NANOBIOMATERIALS 1
AN INTRODUCTION TO SIZE EFFECTS

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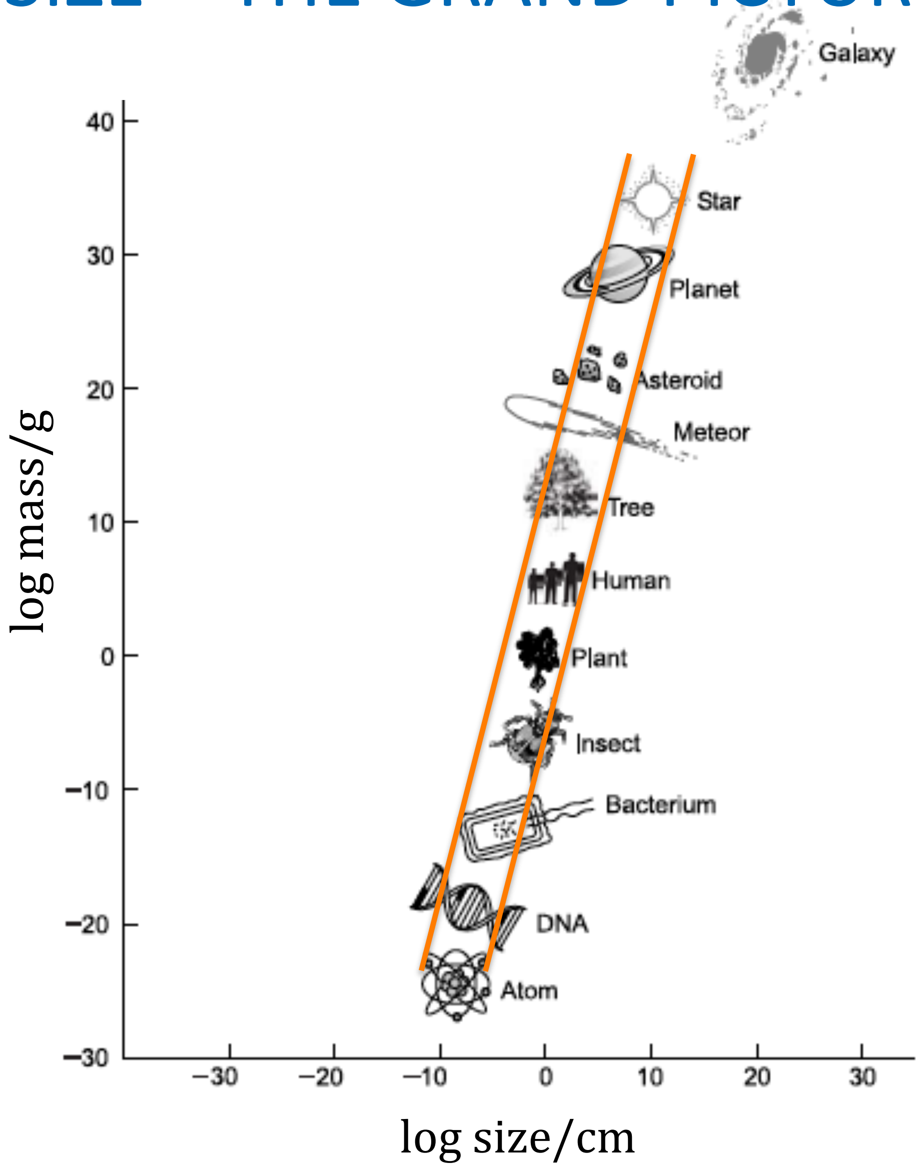
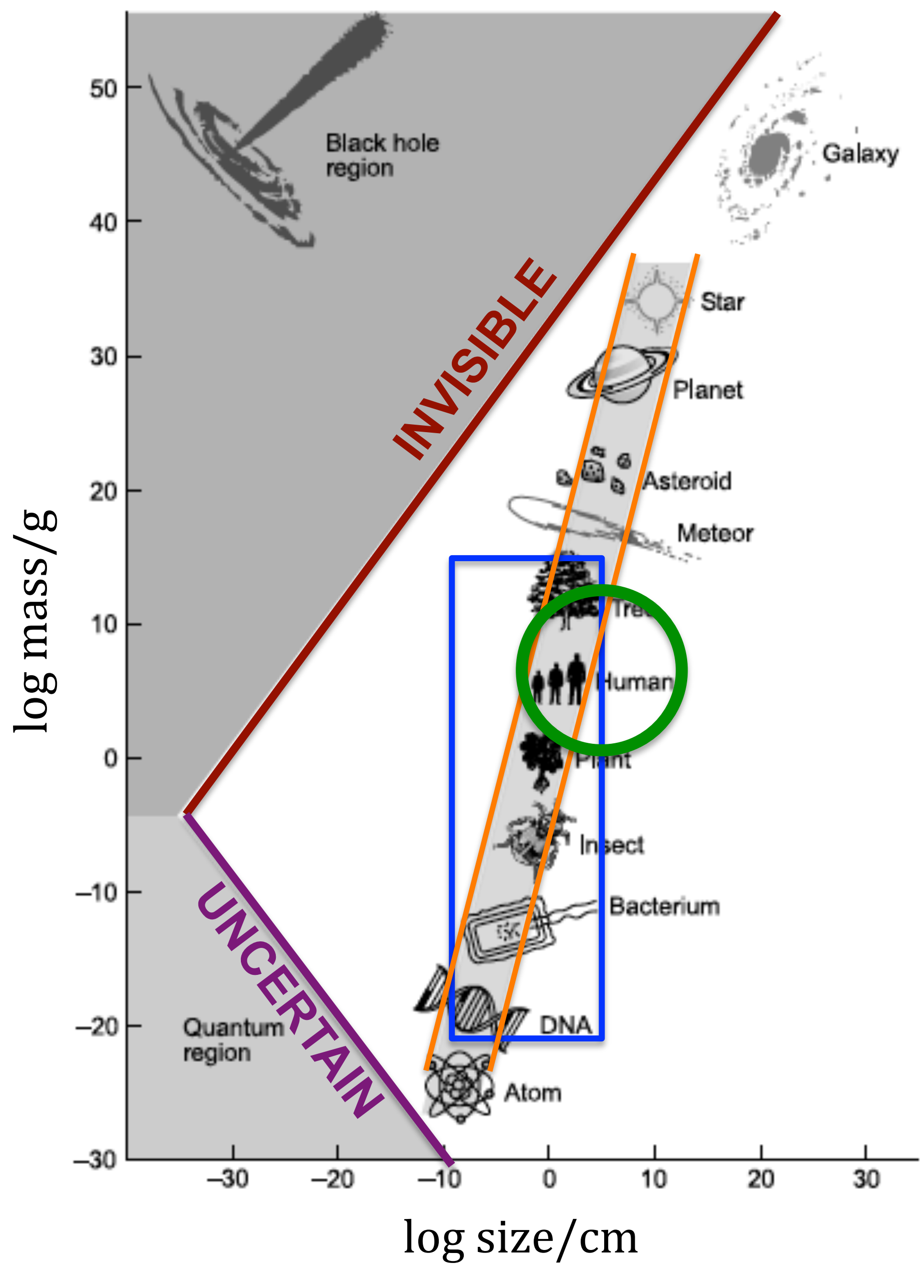
SIZE – THE GRAND PICTURE



mass vs. size of known objects in the universe

balance between opposing forces of Nature:
gravitation ←→ atomic
(resist crushing by grav. forces)
-> **allowed density range**

from J.D. Barrow,
The Artful Universe Expanded



“complex range”:
10^{-10} to 10^{5} cm

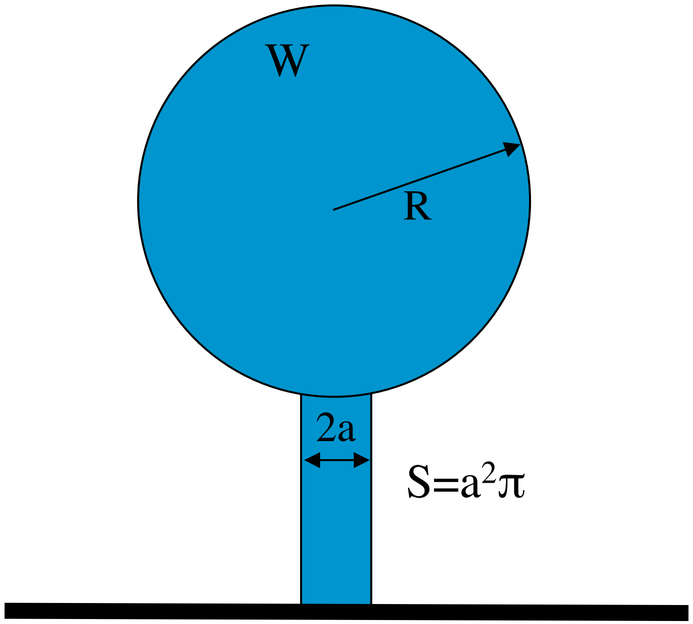
materials:
10^{-7} to 10^{3} cm

human size!

from J.D. Barrow,
The Artful Universe Expanded

BIG ANIMALS BREAK DOWN

“animal”



