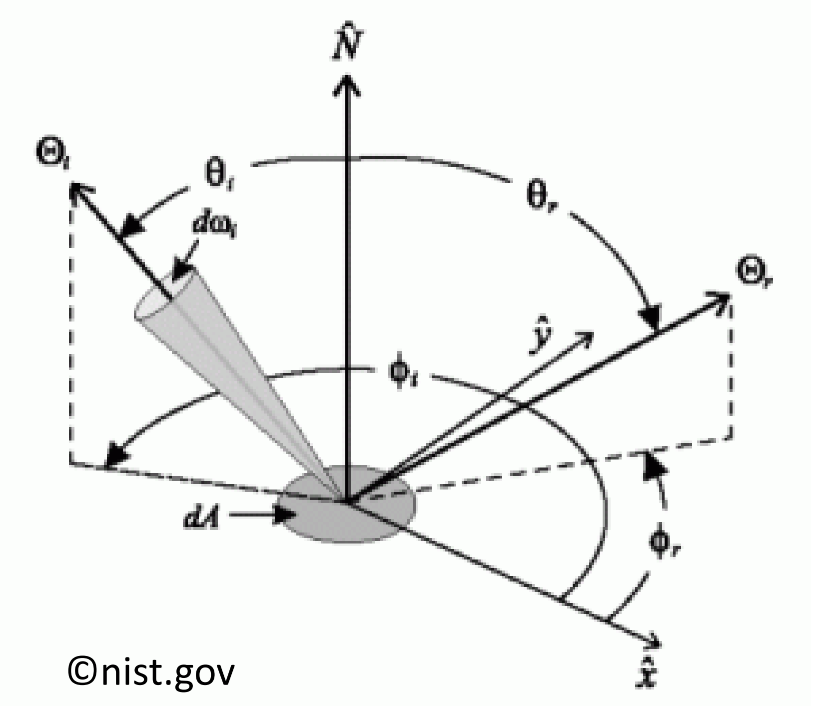
Bidirectional Reflectance Distribution Function (BRDF)

Describes how, *on average,* a surface redistributes the energy of an incident wave in the far field.

P. Chavel *et al.*, "Advocating a statistical definition for the BRDF", NEWRAD International Conference (2021).



©wikipedia.org



BRDF (sr^{-1})

Reflected radiance ($W.m^{-2}.sr^{-1}$)

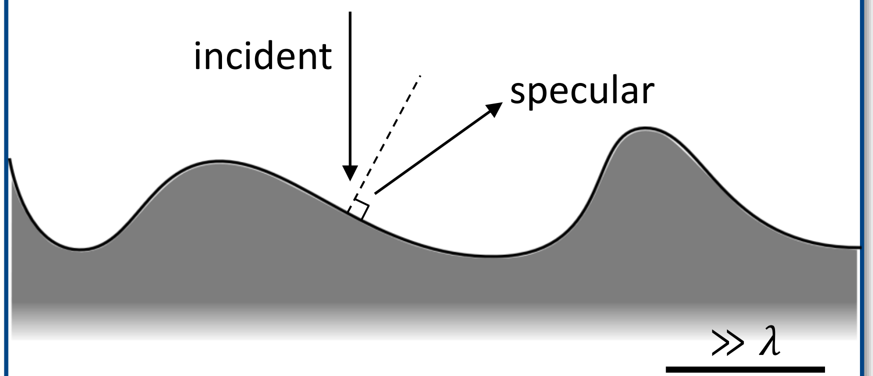
$$f_r(\theta_r, \phi_r, \theta_i, \phi_i; \lambda) = \frac{\langle L_r(\theta_r, \phi_r; \lambda)\rangle}{E_i(\theta_i, \phi_i; \lambda)}$$

Incident irradiance ($W.m^{-2}$)

Classical BRDF models: two limit cases

T. M. Elfouhaily and C.-A. Guérin, Waves Rand. Med. **14**, R1 (2004)

Tangent plane approximation
(Kirchhoff)



- **Locally smooth (flat) surfaces** (large curvature radii vs λ)
- **Specular reflection** from Fresnel equations
- Random tilts broaden the specular reflection peak
- Multiple reflections neglected (in the original formulation)

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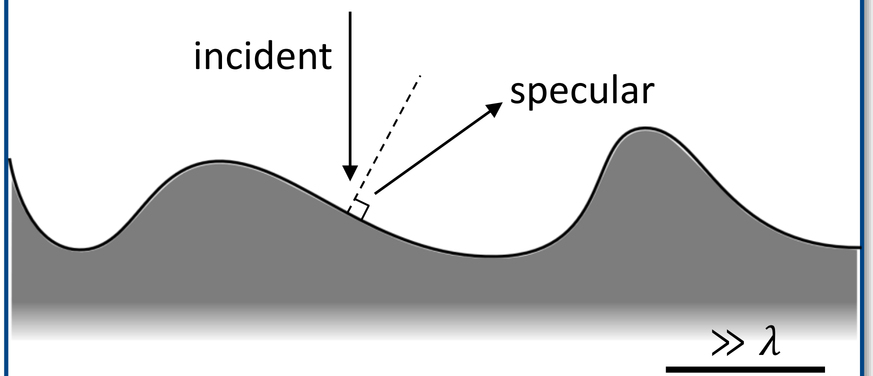

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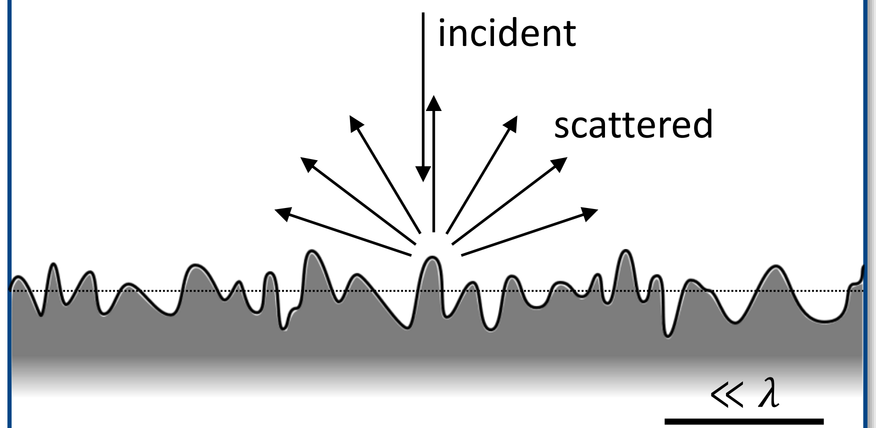
Small perturbation approximation
(Rayleigh-Rice)



- **Tiny variations of height** (vs λ) around an average flat surface
- **Rayleigh scattering** by small polarized volume elements
- Light scattered along all directions with an efficiency varying as $1/\lambda^4$
- Multiple scattering neglected (in the original formulation)

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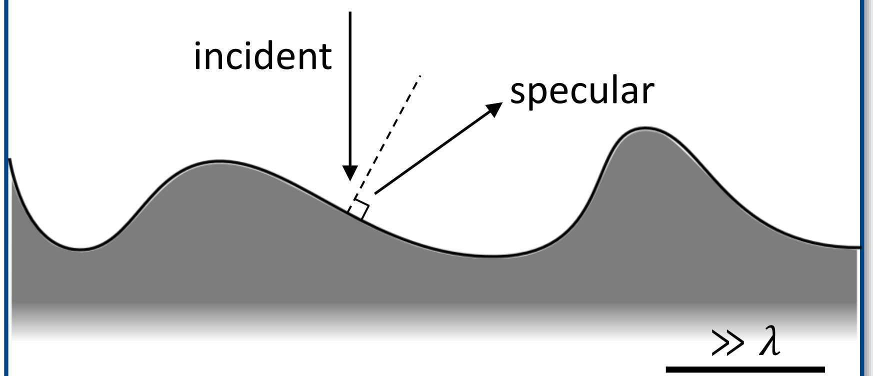

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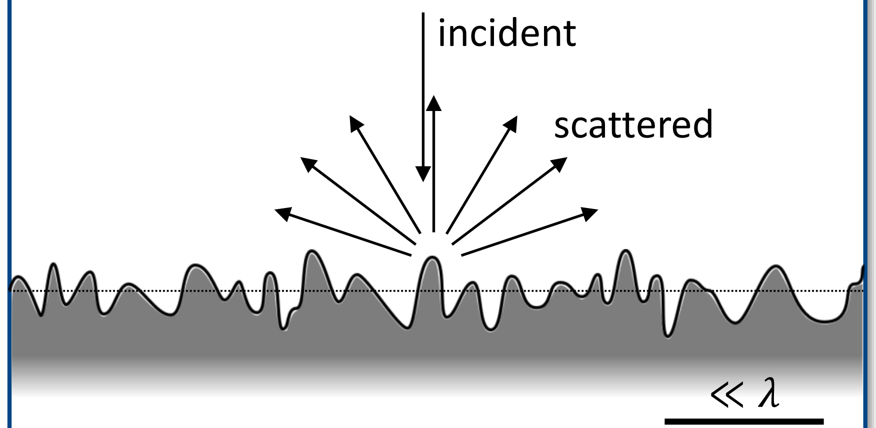

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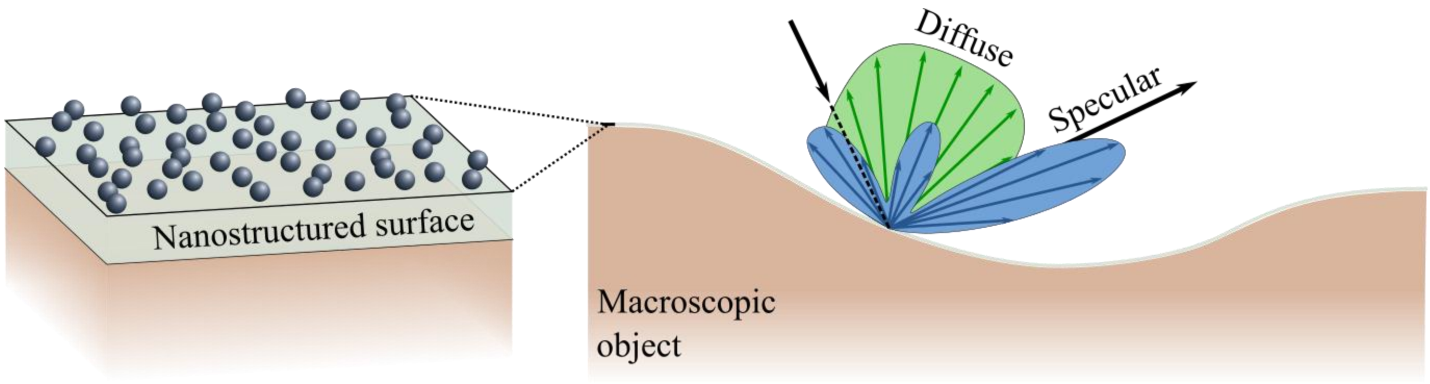
What can we expect from **interacting, wavelength-scale scattering elements** ?

Content of this talk



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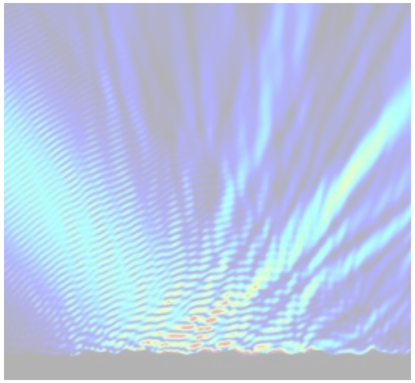
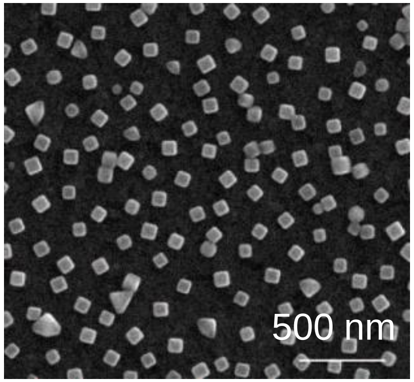
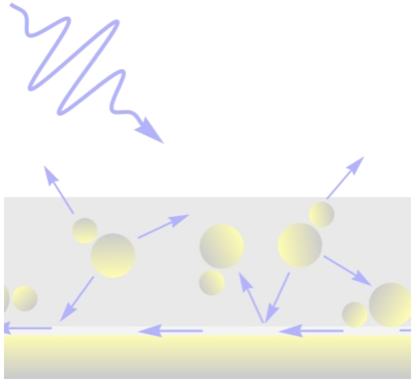
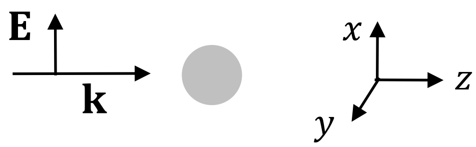


