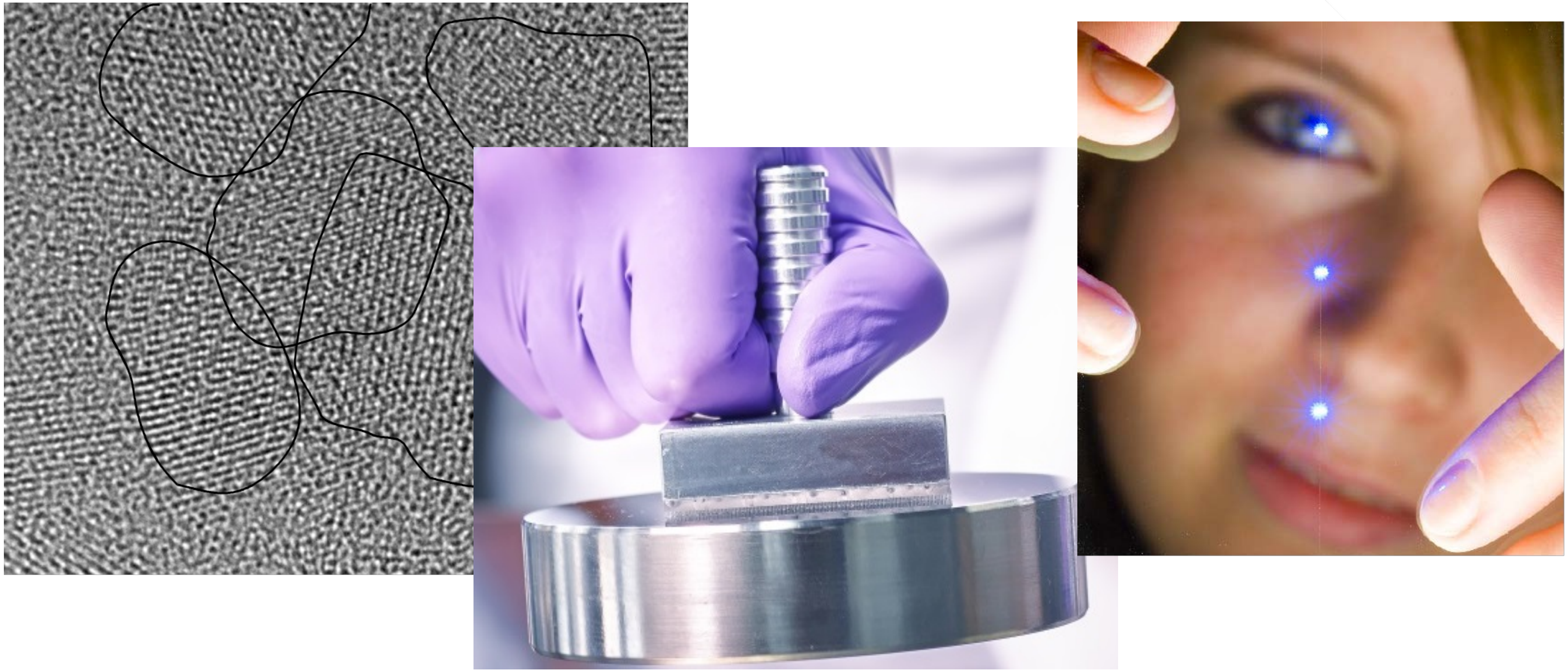
New Ideas. New Materials.