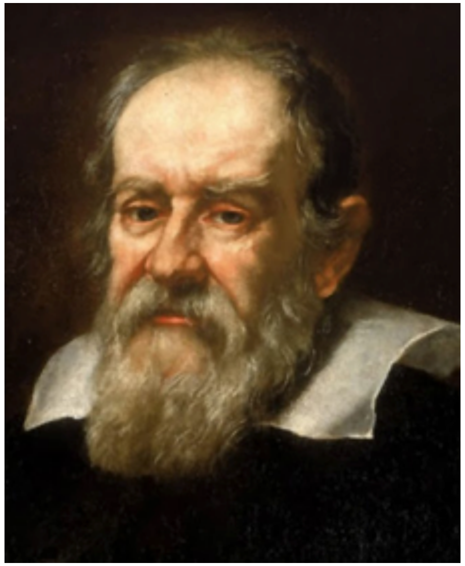
stress calculation

$$weight \sim g(size)^3$$

$$leg\,section \sim (size)^2$$

$$-> stress \sim size.g$$

g..gravitational acceleration



Galileo Galilei
(1564-1642)

- animal size limited by gravitational effects?
- largest dinosaur (*Apatosaurus*): 85 tons
- example for surface/volume effect

BIGGER MAMMALS LIVE LONGER

heat balance

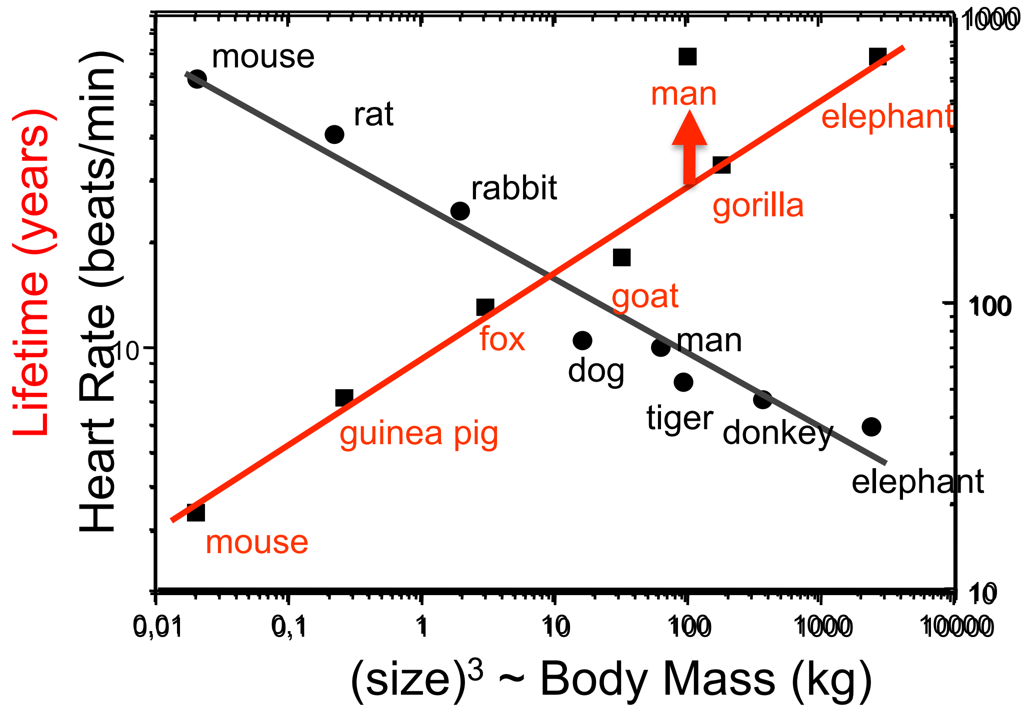
$$+\dot{Q} \sim f_{Hz}\,(size)^3$$

$$-\dot{Q} \sim (size)^2$$

$$-> f_{Hz} \sim 1/(size)$$

$$life \sim 1/f_{Hz} \sim size$$

Q…heat supplied
f_{Hz}…heart beat rate



for a detailed derivation see H. Lin, Am J Phys 50, 72 (1982), T. McMahon, Science 179, 1209 (1973)