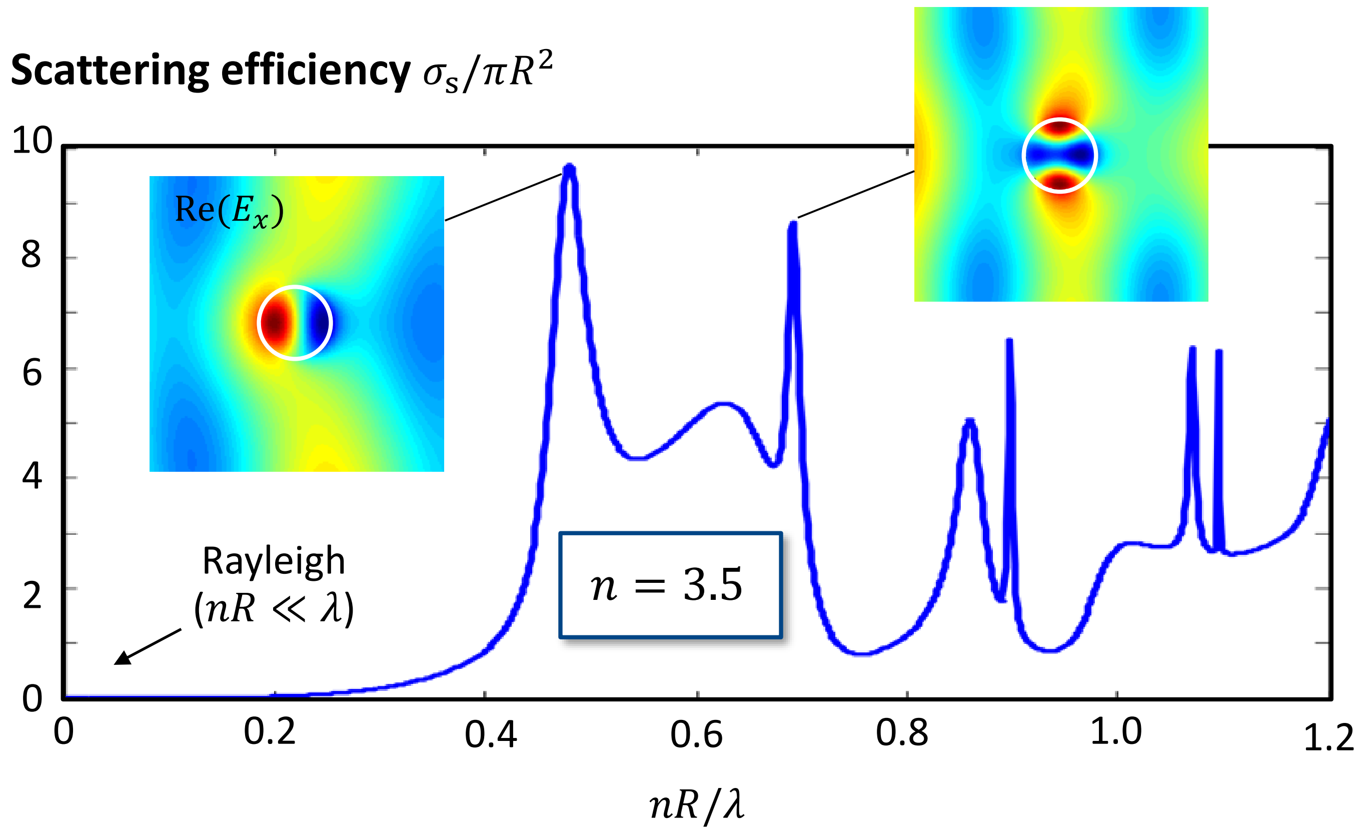




Light scattering by particles / Mie theory

Sphere of radius R and refractive index n illuminated by a planewave at λ



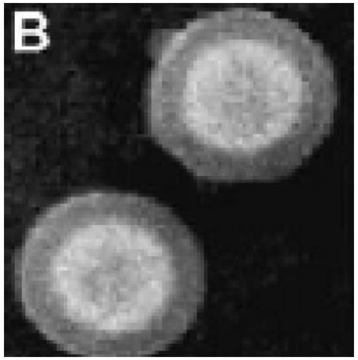


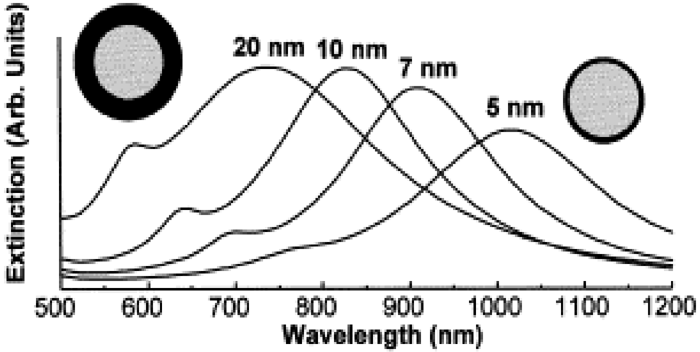
Gustav Mie
(1868-1957)

High-index nanoparticles strongly interact with light

Engineering of dielectric and/or metallic nano-objects

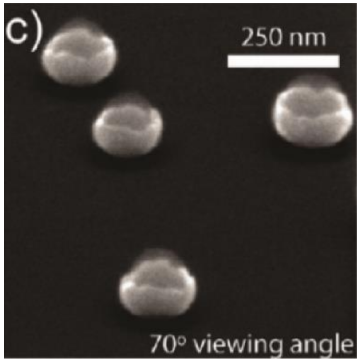
Enabled by **considerable advances in nanofabrication** of **high-index materials** (Si/Ge/..., Ag/Au/...)

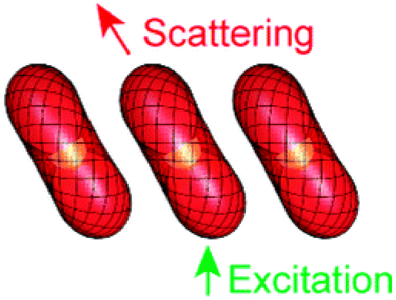




Resonance tunability

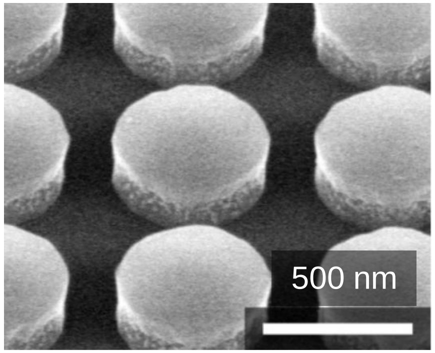
Oldenburg *et al.*,
Chem. Phys. Lett. (1998)

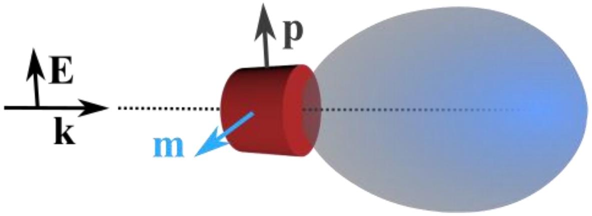




Light bending

Mirin & Halas,
Nano Lett. (2009)



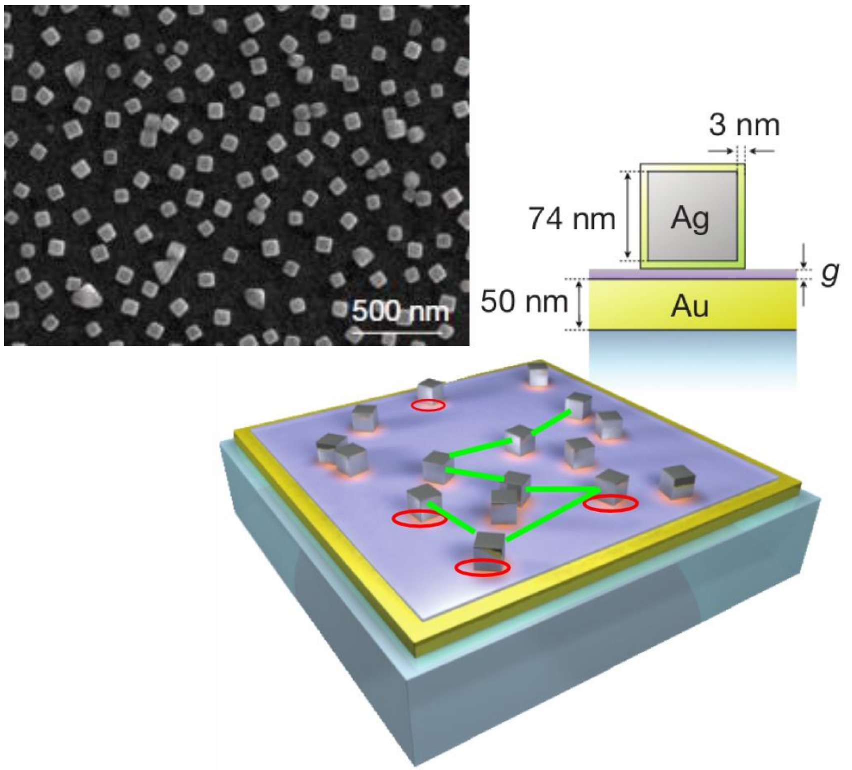


Directive scattering

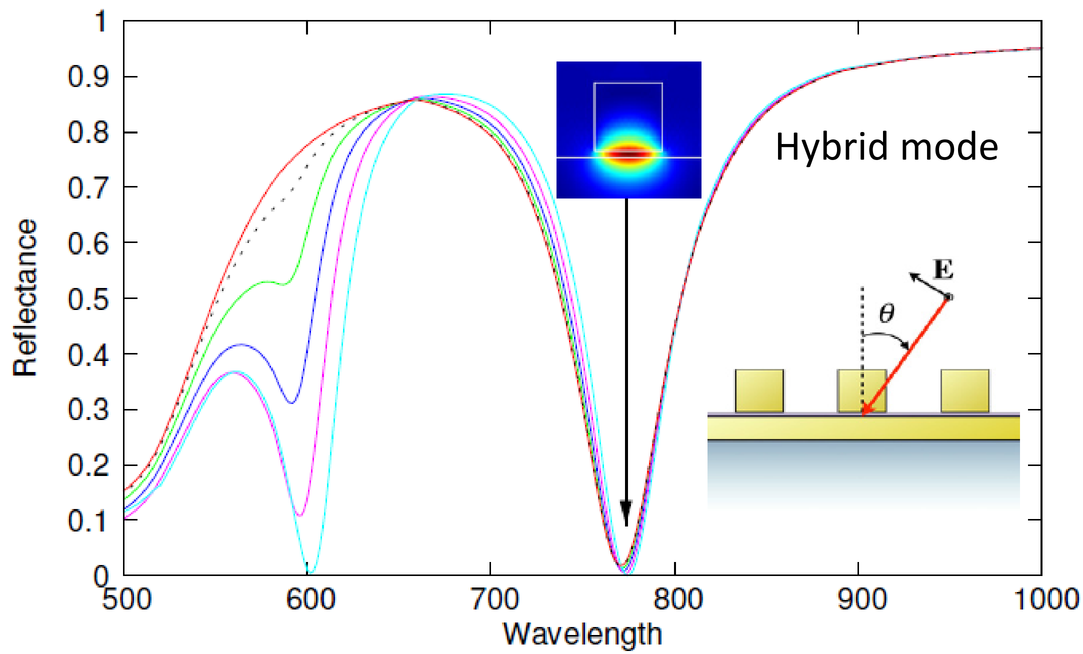
Staude *et al.*,
ACS Nano (2013)

Self-assembly of nanoparticles in layered geometries

Collective response of nanoparticles interacting with planar interfaces can lead to **new optical functionalities**

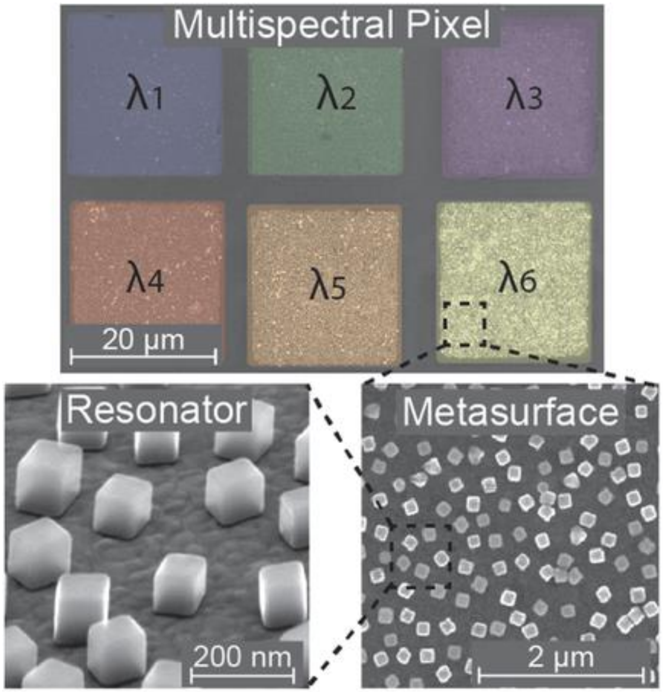


A. Moreau *et al.*,
Nature **492**, 86 (2012)



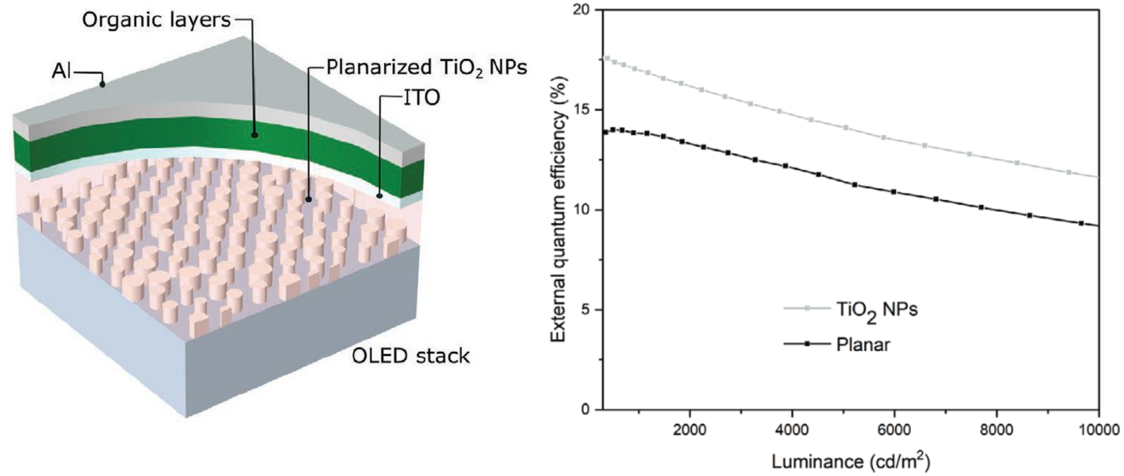
Complex nanostructured surfaces

Colored pixels for security printing, sensing, ...