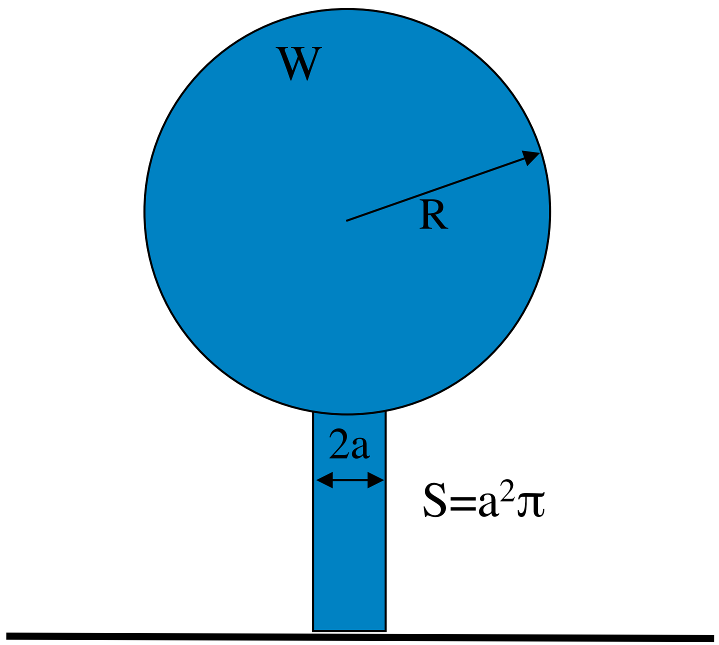


NANOBIOMATERIALS 1
AN INTRODUCTION TO SIZE EFFECTS

Prof. Dr. Eduard Arzt und MitarbeiterInnen
MWWT, Neue Materialien, und INM – Leibniz-Institut für Neue Materialien

LARGE ANIMALS BREAK DOWN

"animal"



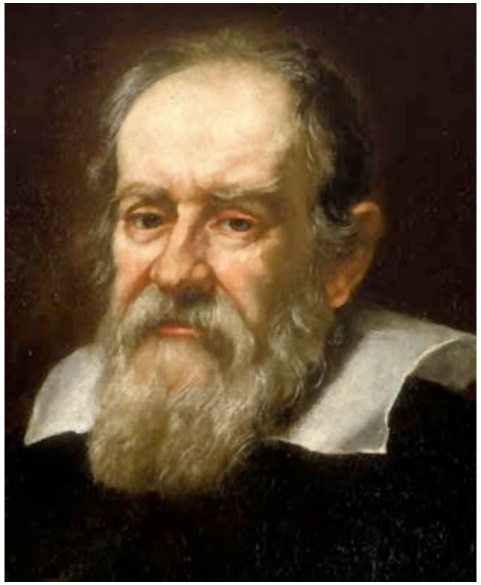
stress calculation

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

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

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

g..gravitational acceleration



Galileo Galilei
(1564-1642)

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

SIZE EFFECTS IN MAMMALS

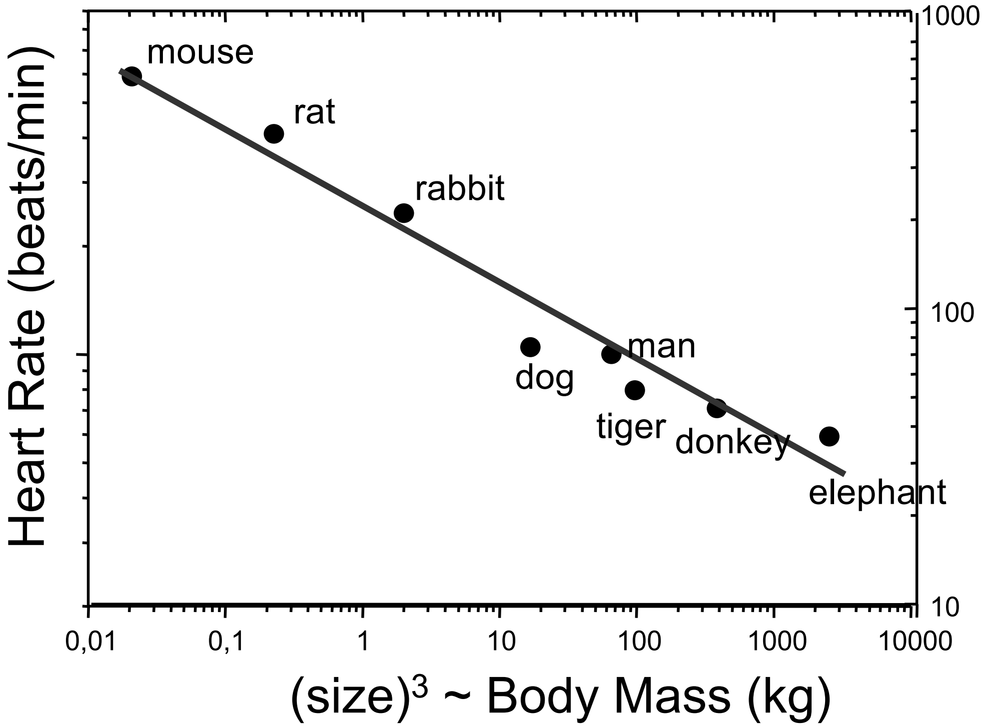
heat balance

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

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

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

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)