LARGE OBJECTS FLY FAST

force balance

$weight\,(volume)$

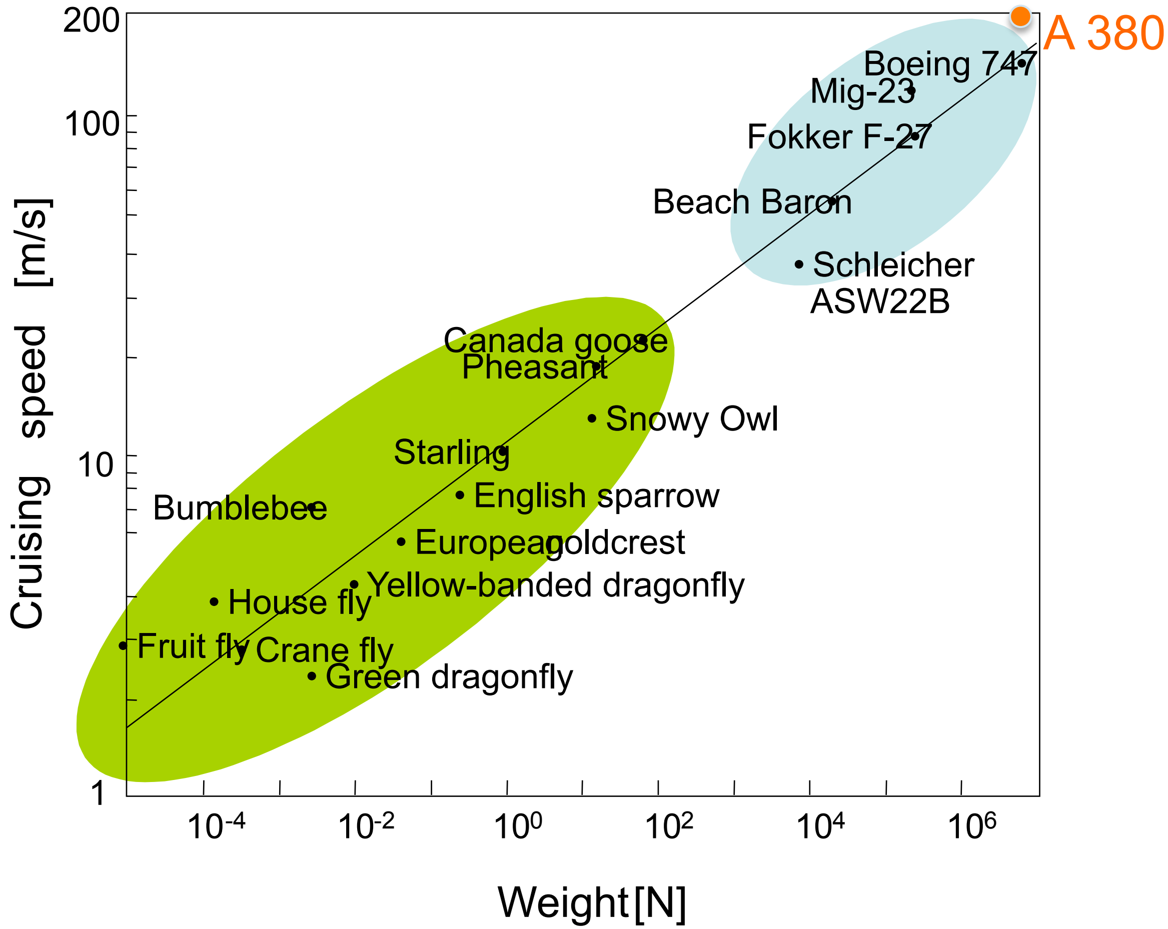
$W \propto R^3$

$lift\,(wing\,area)$

$L \propto V^2 R^2 \rho$

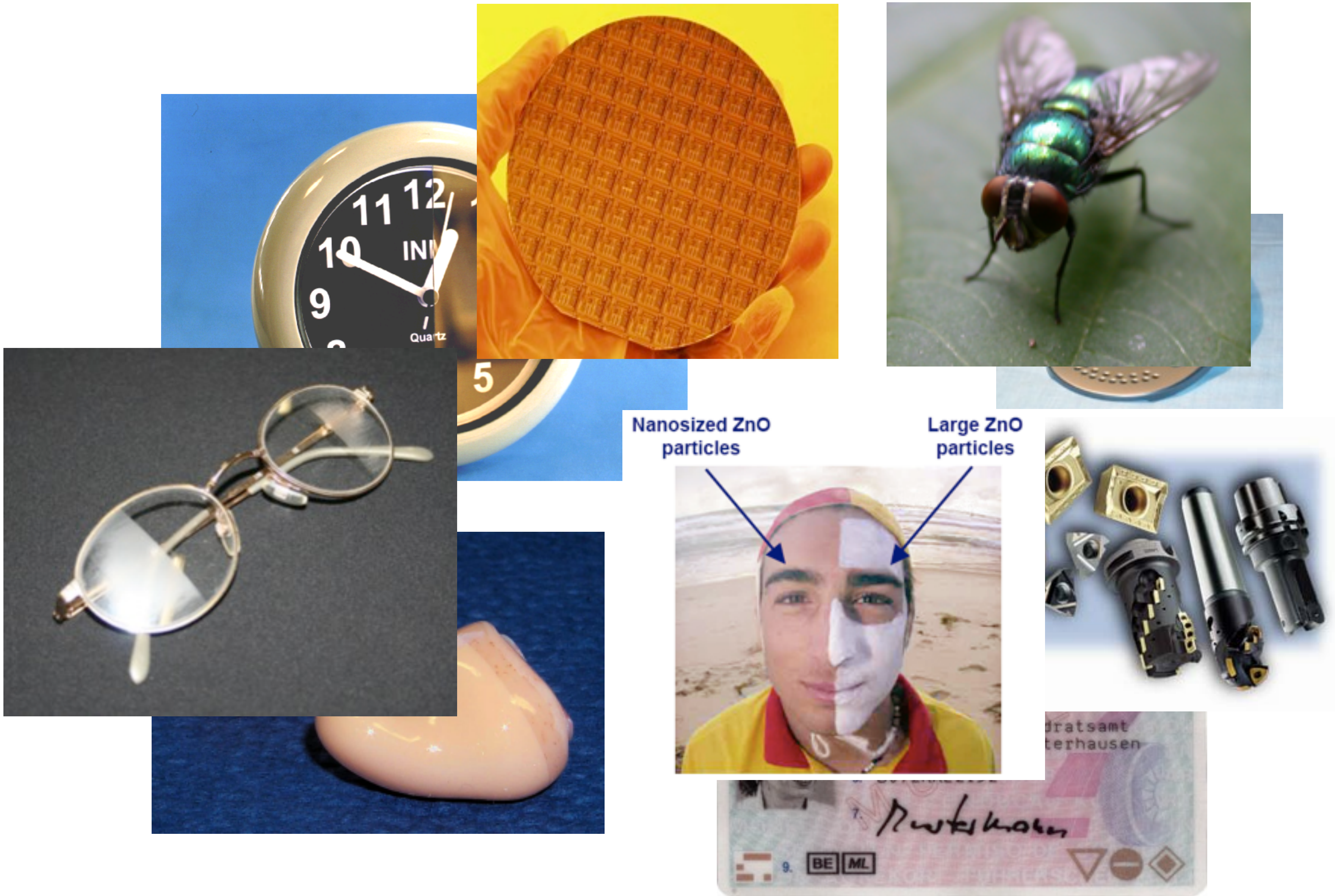
cruising speed

$V \propto W^{1/6} \propto R^{1/2}$

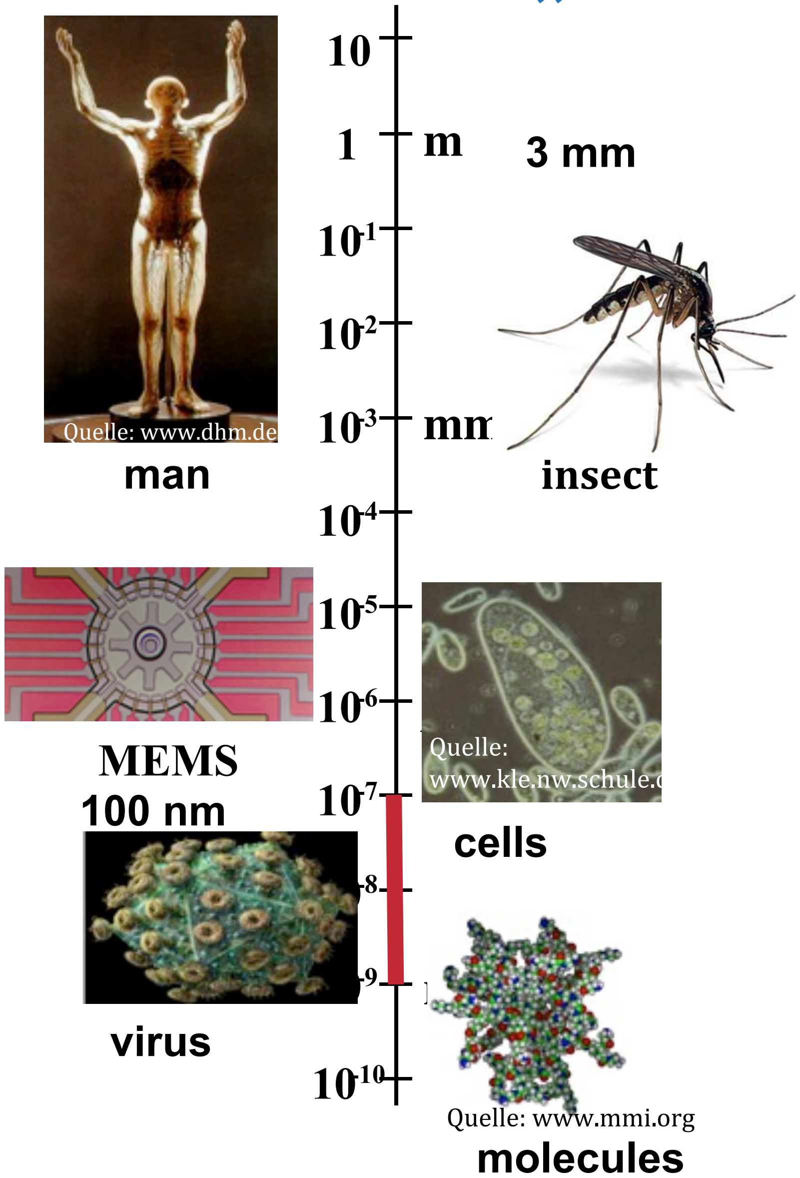


H. Tennekes, The simple science of flight, MIT Press, Cambridge, USA, 1998

NANO IN EVERYDAY LIFE



DEFINITION OF „NANO“



„nano“ von griech. **„Zwerg“**

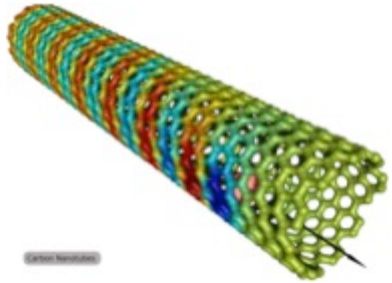
1 Nanometer = 1/1.000.000 mm

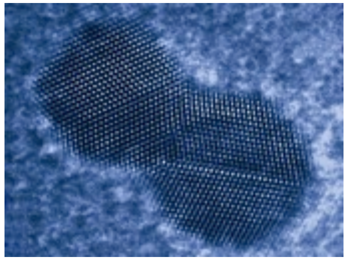
Nanobereich: ca. 1 - 100 nm

NANOMATERIAL ist *„ein natürliches, bei Prozessen anfallendes oder hergestelltes Material, das Partikel in ungebundenem Zustand, als Aggregat oder Agglomerat enthält, und bei dem mindestens 50% der Partikel in der Anzahlgrößenverteilung ein oder mehrere Außenmaße im Bereich von 1 nm bis 100 nm haben.“* (EC, 18.10.11)

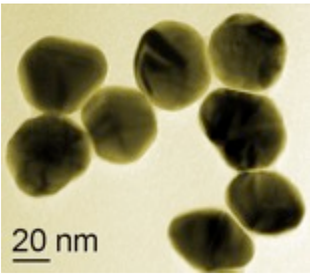
NANOMATERIALS

nanotubes

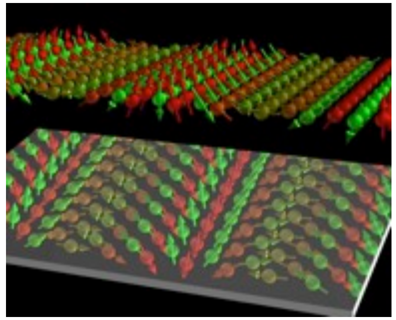




nanoparticles



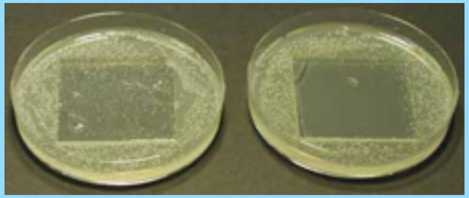
- nanomaterials
  - nano-object
    - nanoparticle
    - nanotube, -wire
    - nanolayers
  - nanostructured material
    - nanocomposite
    - nanostructured surface
    - nanocrystalline material