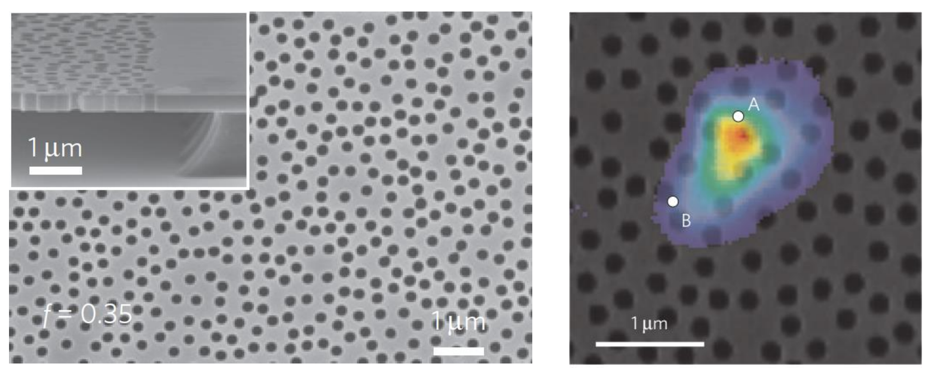
Stewart *et al.*, Adv. Mater. 1602971 (2017)

Controlled light extraction in OLEDs



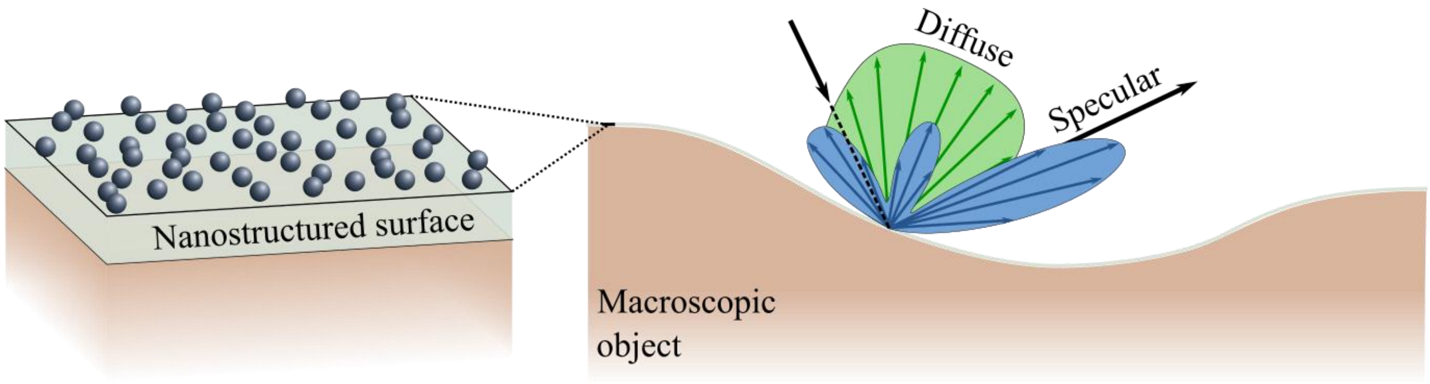
Donie *et al.*, Adv. Opt. Mater. **9**, 2001610 (2021)

Mesoscopic phenomena



Riboli *et al.*, Nature Mater. **13**, 720 (2014)

Content of this talk



I.
Wave scattering by rough surfaces

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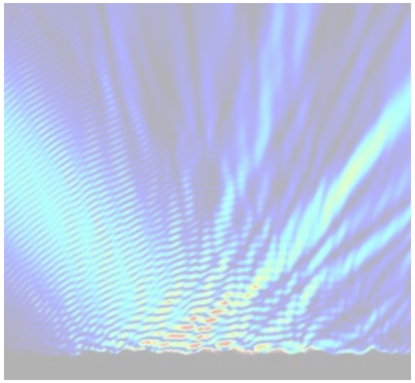
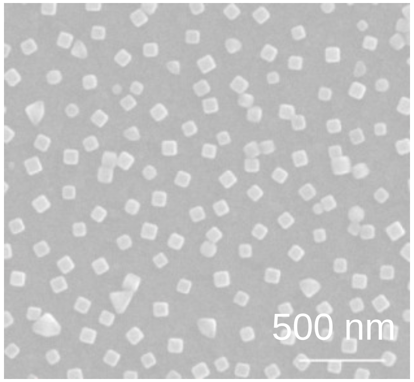
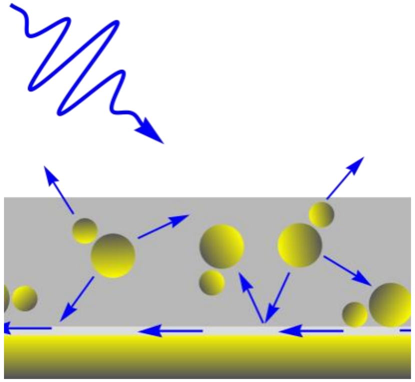
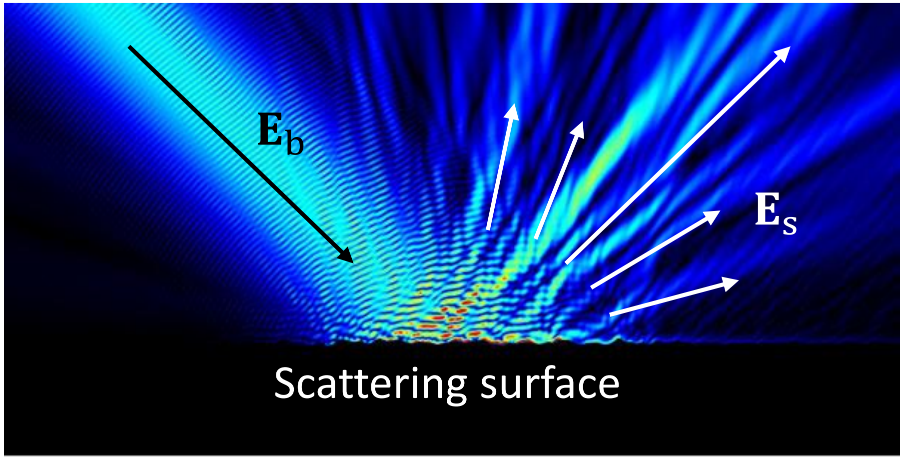
IV.
Application to visual appearance design







Specular and diffuse components of the BRDF



Total electric field $\mathbf{E} = \mathbf{E}_\mathrm{b} + \mathbf{E}_\mathrm{s}$

Incident field ($\mathbf{E}_\mathrm{b}$)

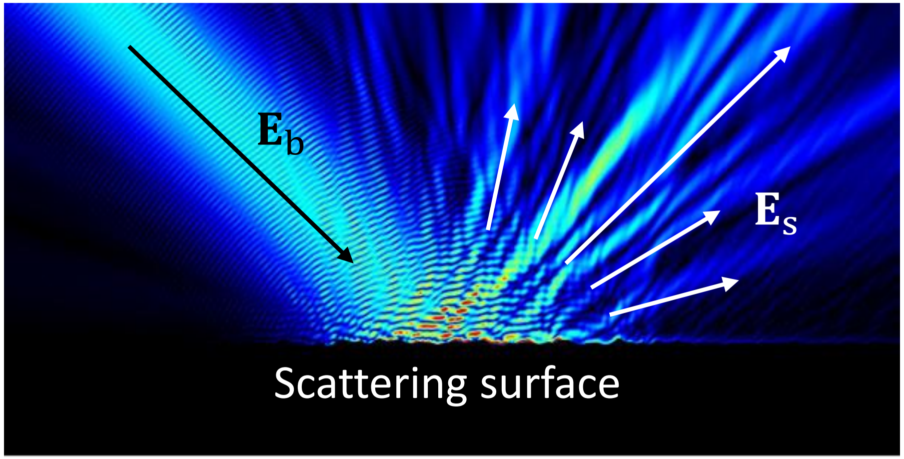
Scattered field ($\mathbf{E}_\mathrm{s}$)

$$\mathbf{E}_\mathrm{s} = \langle \mathbf{E}_\mathrm{s} \rangle + \delta\mathbf{E}_\mathrm{s}$$

average scattered field ($\langle \mathbf{E}_\mathrm{s} \rangle$)

fluctuation around the average with $\langle \delta\mathbf{E}_\mathrm{s} \rangle = 0$ ($\delta\mathbf{E}_\mathrm{s}$)

Specular and diffuse components of the BRDF



Total electric field $\mathbf{E} = \mathbf{E}_\mathrm{b} + \mathbf{E}_\mathrm{s}$

- $\mathbf{E}_\mathrm{b}$: Incident field
- $\mathbf{E}_\mathrm{s}$: Scattered field

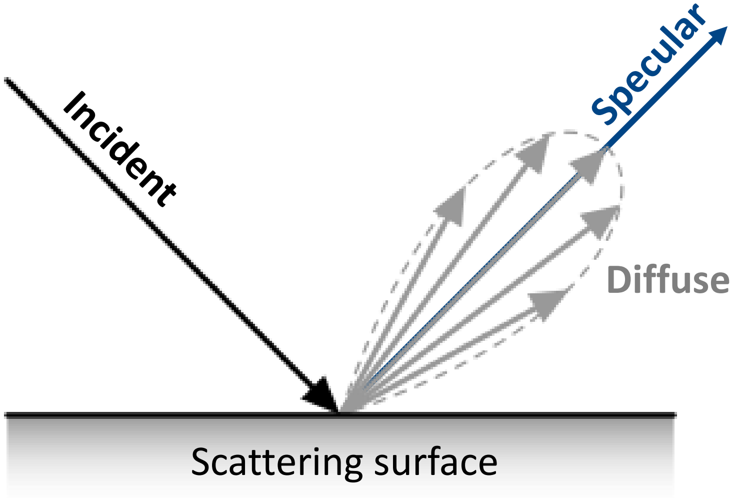
$$\mathbf{E}_\mathrm{s} = \langle \mathbf{E}_\mathrm{s} \rangle + \delta\mathbf{E}_\mathrm{s}$$

- $\langle \mathbf{E}_\mathrm{s} \rangle$: average scattered field
- $\delta\mathbf{E}_\mathrm{s}$: fluctuation around the average with $\langle \delta\mathbf{E}_\mathrm{s} \rangle = 0$

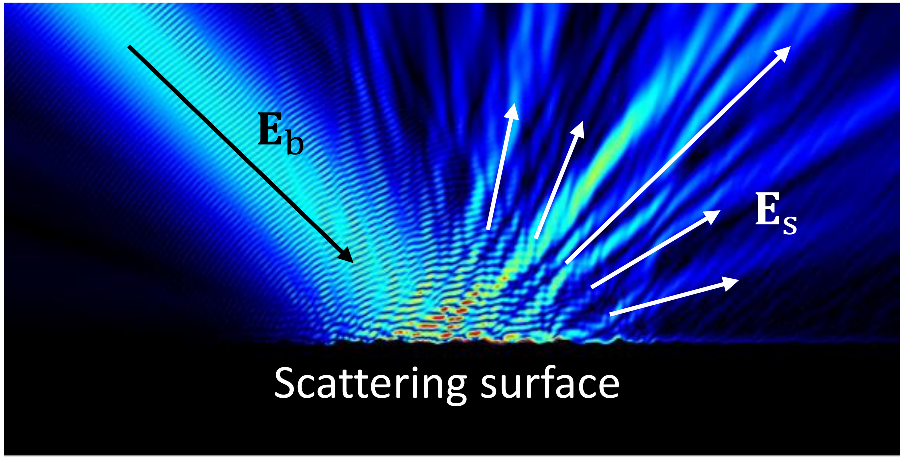
Average intensity

$$\langle I \rangle = \langle |\mathbf{E}|^2 \rangle = |\langle \mathbf{E} \rangle|^2 + \langle |\delta\mathbf{E}_\mathrm{s}|^2 \rangle$$

- $|\langle \mathbf{E} \rangle|^2$: ***Coherent* intensity** (specular)
- $\langle |\delta\mathbf{E}_\mathrm{s}|^2 \rangle$: ***Incoherent* intensity** (diffuse)



Specular and diffuse components of the BRDF



Total electric field $\mathbf{E} = \mathbf{E}_b + \mathbf{E}_s$

Incident field ($\mathbf{E}_b$); Scattered field ($\mathbf{E}_s$)

$$\mathbf{E}_s = \langle \mathbf{E}_s \rangle + \delta\mathbf{E}_s$$

average scattered field ($\langle \mathbf{E}_s \rangle$)