LARGER MAMMALS LIVE LONGER

heat balance

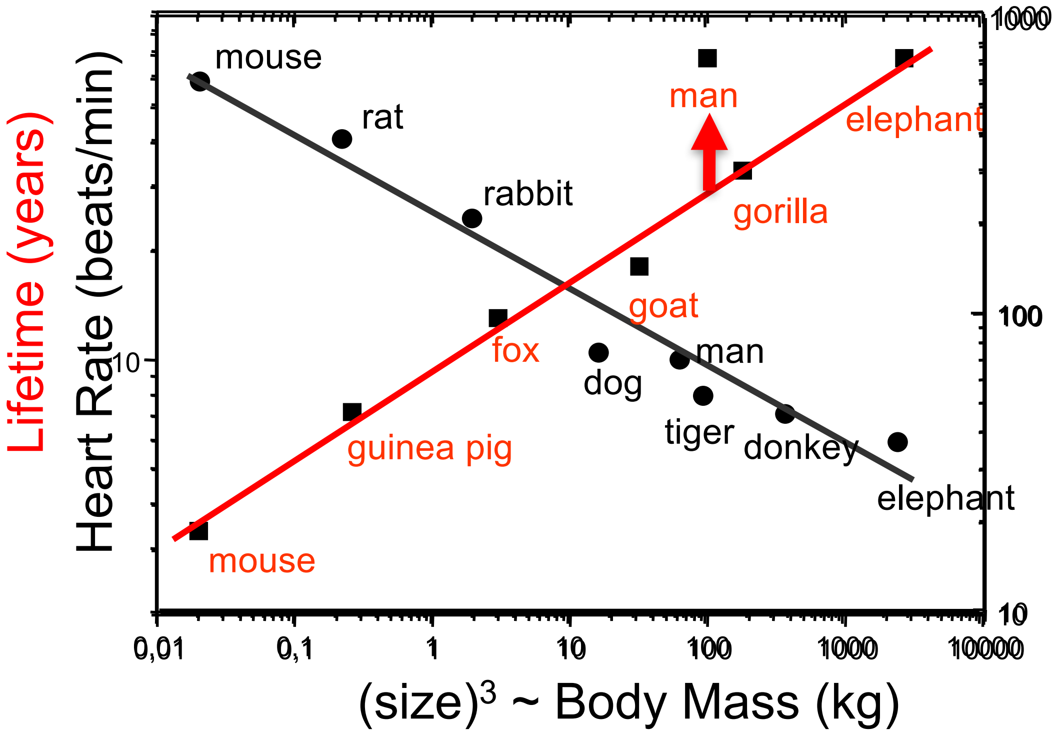
$$+\dot{Q} \sim f_{Hz}\,(size)^3$$

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

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

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

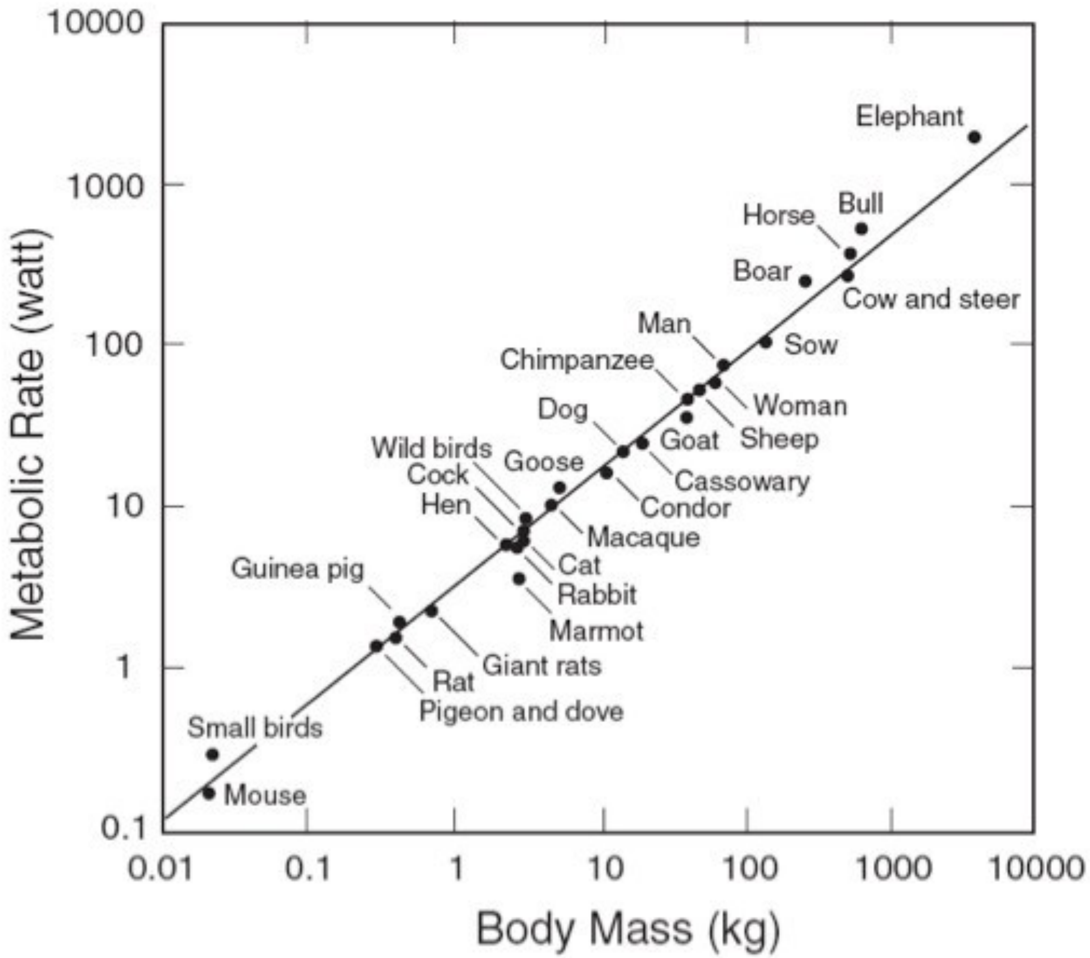
Q…heat supplied
f_{Hz}…heart beat rate

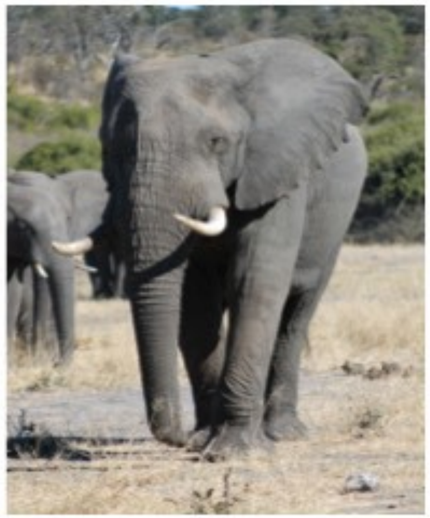


for a detailed derivation see H. Lin, Am J Phys 50, 72 (1982), T. McMahon, Science 179, 1209 (1973)

SCALING EFFECTS

G. West, **Scale: The Universal Laws of Life and Death in Organisms, Cities and Companies**, Weidenfeld&Nicolson 2017





SLOPE = ¾ < 1 SUB-LINEAR ECONOMY OF SCALE

LARGE OBJECTS (MUST) FLY FAST

force balance

weight (volume)