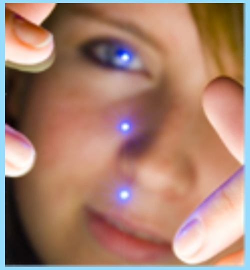
nanolayers

NANOPARTICLES IN APPLICATIONS

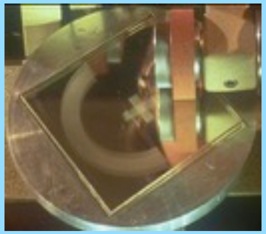
scratch reistance



anti-microbial surfaces



transparent conductive layers



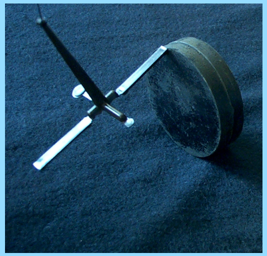
wear resistance

examples:
SiO_2, ZrO_2, TiO_2, CeO_2, ITO, γ-Fe_2O_3, Ag, MoS_2, C, Ag

tailored refractive index

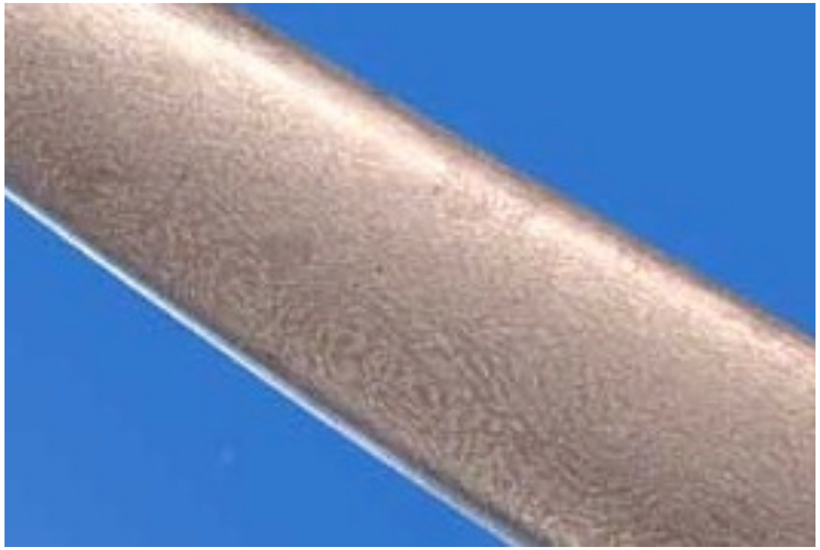
corrosion protection

light management



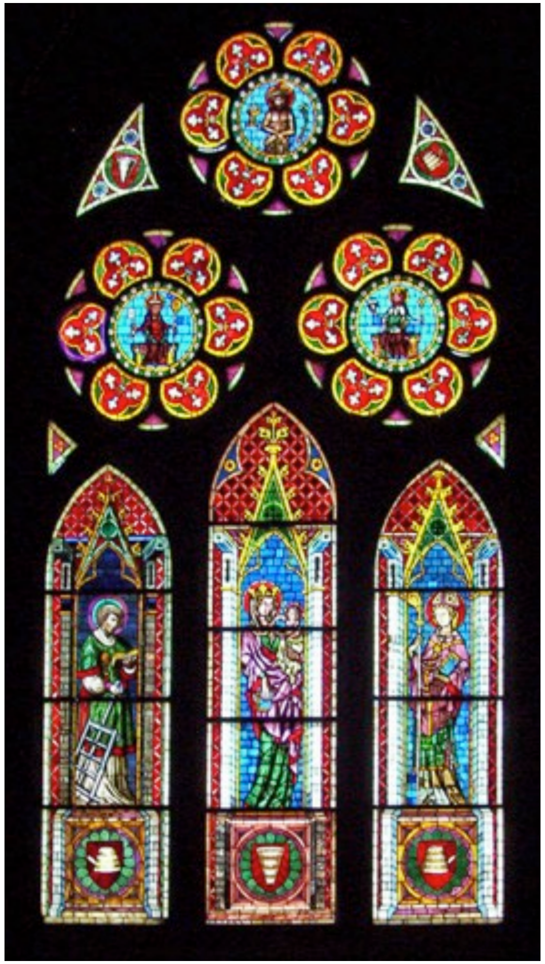
magnetic polymer composites

NANO IN THE DARK AGES



„Damscene steel“
Wieland der Schmied (Mimung)

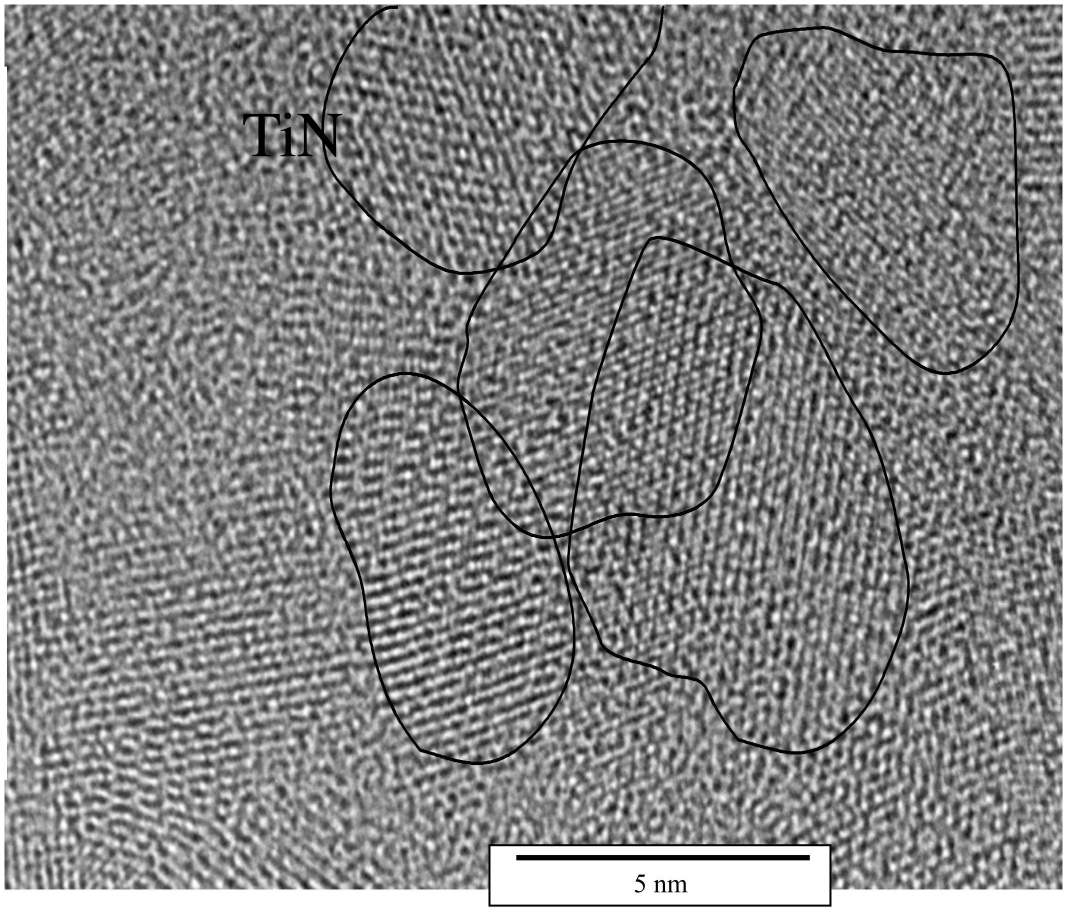
SMALL IS STRONG!



stained-glass windows with Au particles (Freiburger Münster)

TYPICAL NANOCOMPOSITES

ARM 1250 kV



small (nano)crystals have high strength!

SIZE EFFECTS IN MATERIALS: TYPES

1. surface/ volume

→ scaling effects

→ curvature effects

nanochemistry/ nanomechanics

new batteries

adhesion devices

nanofilters

cosmetics, lacquers

2. size matching

→ light interaction (λ)

→ free mean path(e,ph)