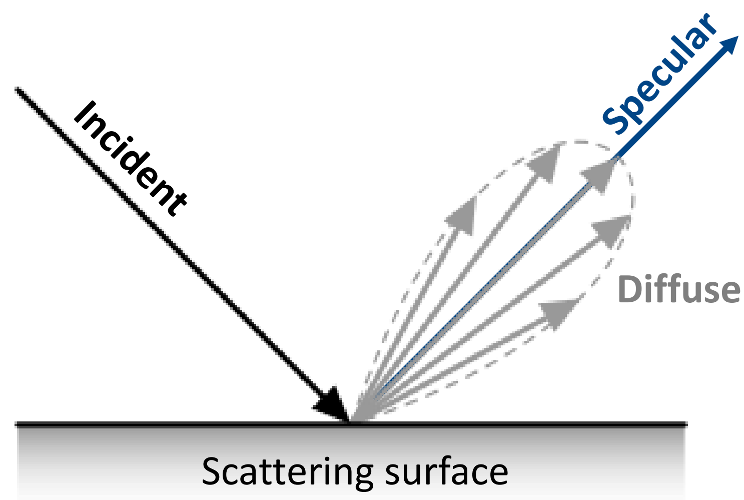
fluctuation around the average with $\langle \delta\mathbf{E}_s \rangle = 0$

Average intensity

$$\langle I \rangle = \langle |\mathbf{E}|^2 \rangle = |\langle \mathbf{E} \rangle|^2 + \langle |\delta\mathbf{E}_s|^2 \rangle$$

Coherent **intensity** (specular) — $|\langle \mathbf{E} \rangle|^2$

Incoherent **intensity** (diffuse) — $\langle |\delta\mathbf{E}_s|^2 \rangle$

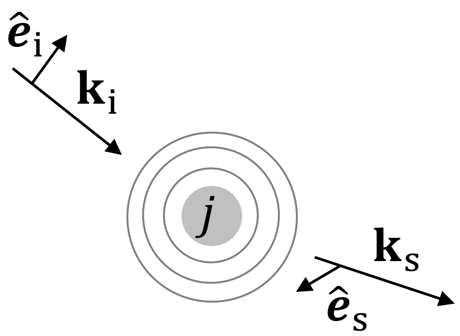


BRDF

$$f_r = f_r^{spe} + f_r^{dif}$$

- f_r^{spe} evaluated from $|\langle \mathbf{E} \rangle|^2$
- f_r^{dif} evaluated from $\langle |\mathbf{E}|^2 \rangle - |\langle \mathbf{E} \rangle|^2 = \langle |\mathbf{E}_s|^2 \rangle - |\langle \mathbf{E}_s \rangle|^2$

Scattering by *non-interacting* particles

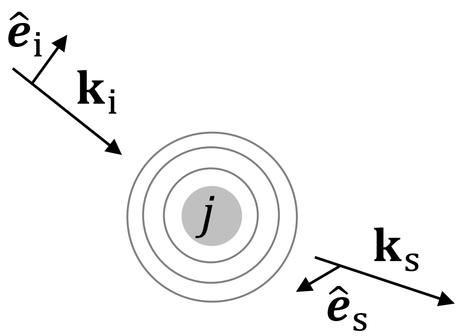


Scattering amplitude describing how an incoming planewave is scattered as an outgoing spherical wave

$$\mathbf{E}_\mathrm{s}^j(\mathbf{r}) = \mathbf{f}_j(\mathbf{k}_\mathrm{s}, \mathbf{k}_\mathrm{i})\, \mathbf{E}_\mathrm{b}^j \frac{\exp[ikr]}{r}$$

Scattering amplitude of particle j

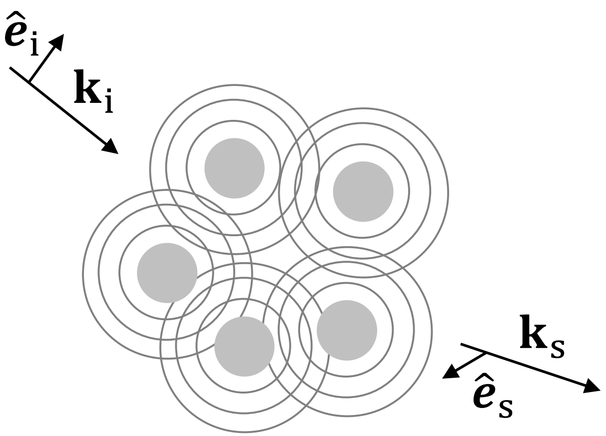
Scattering by *non-interacting* particles



Scattering amplitude describing how an incoming planewave is scattered as an outgoing spherical wave

$$\mathbf{E}_\mathrm{s}^{j}(\mathbf{r}) = \mathbf{f}_j(\mathbf{k}_\mathrm{s}, \mathbf{k}_\mathrm{i})\ \mathbf{E}_\mathrm{b}^{j} \frac{\exp[ikr]}{r}$$

Scattering amplitude of particle *j*

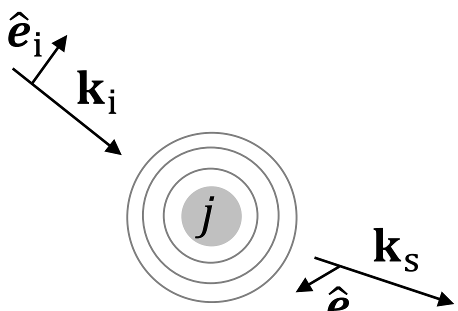


Scattering amplitude for N *non-interacting* particles

$$\mathbf{A}(\mathbf{k}_\mathrm{s}, \mathbf{k}_\mathrm{i}) = \sum_{j=1}^{N} \mathbf{f}_j(\mathbf{k}_\mathrm{s}, \mathbf{k}_\mathrm{i}) \exp\left[i\underbrace{(\mathbf{k}_\mathrm{i} - \mathbf{k}_\mathrm{s}) \cdot \mathbf{r}_j}\right]$$

Dephasing between the incident and scattered waves
→ Interferences

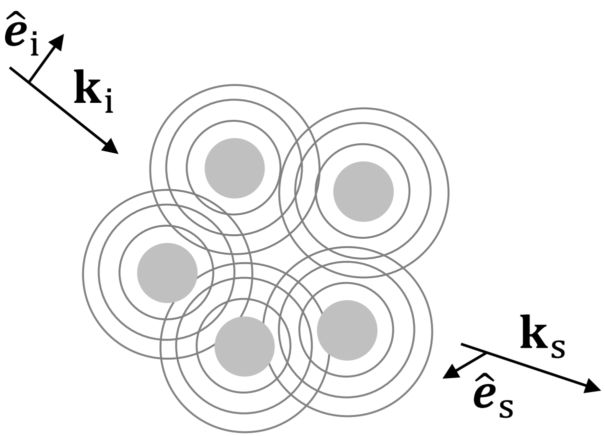
Scattering by *non-interacting* particles



Scattering amplitude describing how an incoming planewave is scattered as an outgoing spherical wave

$$\mathbf{E}_\mathrm{s}^j(\mathbf{r}) = \mathbf{f}_j(\mathbf{k}_\mathrm{s}, \mathbf{k}_\mathrm{i})\ \mathbf{E}_\mathrm{b}^j \frac{\exp[ikr]}{r}$$

Scattering amplitude of particle j (for $\mathbf{f}_j$)



Scattering amplitude for N *non-interacting* particles

$$\mathbf{A}(\mathbf{k}_\mathrm{s}, \mathbf{k}_\mathrm{i}) = \sum_{j=1}^{N} \mathbf{f}_j(\mathbf{k}_\mathrm{s}, \mathbf{k}_\mathrm{i}) \exp\big[i\underbrace{(\mathbf{k}_\mathrm{i} - \mathbf{k}_\mathrm{s}) \cdot \mathbf{r}_j}\big]$$

Dephasing between the incident and scattered waves
→ Interferences

Scattered intensity for N non-interacting *identical* particles ($\mathbf{f}_j = \mathbf{f}$) between $\hat{\boldsymbol{e}}_\mathrm{i}$ and $\hat{\boldsymbol{e}}_\mathrm{s}$

$$|\hat{\boldsymbol{e}}_\mathrm{s} \cdot \mathbf{A}(\mathbf{k}_\mathrm{s}, \mathbf{k}_\mathrm{i})\hat{\boldsymbol{e}}_\mathrm{i}|^2 = |\hat{\boldsymbol{e}}_\mathrm{s} \cdot \mathbf{f}(\mathbf{k}_\mathrm{s}, \mathbf{k}_\mathrm{i})\hat{\boldsymbol{e}}_\mathrm{i}|^2 \sum_{j,k=1}^{N} \exp\big[\underbrace{i(\mathbf{k}_\mathrm{i} - \mathbf{k}_\mathrm{s}) \cdot (\mathbf{r}_j - \mathbf{r}_k)}\big]$$

Dephasing between pairs of particles

Form and structure factors

Scattered intensity for N identical, non-interacting particles ($\mathbf{f}_j = \mathbf{f}$) between $\hat{\boldsymbol{e}}_\mathrm{i}$ and $\hat{\boldsymbol{e}}_\mathrm{s}$

$$|\hat{\boldsymbol{e}}_\mathrm{s} \cdot \mathbf{A}(\mathbf{k}_\mathrm{s}, \mathbf{k}_\mathrm{i})\hat{\boldsymbol{e}}_\mathrm{i}|^2 = |\hat{\boldsymbol{e}}_\mathrm{s} \cdot \mathbf{f}(\mathbf{k}_\mathrm{s}, \mathbf{k}_\mathrm{i})\hat{\boldsymbol{e}}_\mathrm{i}|^2 \sum_{j,k=1}^{N} \exp\left[i(\mathbf{k}_\mathrm{i} - \mathbf{k}_\mathrm{s}) \cdot \left(\mathbf{r}_j - \mathbf{r}_k\right)\right]$$

Average scattered intensity

$$\langle|\hat{\boldsymbol{e}}_\mathrm{s} \cdot \mathbf{A}(\mathbf{k}_\mathrm{s}, \mathbf{k}_\mathrm{i})\hat{\boldsymbol{e}}_\mathrm{i}|^2\rangle = NF(\mathbf{k}_\mathrm{s}, \mathbf{k}_\mathrm{i})S(\mathbf{k}_\mathrm{s}, \mathbf{k}_\mathrm{i})$$

Form factor = scattering diagram of the individual particle

$$F(\mathbf{k}_\mathrm{s}, \mathbf{k}_\mathrm{i}) = |\hat{\boldsymbol{e}}_\mathrm{s} \cdot \mathbf{f}(\mathbf{k}_\mathrm{s}, \mathbf{k}_\mathrm{i})\hat{\boldsymbol{e}}_\mathrm{i}|^2$$

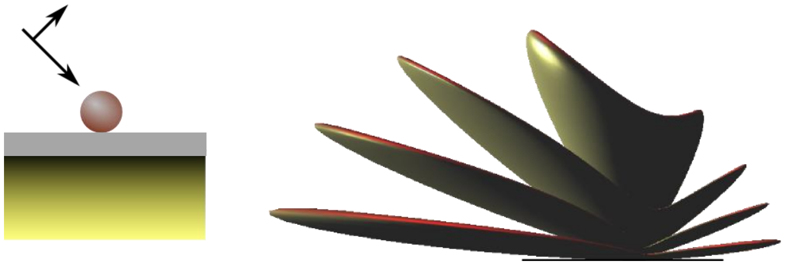
Structure factor = Effect of correlations of particle pairs on scattering

$$S(\mathbf{k}_\mathrm{s}, \mathbf{k}_\mathrm{i}) = 1 + \frac{1}{N}\left\langle\sum_{k\neq j} \exp\left[i(\mathbf{k}_\mathrm{i} - \mathbf{k}_\mathrm{s}) \cdot \left(\mathbf{r}_j - \mathbf{r}_k\right)\right]\right\rangle$$

($S = 1$ in uncorrelated random media)

Structural correlations are an additional degree of freedom to control light scattering

Strategy for predictive rendering

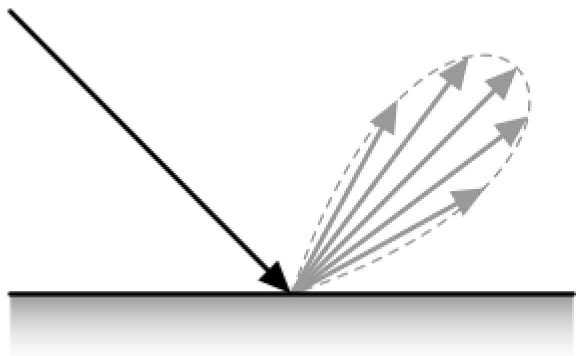


Resolution of the **electromagnetic problem** for a *single* scatterer at the nanoscale