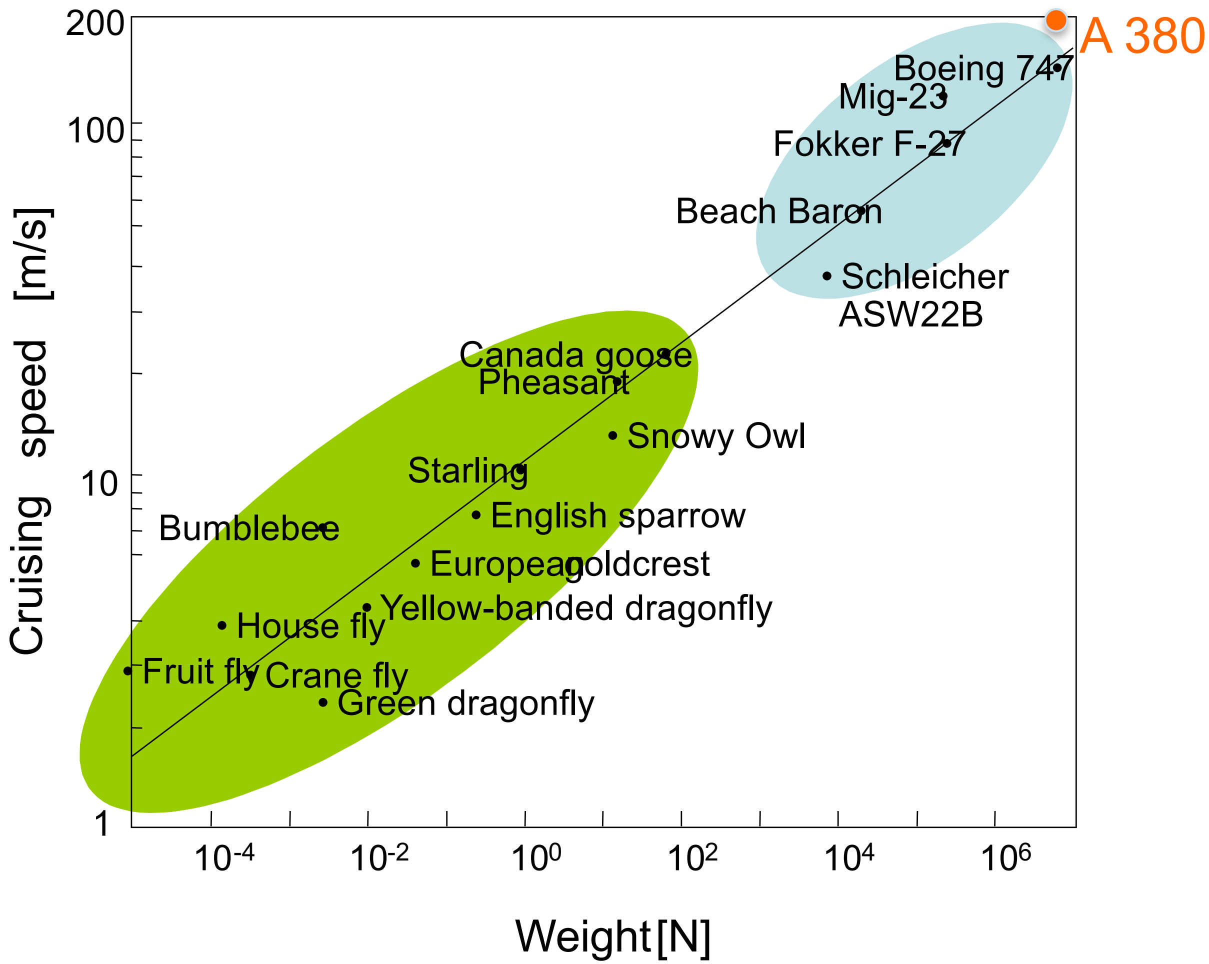
$$W \propto R^3$$

lift (wing area)