nano-optics

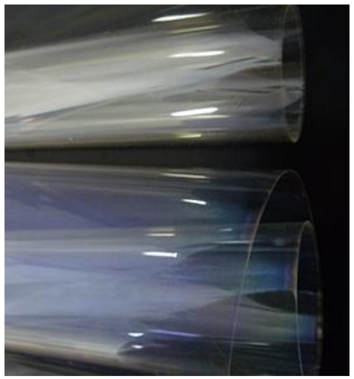
light management

anti-reflection

new lenses

heat insulation

electrosorption



3. quantum effects

→ emission/absorption

→ band gap engineering

nanoelectronics

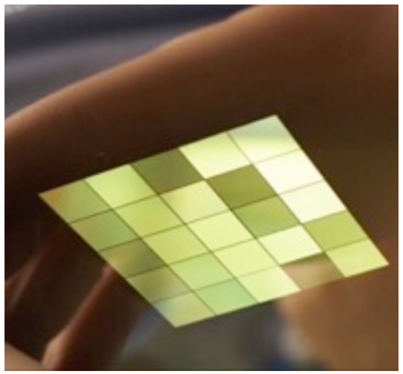
efficient lighting

new memories

better solar cells

new magnets

self-cleaning



4. bio interaction

→cell behavior

→medical surfaces

nano-bio

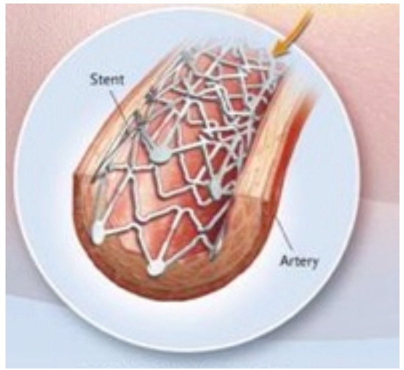
implant engineering

diagnostics

cancer therapy

nanotoxicity

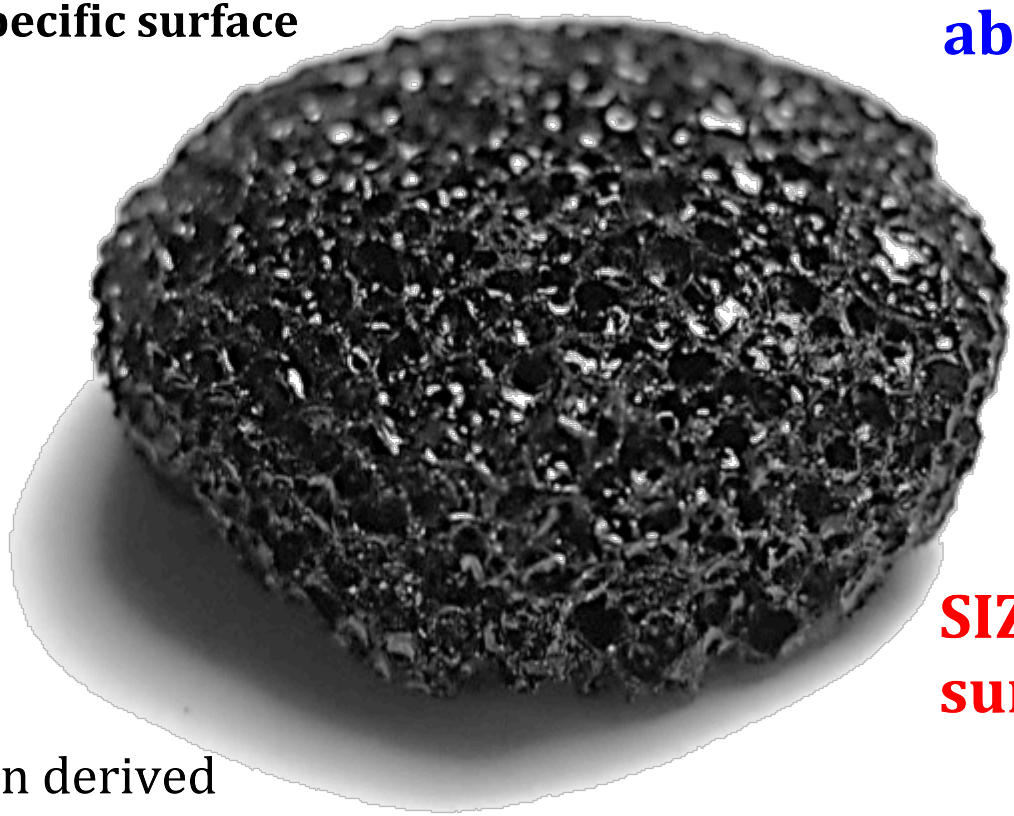
sustainability



ENERGY STORAGE : SUPERCAP ELECTRODES

electric energy storage by electrosorption of ions: Capacitance ~ ions adsorbed per volume: specific surface

SIZE EFFECT 2: absolute pore size = ca. size of electrolyte ion



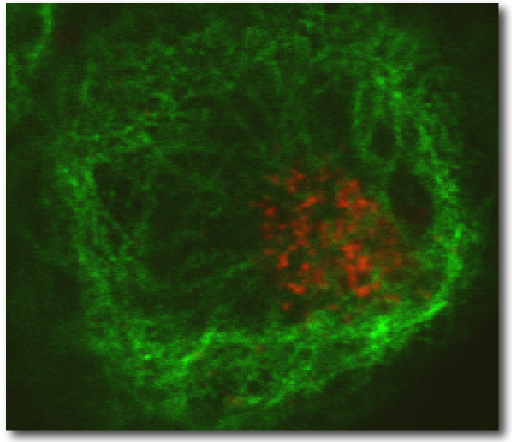
porous carbon derived
from Si-O-C foam
pore sizes 1nm – 100 µm

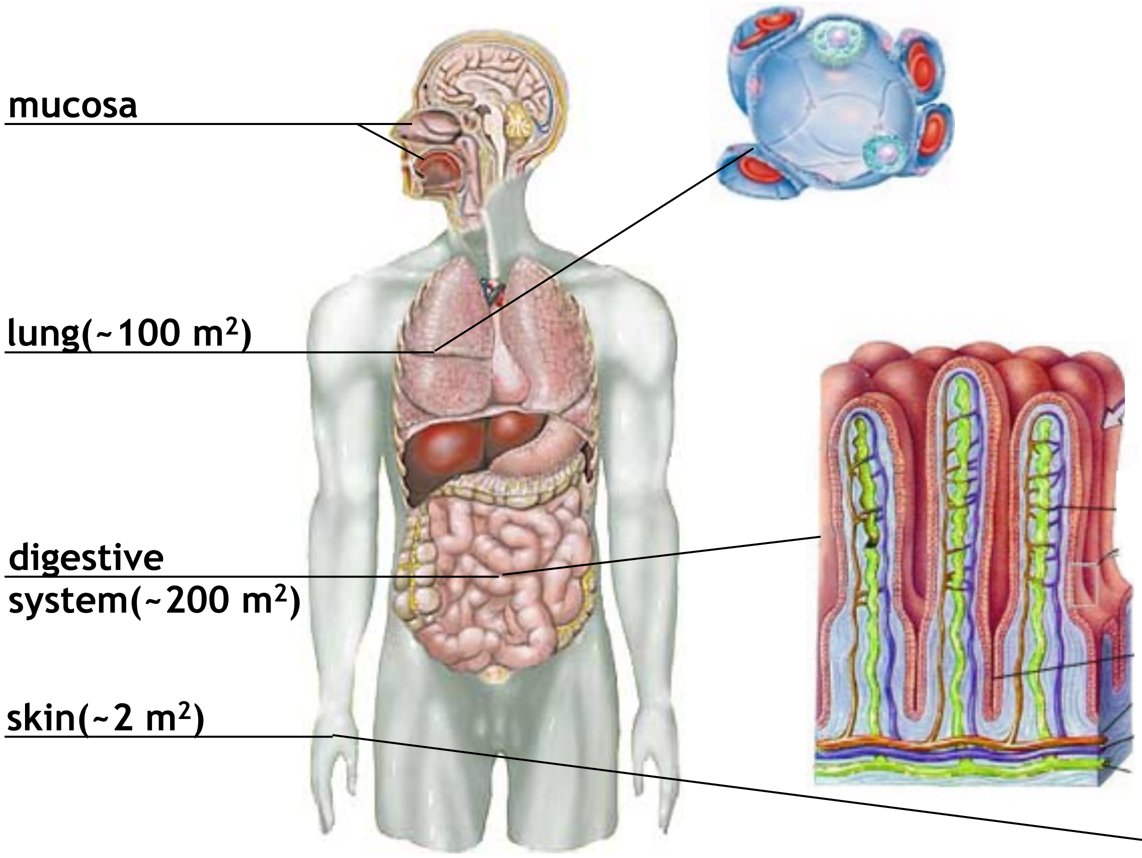
SIZE EFFECT 1: surface/volume ~ 1 / charact. size