Feedback

Synthetic images of macroscopic objects in realistic environments

Approximate BRDF model

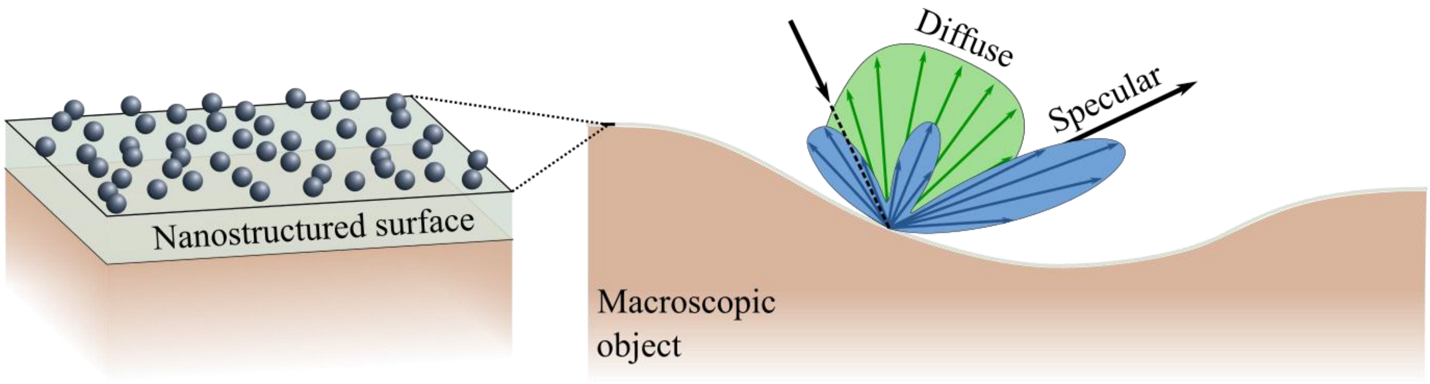


BRDF of the *infinitely large* nanostructured surface

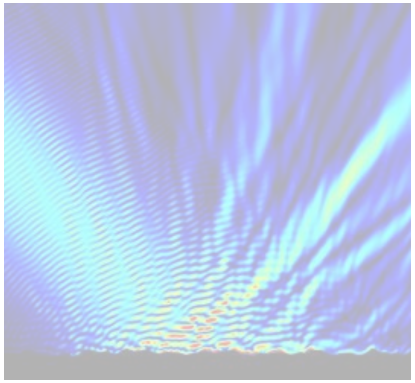
Multispectral rendering engine

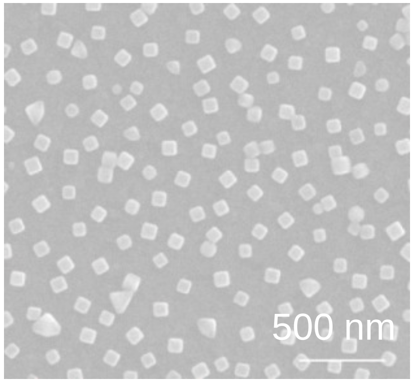
K. Vynck *et al.*,
Nature Materials **21**, 1035 (2022)

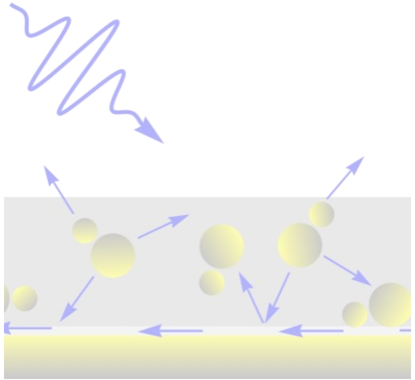
Content of this talk



I.	II.	III.	IV.
Wave scattering by rough surfaces	Complex resonant nanostructures	Modelling of complex nanostructures	**Application to visual appearance design**

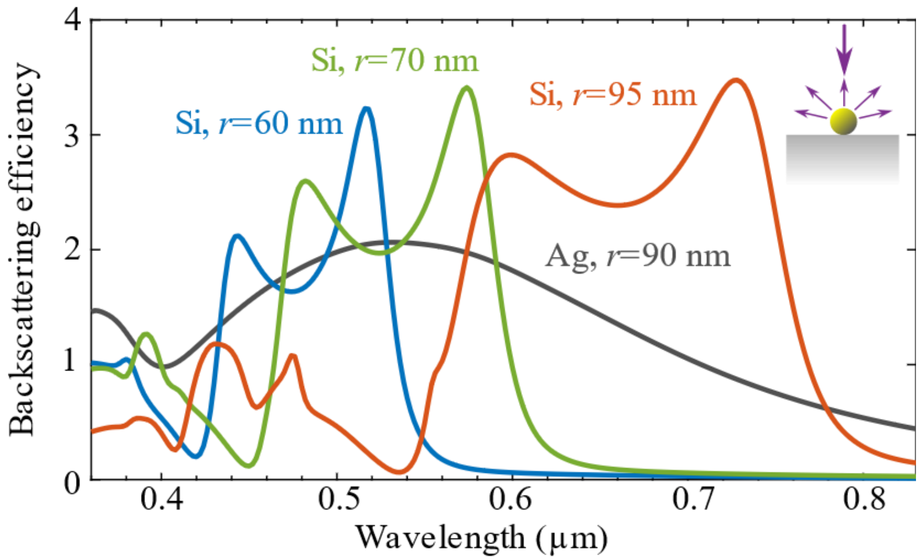




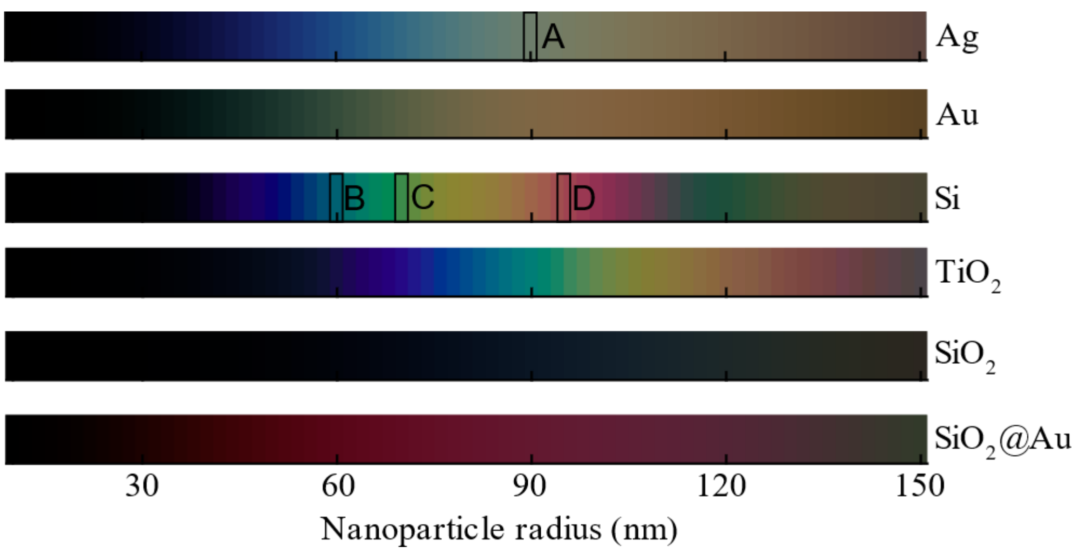


Engineering of the individual particle

Scattering efficiency spectra

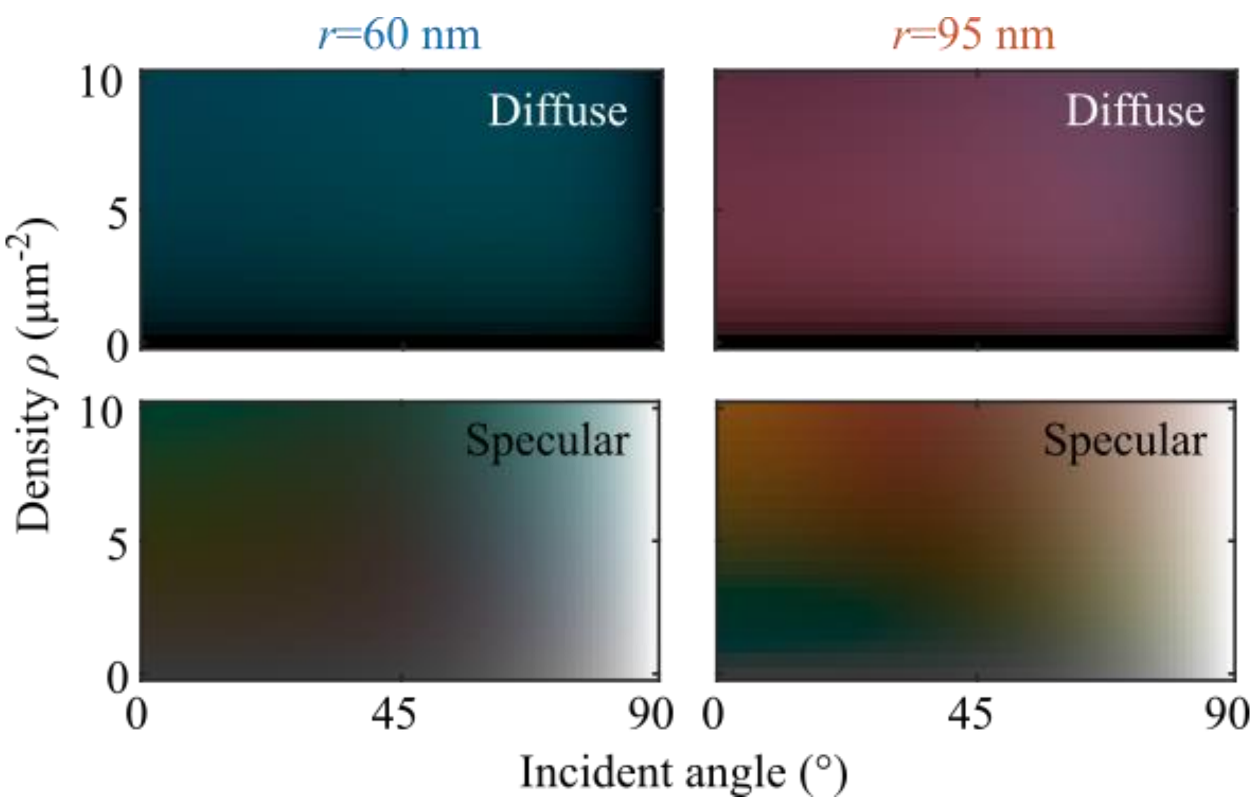


Colours predicted from the spectra



The individual particle (on a dielectric substrate) is expected to provide the **dominant color of the surface**.

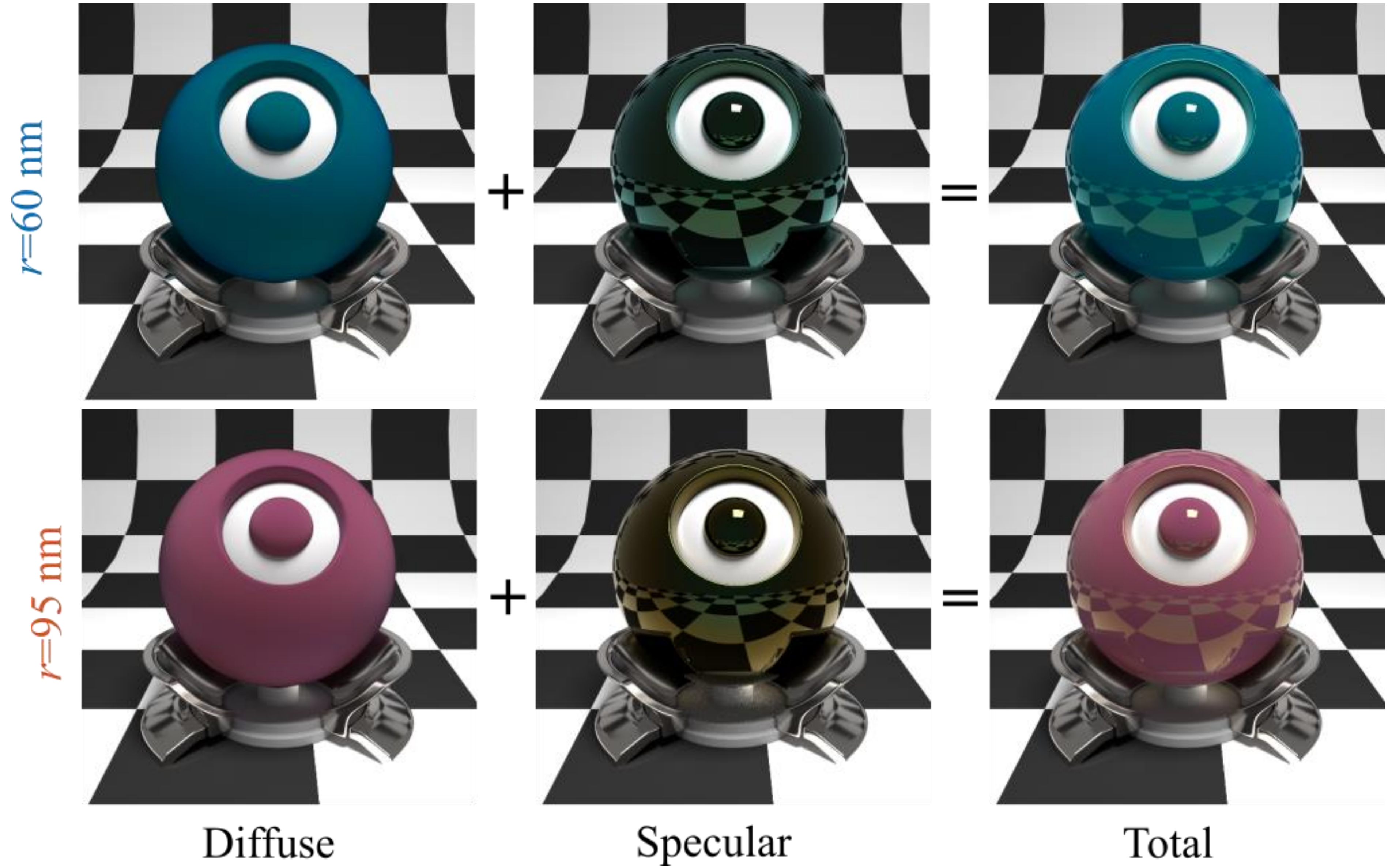
This simple analysis misses most of what matters for perception