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

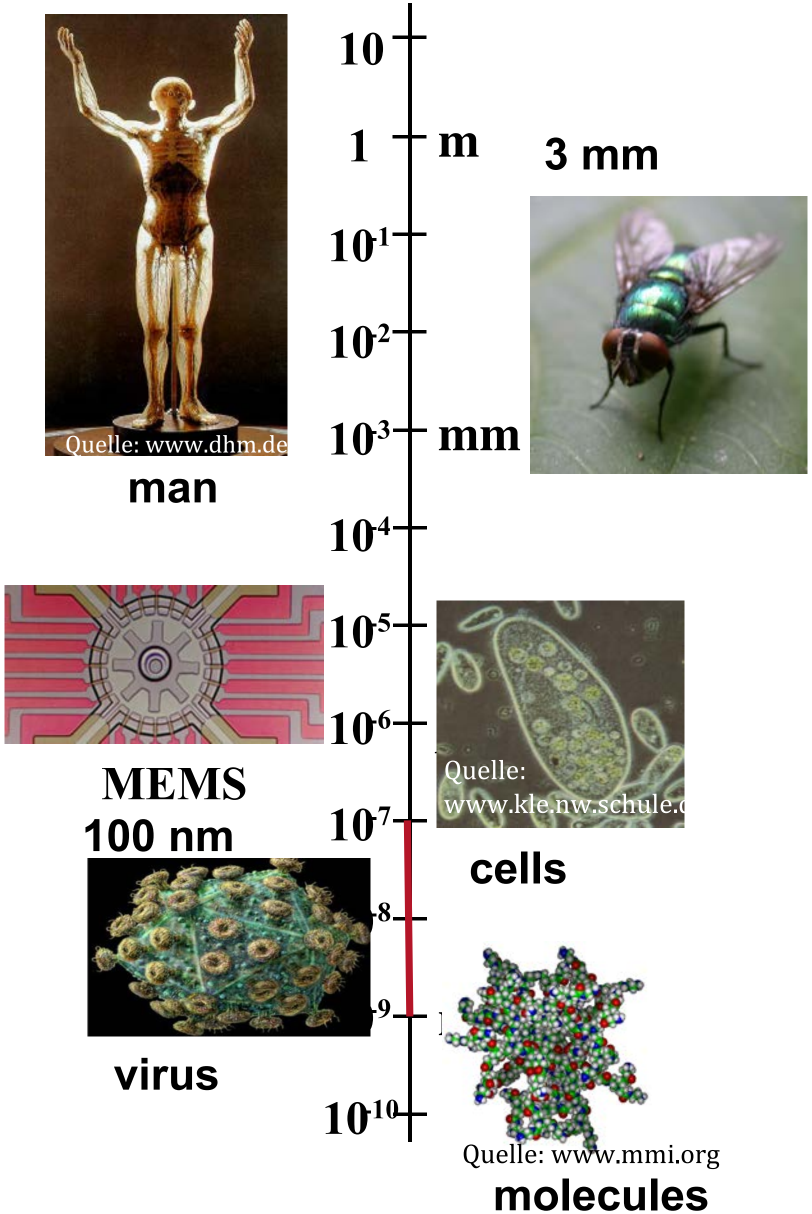
cruising speed

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



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

DEFINTION OF „nano“



„**nano**“ von griech. „**Zwerg**“

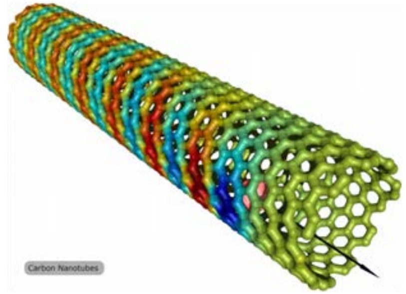
1 Nanometer = 1/1.000.000 mm

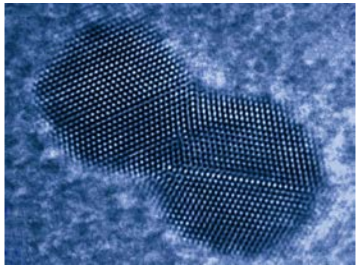
Nanobereich: ca. 1 - 100 nm

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)

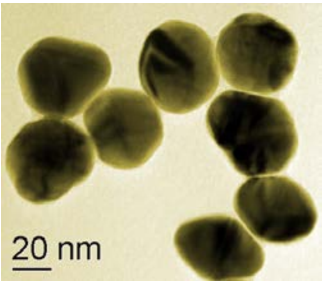
NANOMATERIALS - TERMINOLOGY

nanotubes

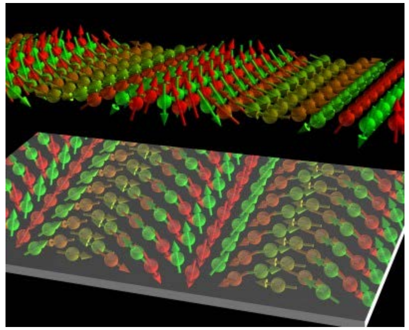




nanoparticles

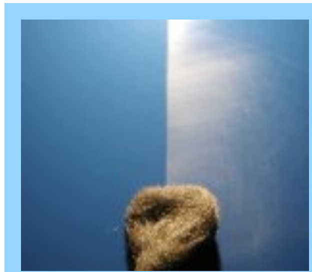


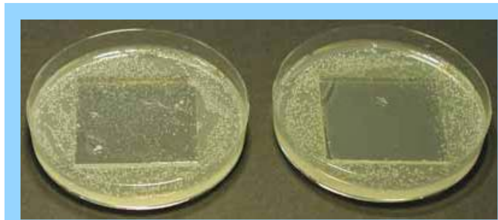
- nanomaterials
  - nano-object
    - nanoparticle
    - nanotube, -wire
    - nanolayers
  - nanostructured material
    - nanocomposite
    - nanostructured surface
    - nanocrystalline material