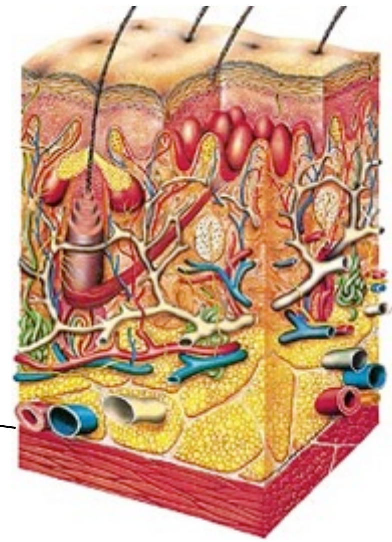
V. Presser, INM

POTENTIAL HAZARDS DUE TO NANO-OBJECTS

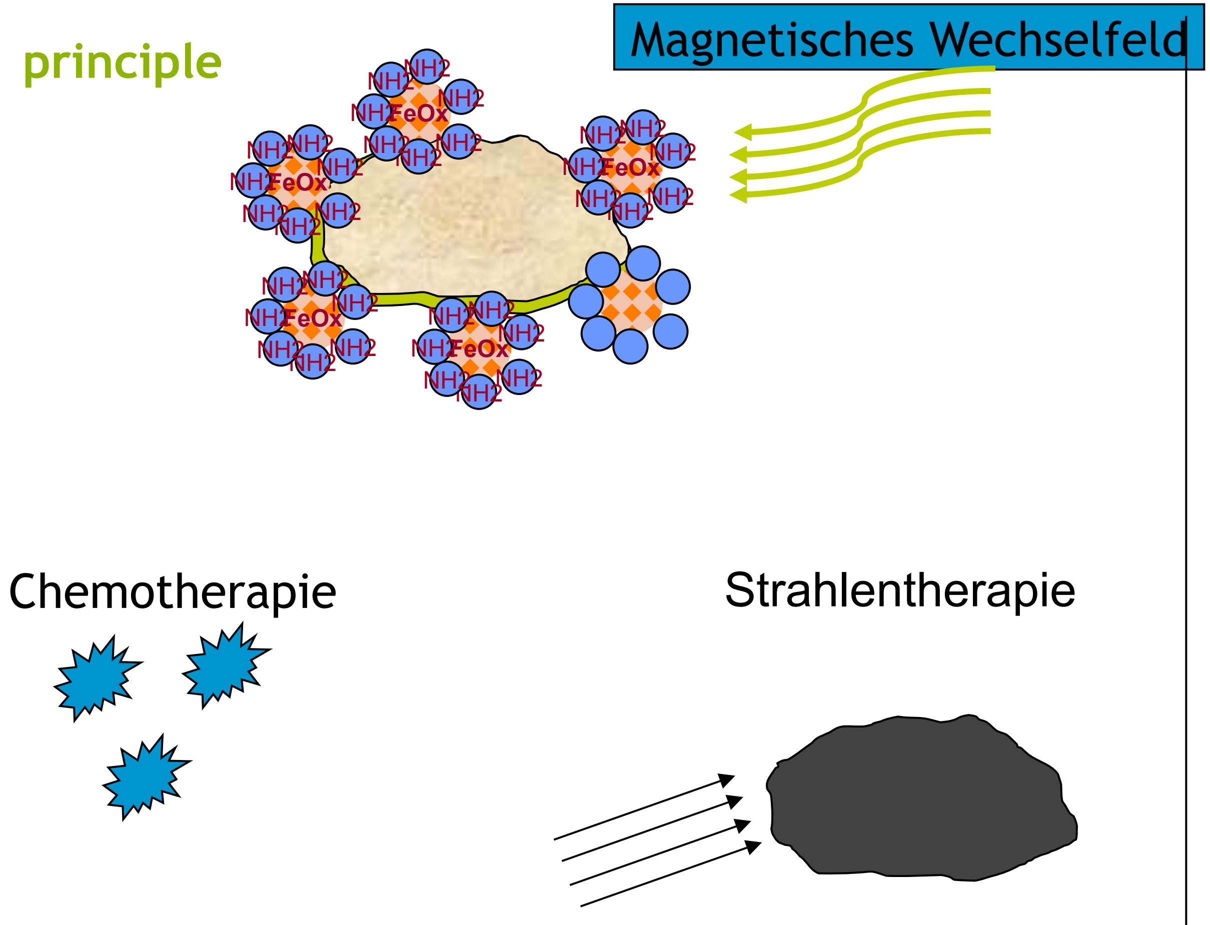
see A. Kraegeloh





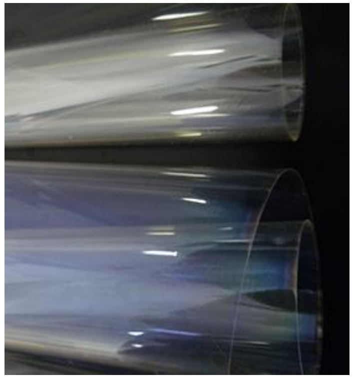


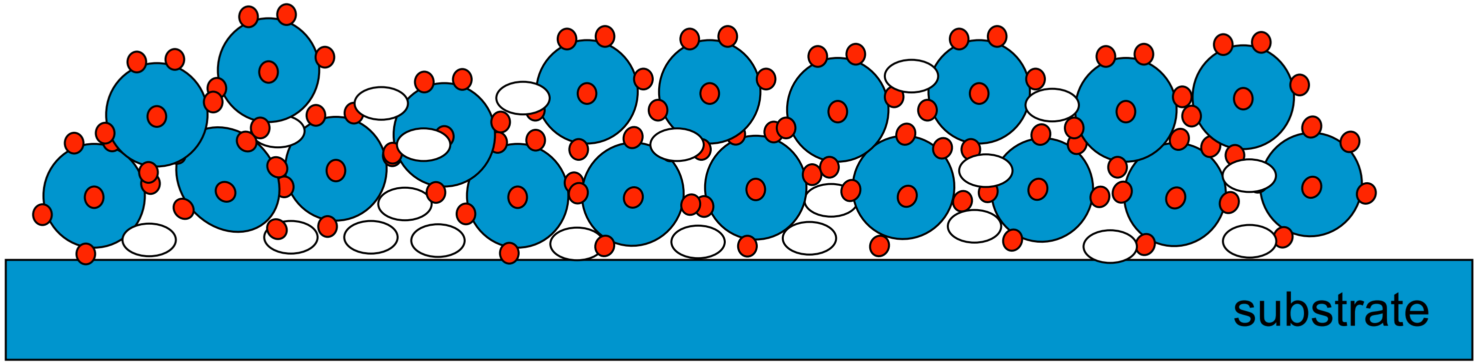
NANOPARTICLES IN CANCER THERAPY



- Injektion der Partikel in Tumor
- Aufnahme der Partikel in die Tumorzellen
- Tumorgewebe wird auf 41-45°C erwärmt
- Die Tumorzellen sind jetzt sensibilisiert.
- Tumorzellen werden per Chemo- / Radiotherapie abgetötet

LIGHT MANAGEMENT/ANTIREFLECTIVE

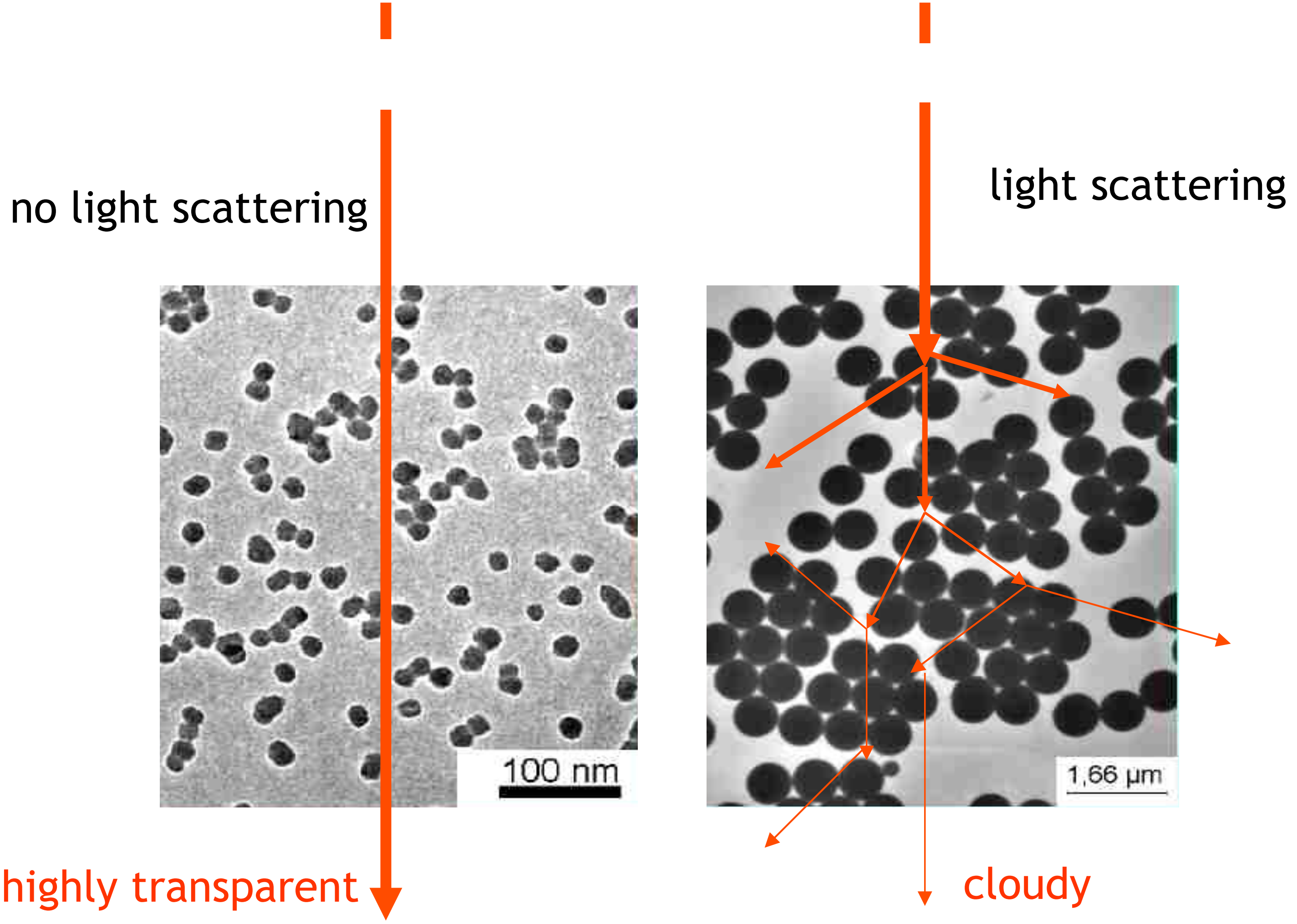




- TiO_2 crystallite: 2-7 nm (PHOTOCATALYTIC)
- SiO_2 amorphous: 30-50 nm (SCRATCH-RES.)
- Pore, void: different sizes (INDEX MATCH)