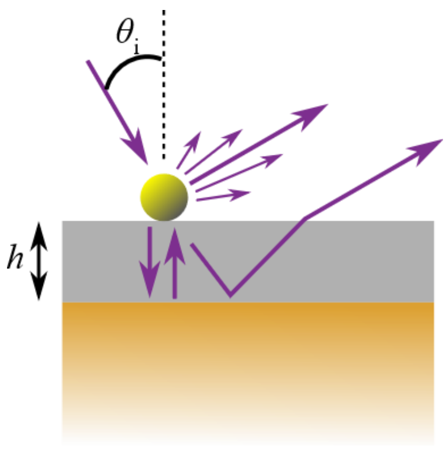
Angle-independent colors, nearly independent of density

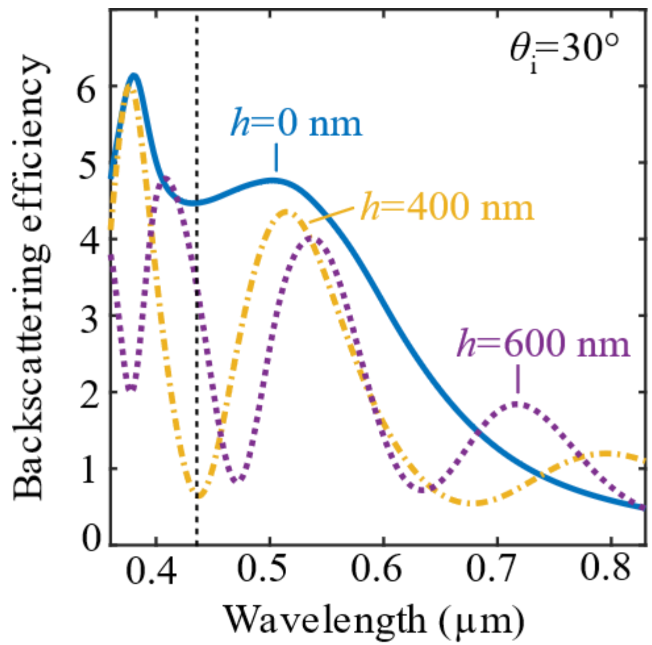
Iridescence that depends strongly on the particle density

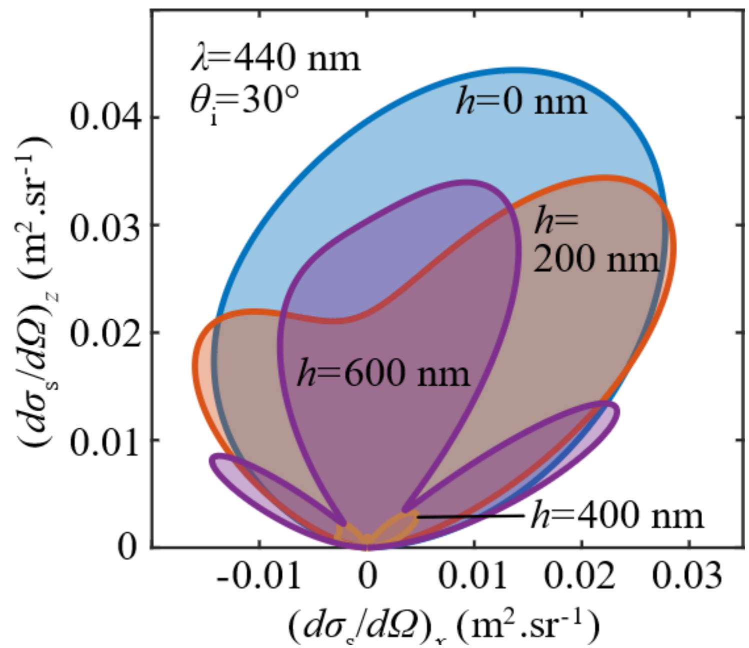
Both components are essential to visual appearance



Engineering of the substrate





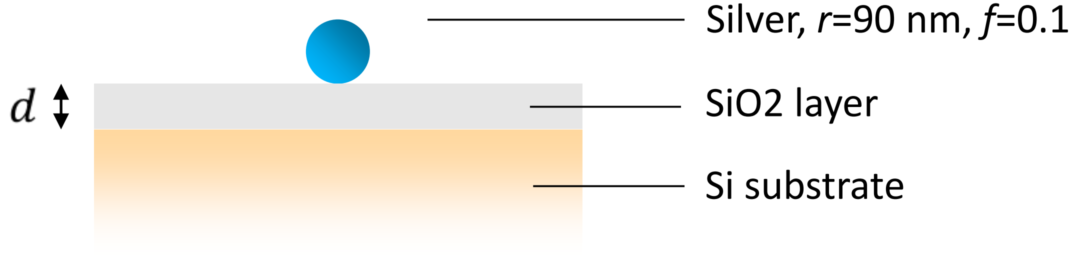


Interference between light reflected from the substrate and scattered by the particle.

Diffuse iridescence (not thin-film iridescence)

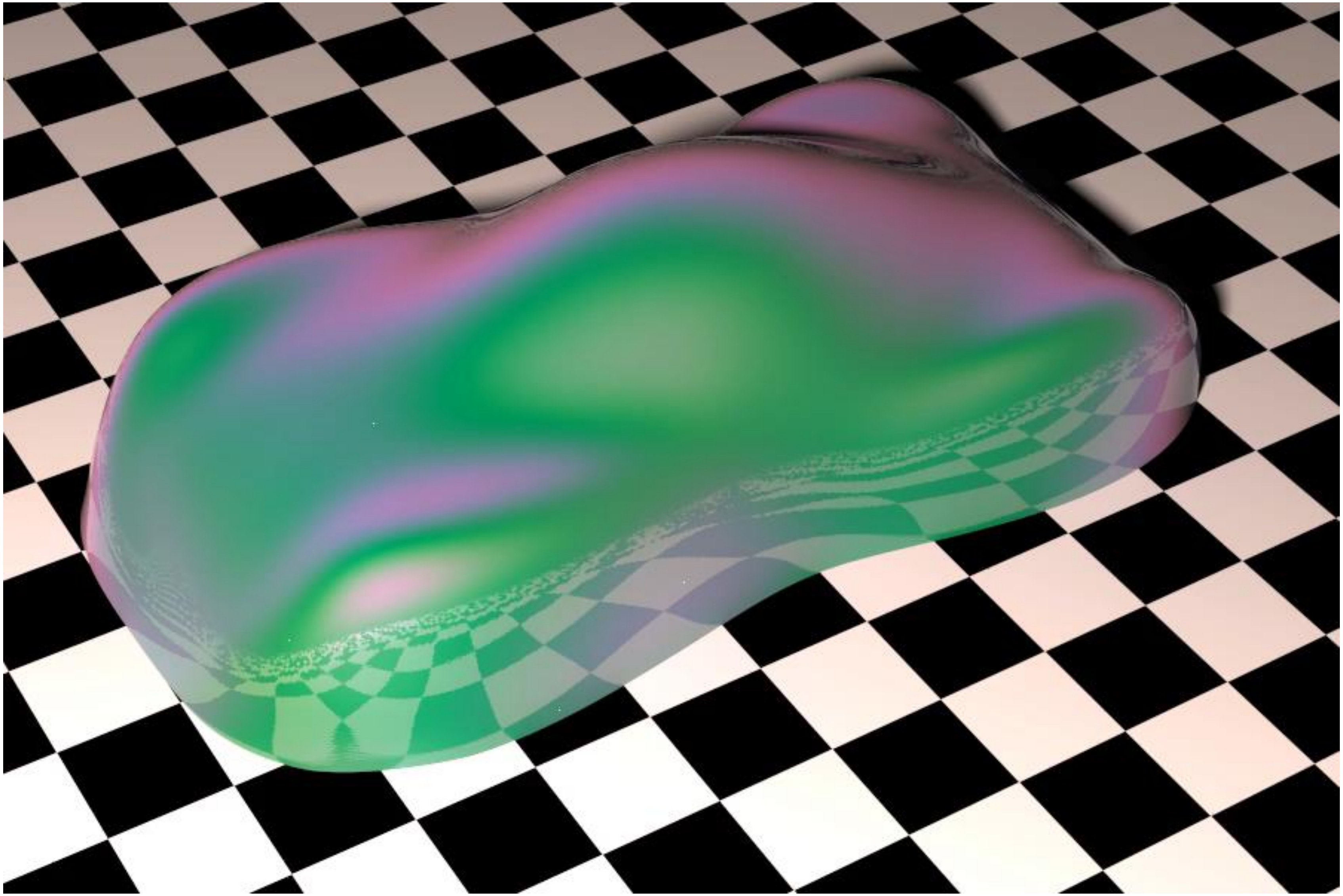
$d = 0$ nm

$d = 200$ nm



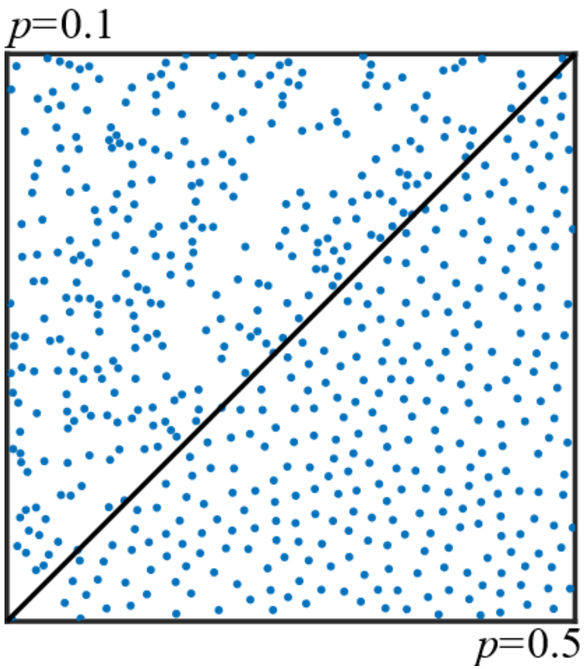
$d = 400$ nm

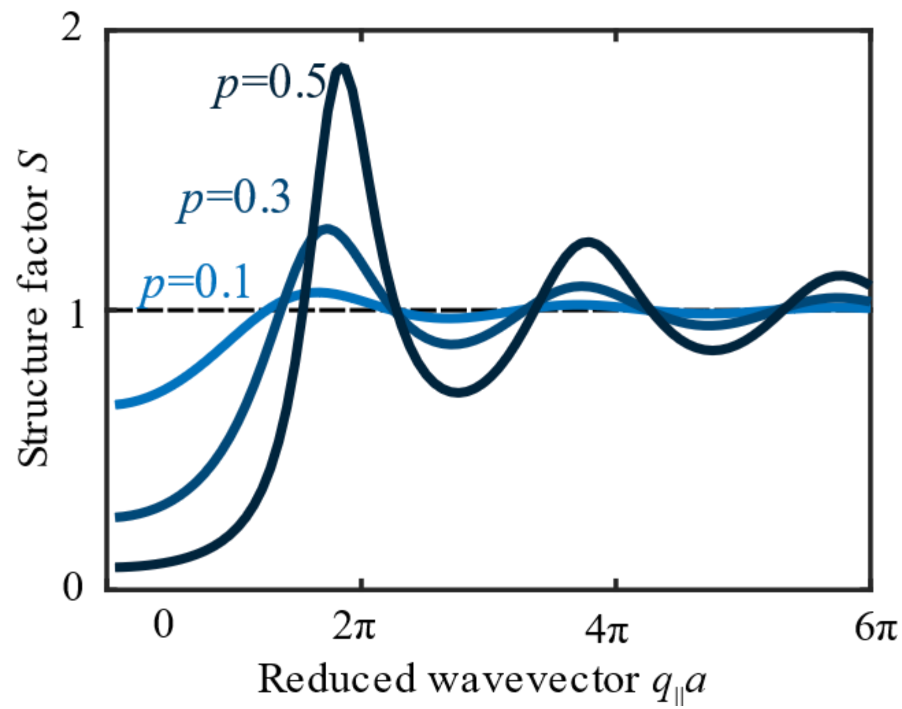
Diffuse iridescence is very different from thin-film iridescence!