P. de Oliveira, INM

HIGH TRANSPARENCY VIA SMALL PARTICLE SIZE



C. Becker-Willinger

NANOPARTICLES CAN MODIFY OPTICAL PROPERTIES

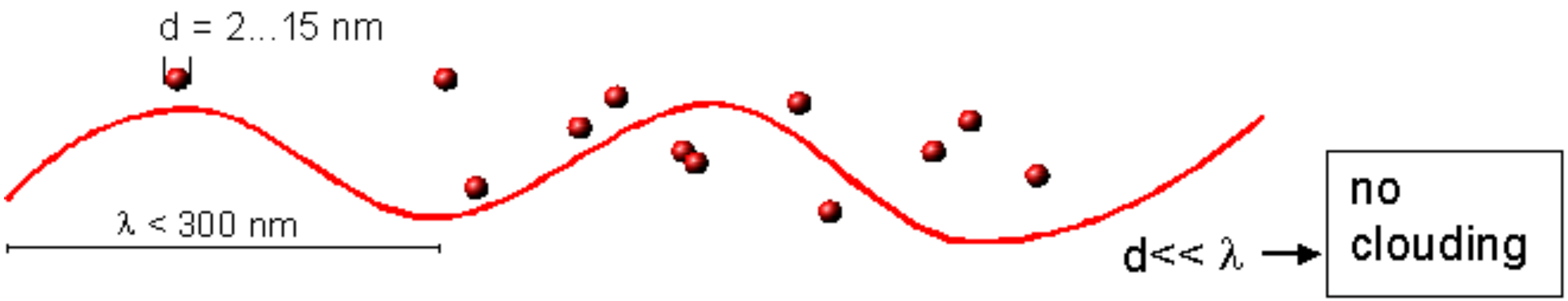
$$n = n_1(1-c) + n_2 c$$

n ... refractive index of composite
n_1...refractive index of matrix
n_2...refractive index of particle
c....vol% particles

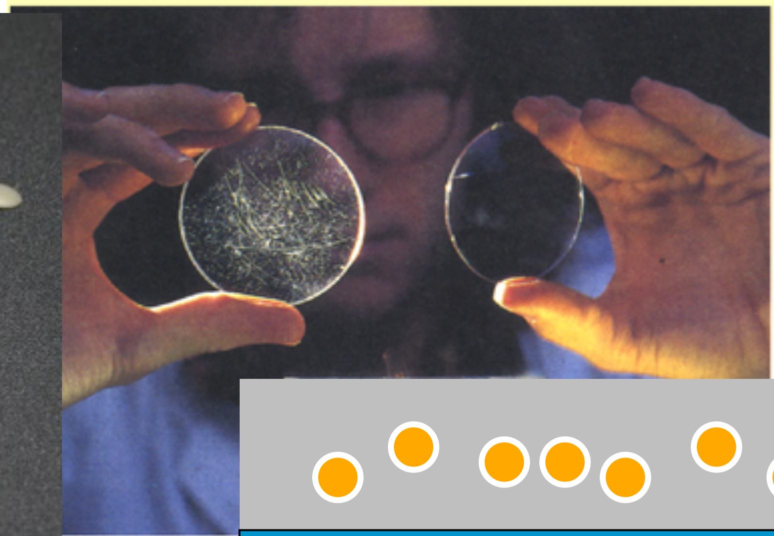
$$\frac{I_{sc}}{I_0} \propto c \frac{D^6}{\lambda^4} \frac{n_2 - n_1}{n_1^2}$$

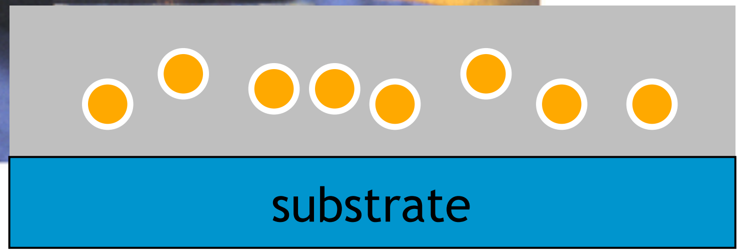
I_{sc}...scattered intensity
I_o...initial intensity
D...particle diameter
λ...wavelength (λ_0/n_1)

transparency: D_{max} < 0.05 λ (ca. 20 nm), no clusters



SCRATCH RESISTANT *AND* TRANSPARENT





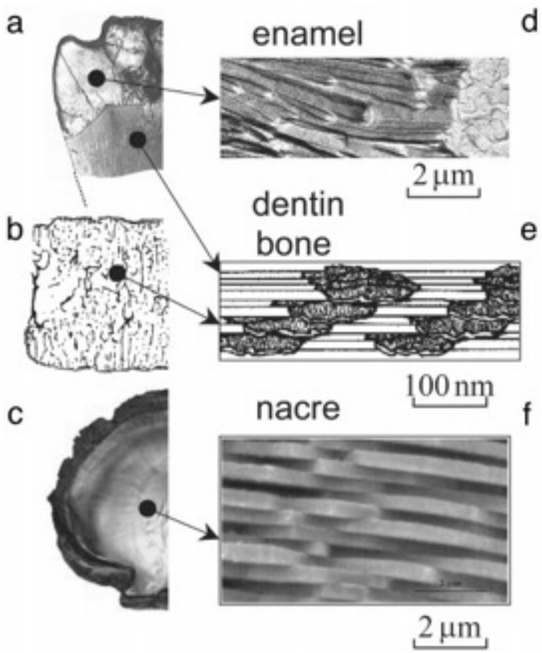
Nanomer® coating for plastic lenses

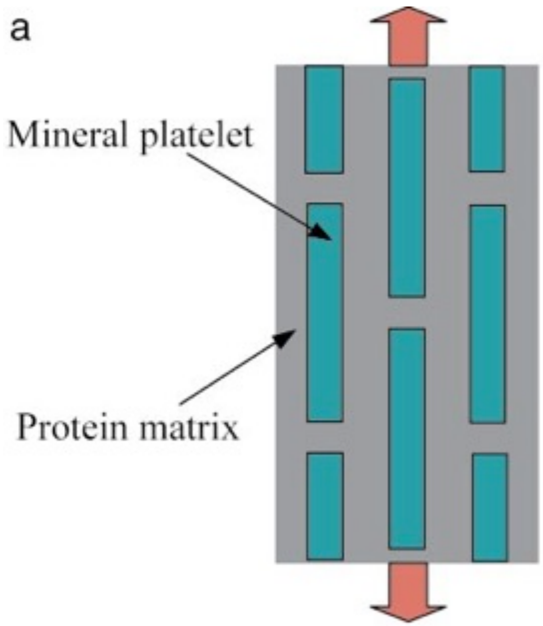
EU driver license

C. Becker-Willinger, INM

ELASTICITY, STRENGTH AND FRACTURE: SMALL = STRONG!

ELASTICITY: no size effect (property of the bond)
PLASTICITY: smaller objects are stronger (plastic deformation impeded)
FRACTURE: small fail later (only small cracks allowed)





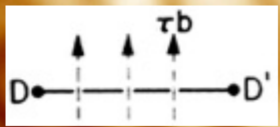
Plastic Strength

plastic (permanent) deformation in crystals is mediated by lattice defects (dislocations)

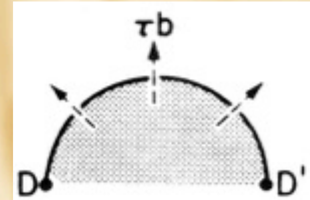
dislocations need space to move and multiply

the shear stress for a dislocation to bend to a circle of diameter L is given by the Orowan stress:

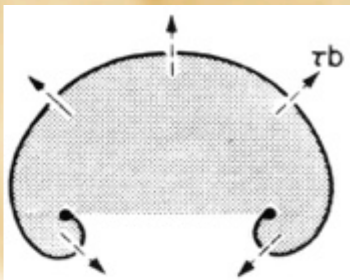
$$\tau \approx \frac{Gb}{L}$$



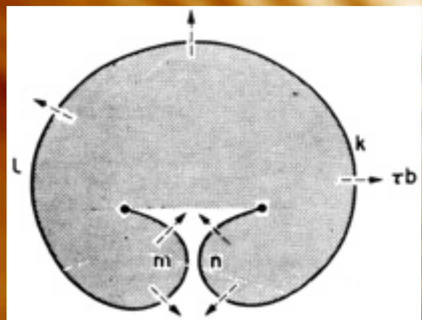
(a)



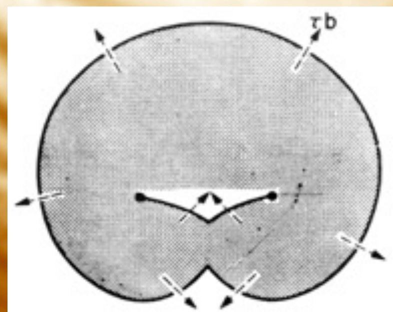
(b)



(c)



(d)