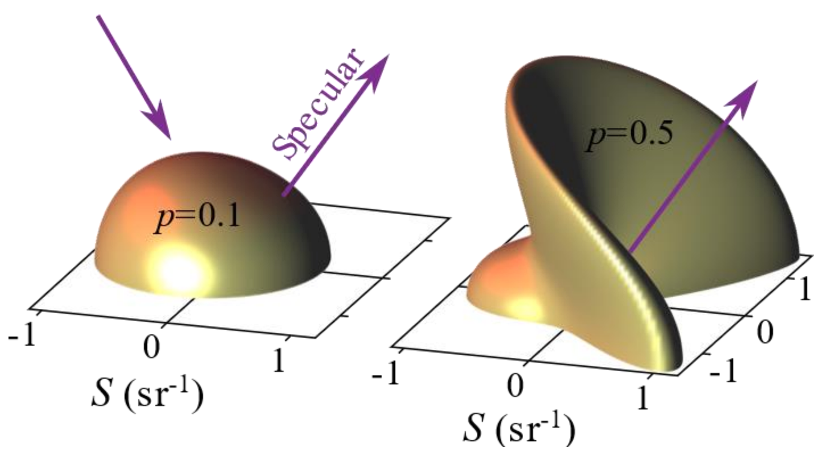


Predictive rendering by **Romain Pacanowski** (*INRIA Bordeaux Sud-Ouest*)

Engineering of structural correlations



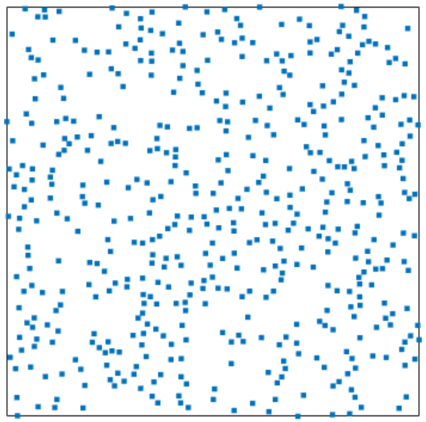




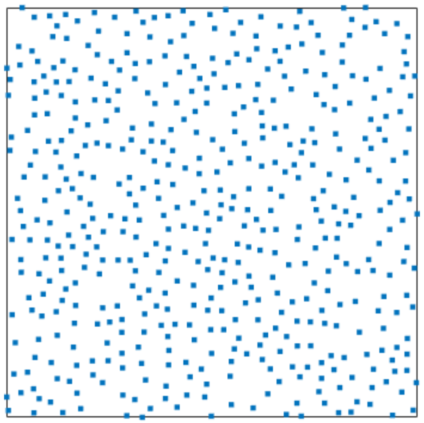
- **Suppression of the diffuse intensity** near the direction of specular reflection
- Sharp **high-intensity lobes** at larger angles

Diffuse halo

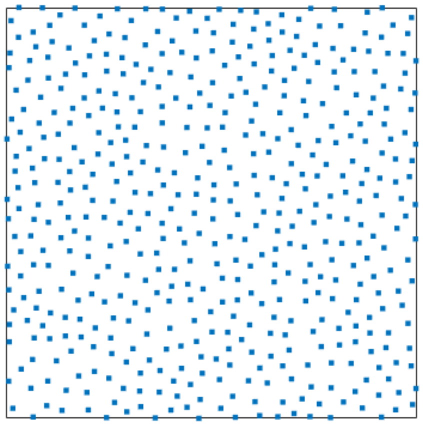
Silver, *r*=90 nm, on glass, *ρ*=5 μm^{-2}



$p = 0.1$

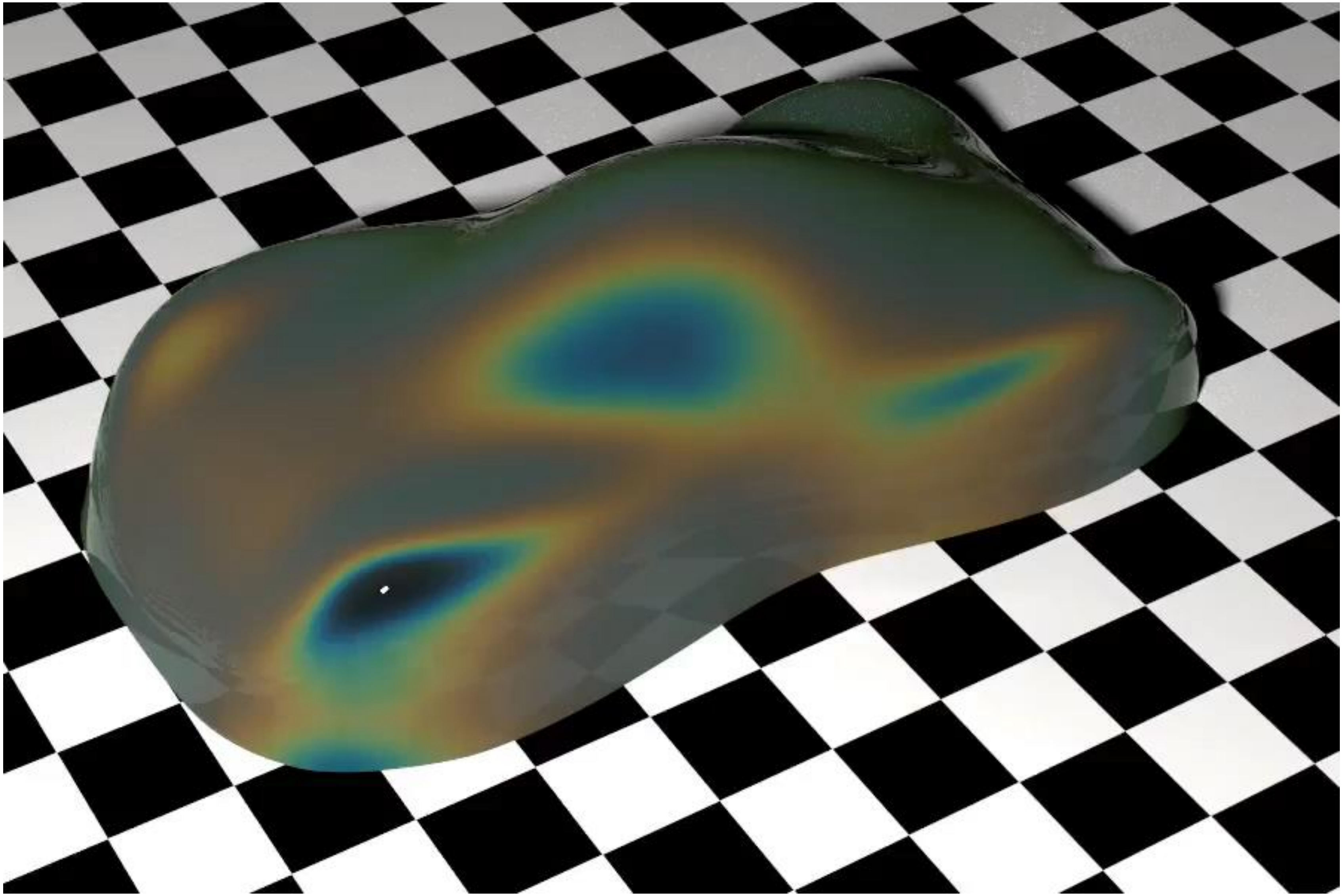


$p = 0.3$



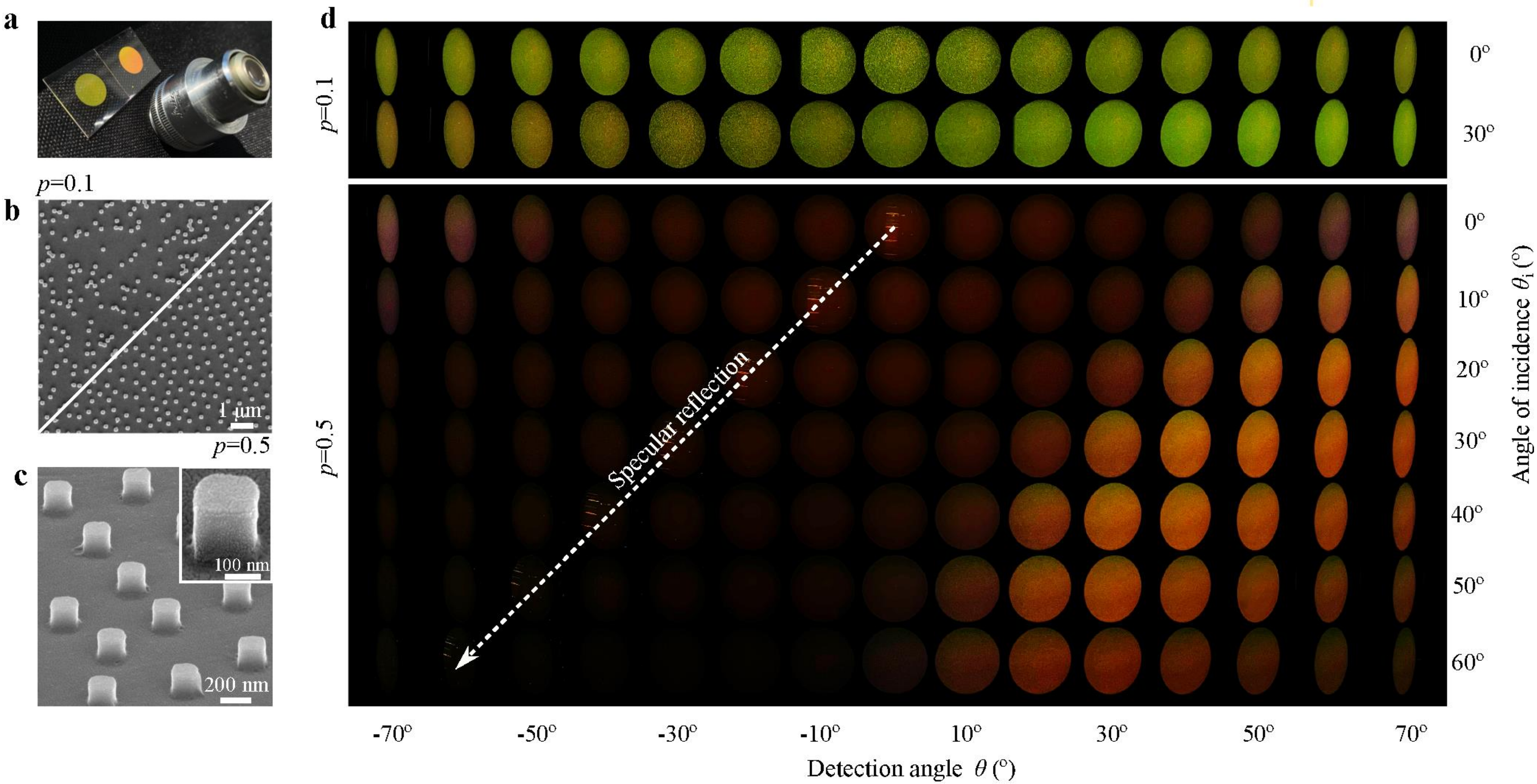
$p = 0.5$

Correlated disorder yields very unusual visual effects



Predictive rendering by **Romain Pacanowski** (*INRIA Bordeaux Sud-Ouest*)

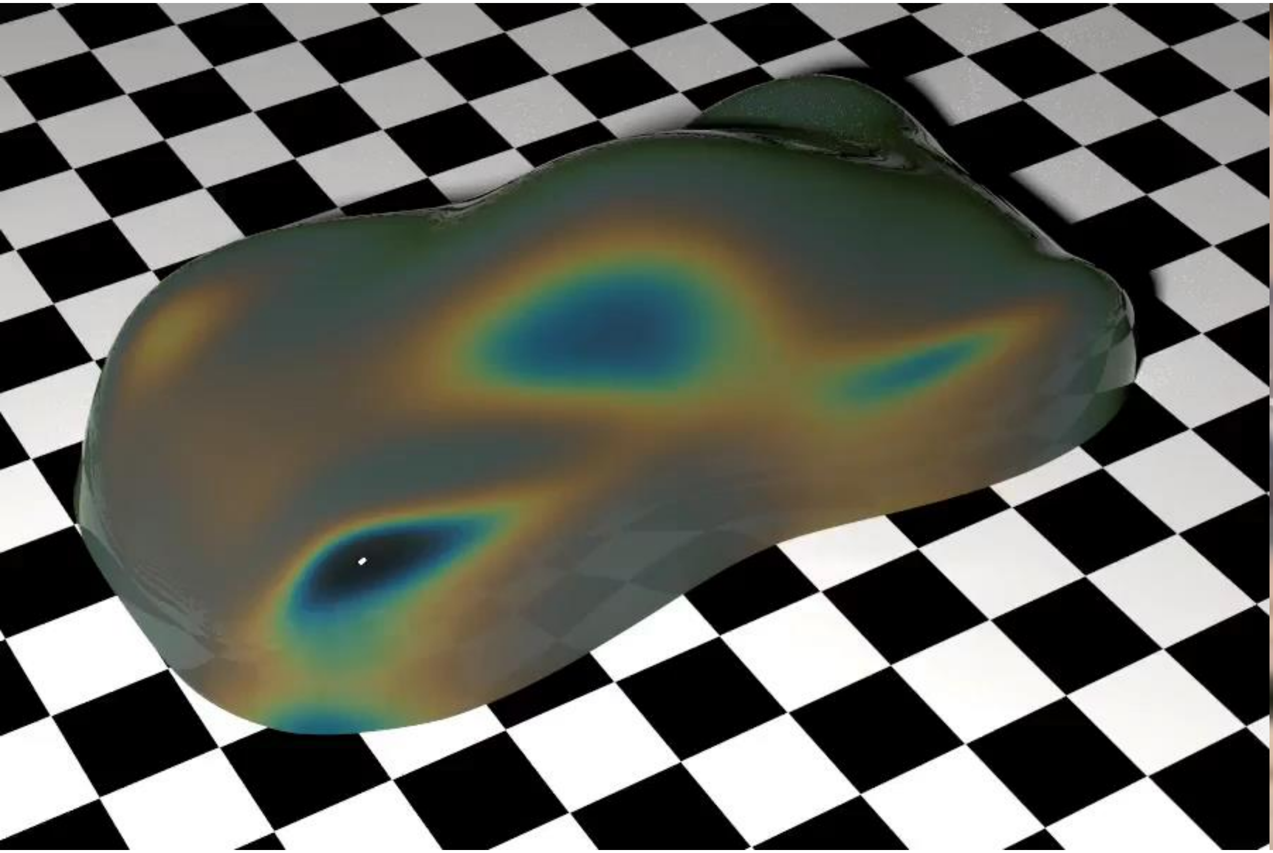
Experimental demonstration (top-down nanofabrication)

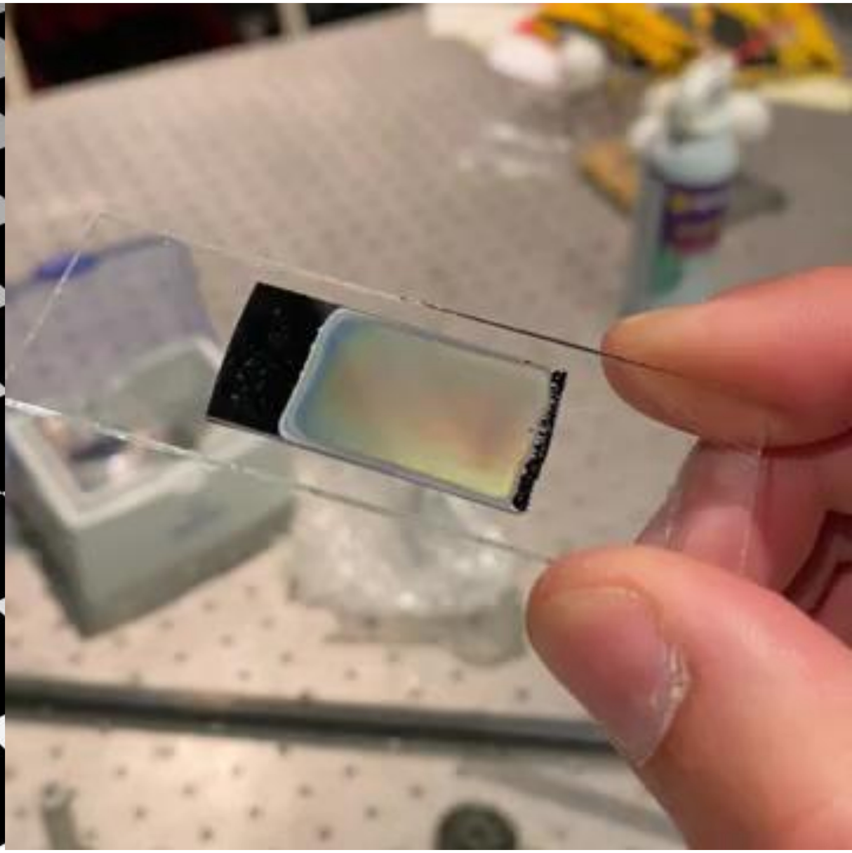


Samples by **Frank Carcenac** (LAAS, Toulouse)
Optical characterization by **Adrian Agreda**, **Philippe Lalanne** (LP2N, Bordeaux)

K. Vynck *et al.*,
Nature Materials **21**, 1035 (2022)

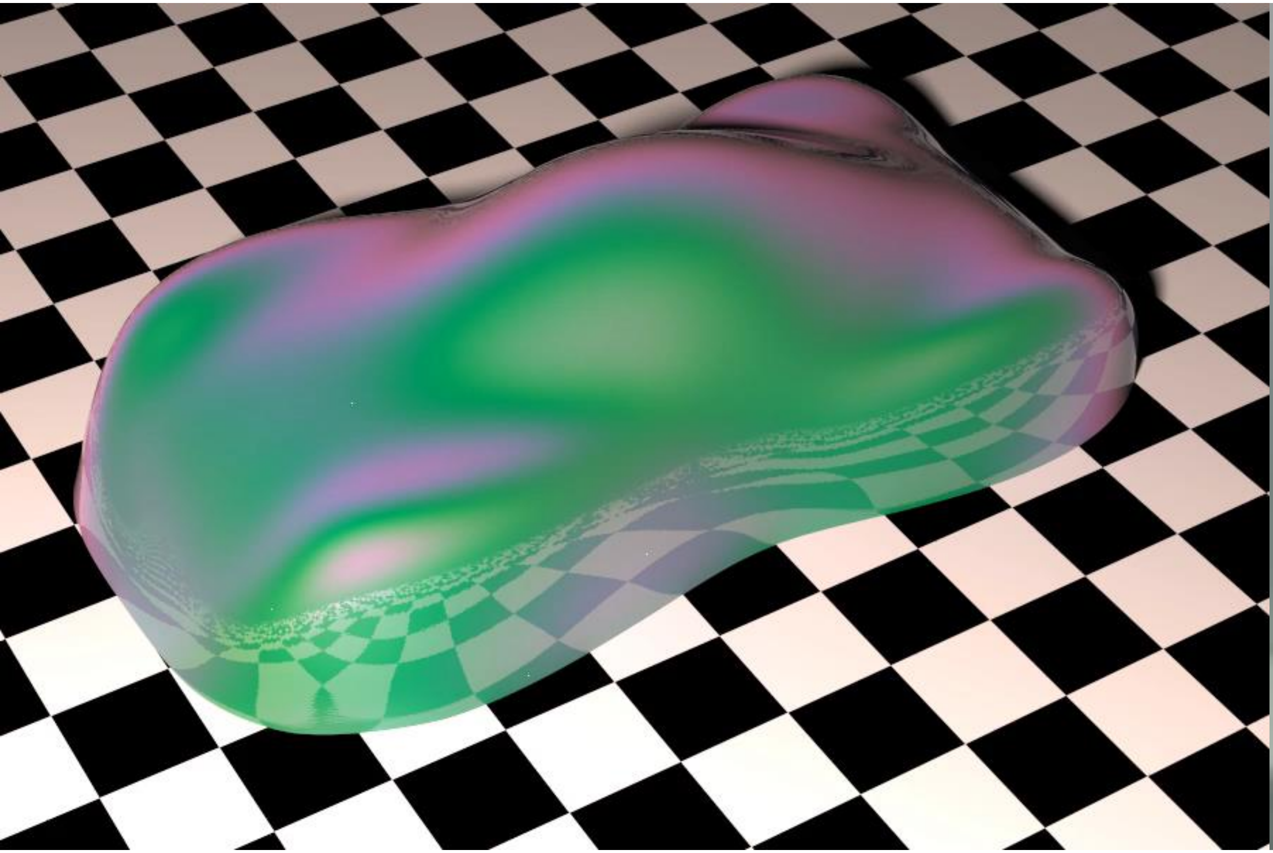
Diffuse halo observed on *bottom-up* cm-scale samples

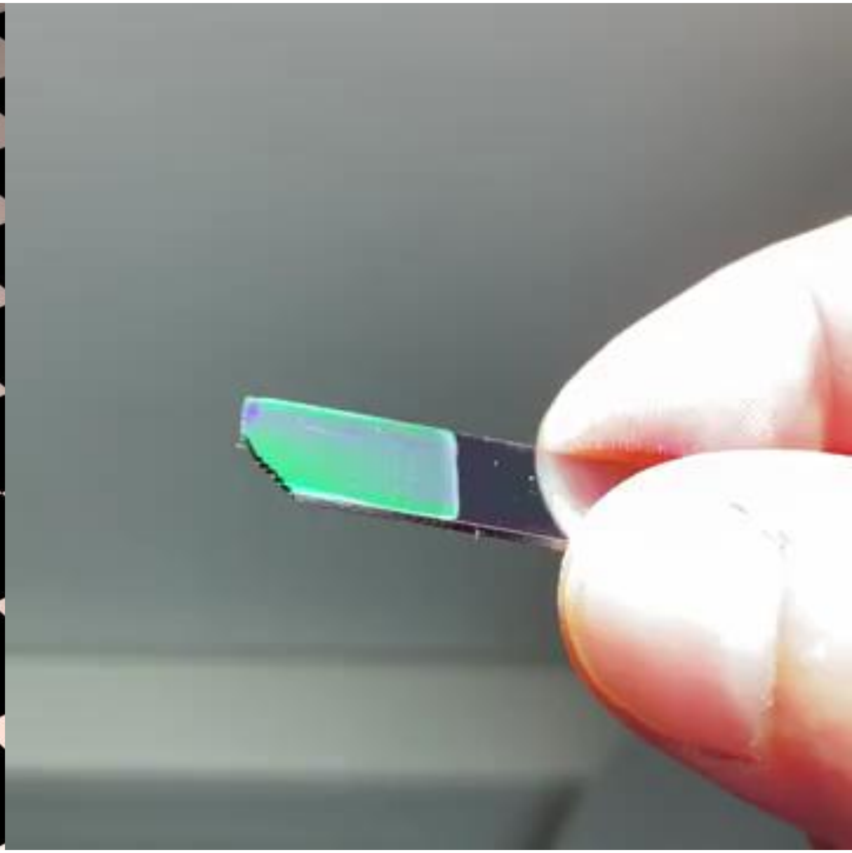




Samples by **Adrian Hereu**, **Glenna Drisko**, **Mona Treguer-Delapierre** (ICMCB, Bordeaux)

Diffuse iridescence observed on *bottom-up* cm-scale samples

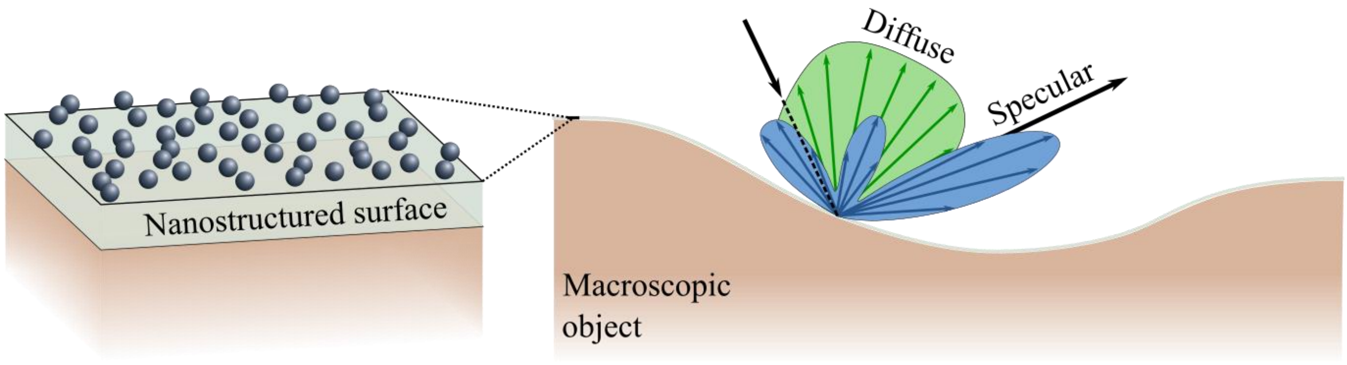




Samples by **Adrian Hereu**, **Glenna Drisko**, **Mona Treguer-Delapierre** (ICMCB, Bordeaux)

A. Agreda, T. Wu, *et al.*, ACS Nano **17**, 6362 (2023)

Content of this talk



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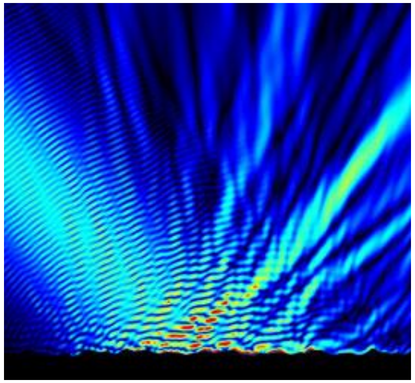
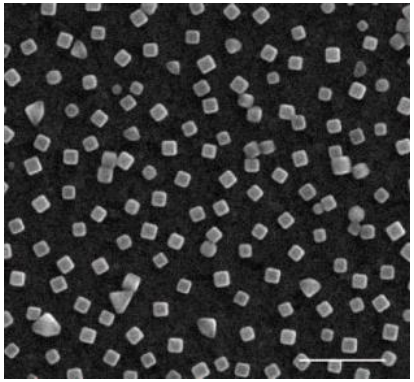
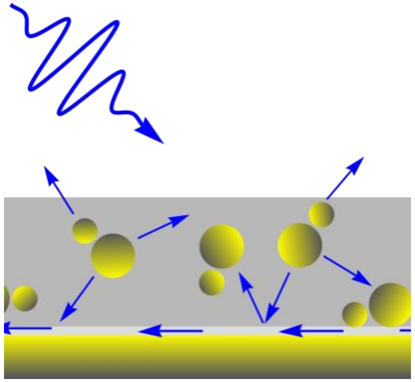






Acknowledgments

LP2N
Laboratoire Photonique Numérique & Nanosciences

Philippe Lalanne   Adrian Agreda

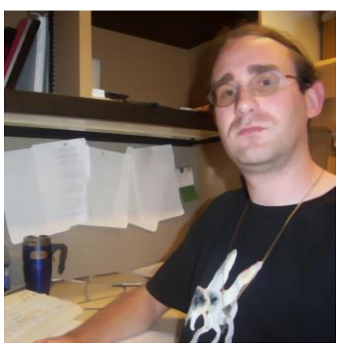
icmcb
institut de chimie de la matière condensée de bordeaux

Glenna Drisko

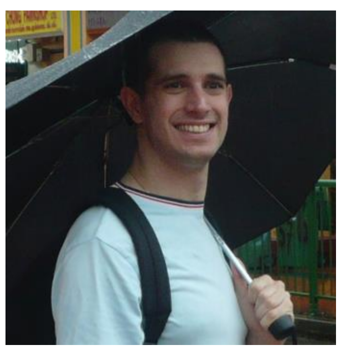
Mona Tréguer Delapierre

Adrian Hereu

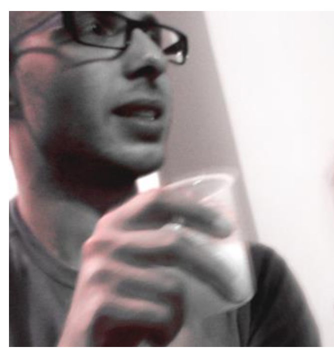
Inria
INVENTEURS DU MONDE NUMÉRIQUE



Xavier Granier



Romain Pacanowski



Pascal Barla

LABORATOIRE CHARLES FABRY

Jean-Paul Hugonin