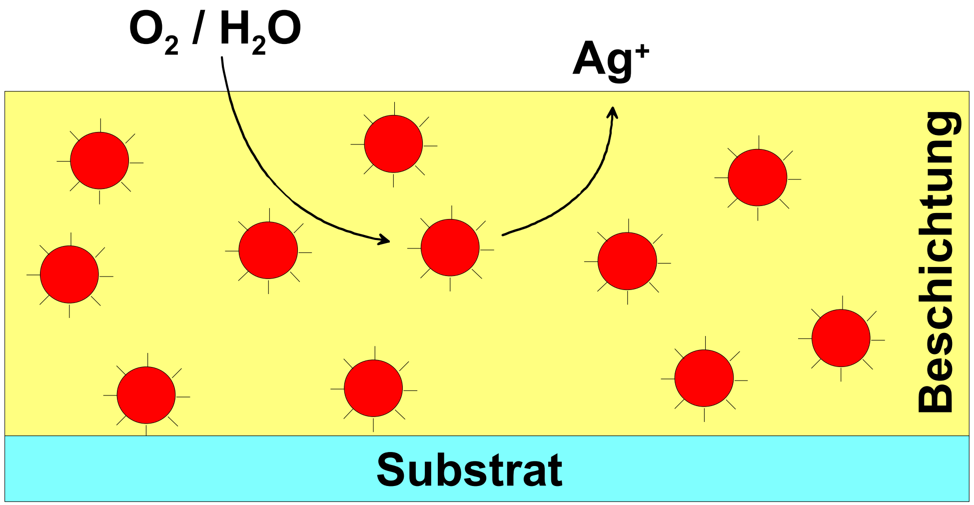


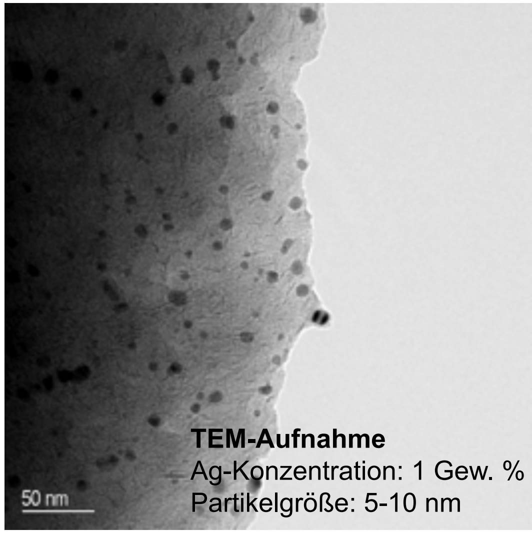
(e)

(where G is the shear modulus, b the Burgers vector)

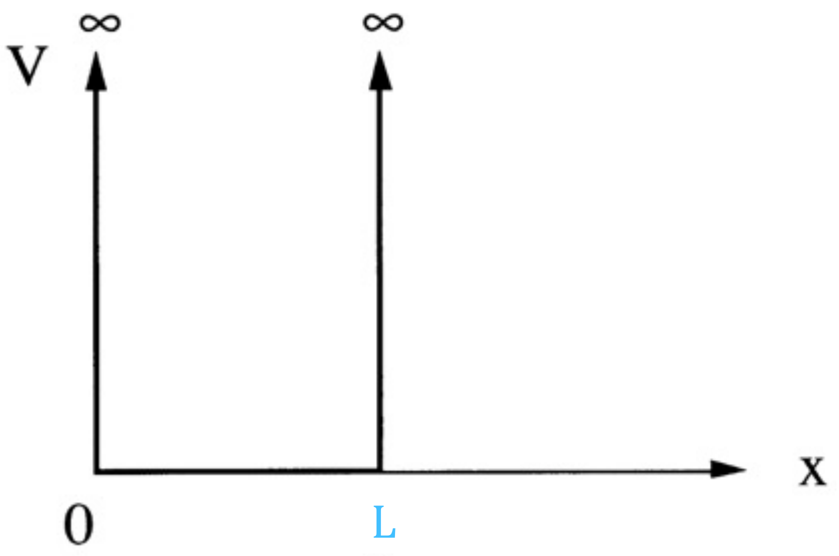
ANTIBACTERIAL SURFACES

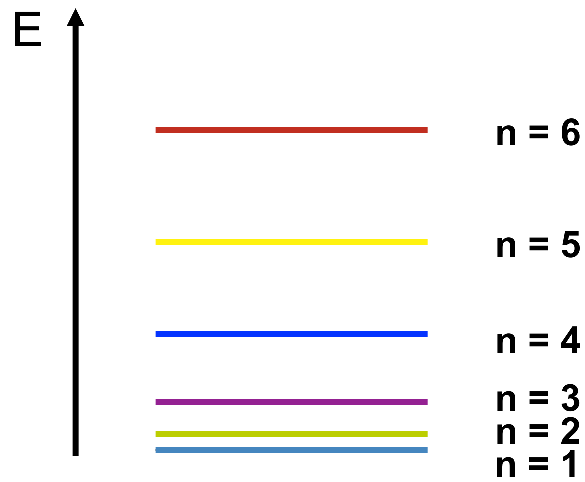
Ag^+ ions kill cells: form in presence of water





REMINDER: QUANTUM CONFINEMENT OF ELECTRON IN INFINITE WELL





energy quantisation

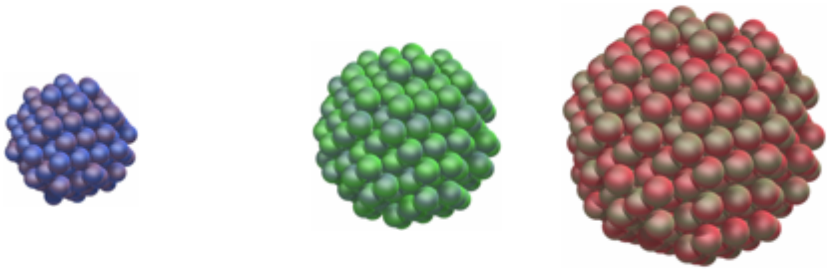
$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} \cdot n^2$$

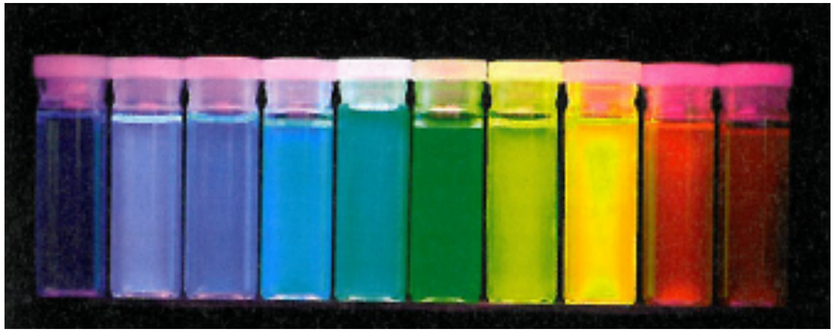
>> small systems have *higher* energy levels and differences between them, therefore transitions are associated with *smaller* wavelength radiation („blue shift“ with smaller size)

COLOR EFFECTS IN NANOPARTICLES

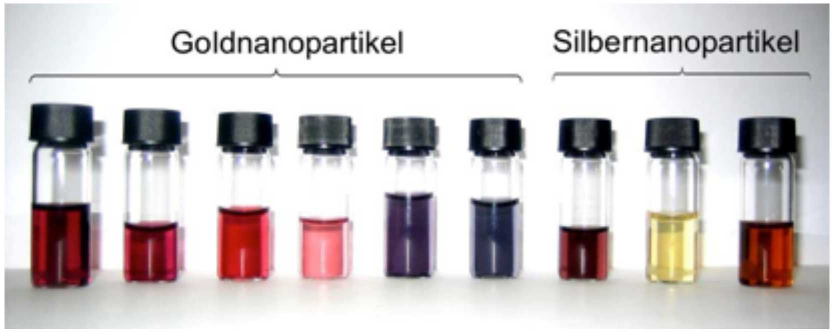
semi-conductors (quantum confinement)

metals (plasmon resonance)





CdSe quantum dots [Niemeyer, 2005]



metallic nanoparticles [Wagner, 2007]

after A. Kraegeloh, INM

SOME TAKE HOME QUESTIONS & MORE

- How is the “nano-range” defined? What are nanomaterials, nanoobjects?
- Which generic kinds of size effects can be distinguished? Examples?
- How does size affect the elastic properties? What is elasticity? Which law governs elastic behavior?
- What is strength? stiffness? toughness?
- How does size affect plastic strength? What is plasticity? Which materials constants are used to describe it?
- *How does size affect fatigue of metals? What is fatigue?*
- *How does size affect the magnetic properties? What is superparamagnetism?*
- Why are most materials in nature nanocomposites? Examples?
- How can nanoparticles affect optical properties? Why are nanoparticles needed to form scratchresistant transparent coating?
- How is an electron affected by a square potential? How does size affect energy levels and transitions between states?
- What is meant by plasmon resonance?
- Why are nanoobjects of interest in biology and medicine?

ABSORPTION/EMISSION (PHOTON INTERACTION)

transition between levels n and n+1 (photoluminescence):

$$\Delta E = \frac{\hbar^2 \pi^2}{2mL^2} \cdot (2n+1)$$

leads to emission/absorption: $\Delta E = h\nu = hc/\lambda$

$$\lambda \propto L^2$$

>> small systems have *higher* energy levels and differences between them, therefore transitions are associated with *smaller* wavelength radiation („blue shift“ with smaller size)