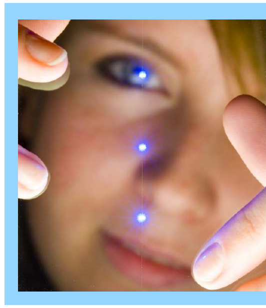


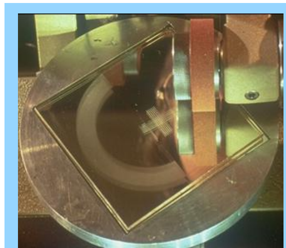
nanolayers

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

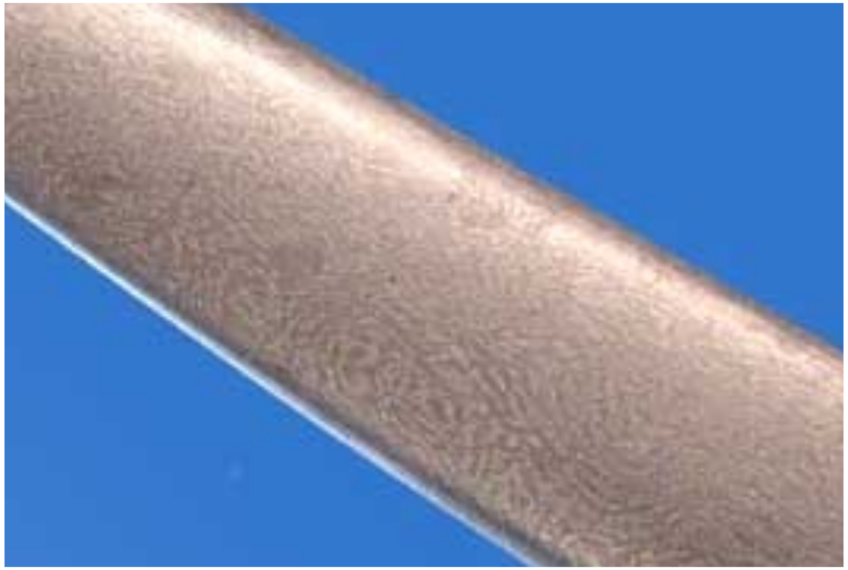

tailored refractive index


corrosion protection


light management


magnetic polymer composites

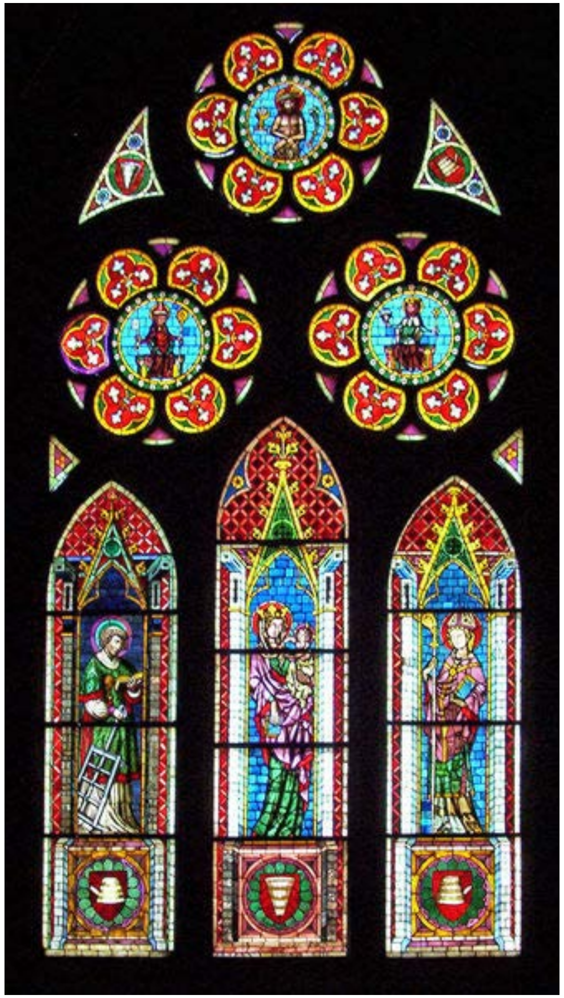
NANO IN THE DARK AGES



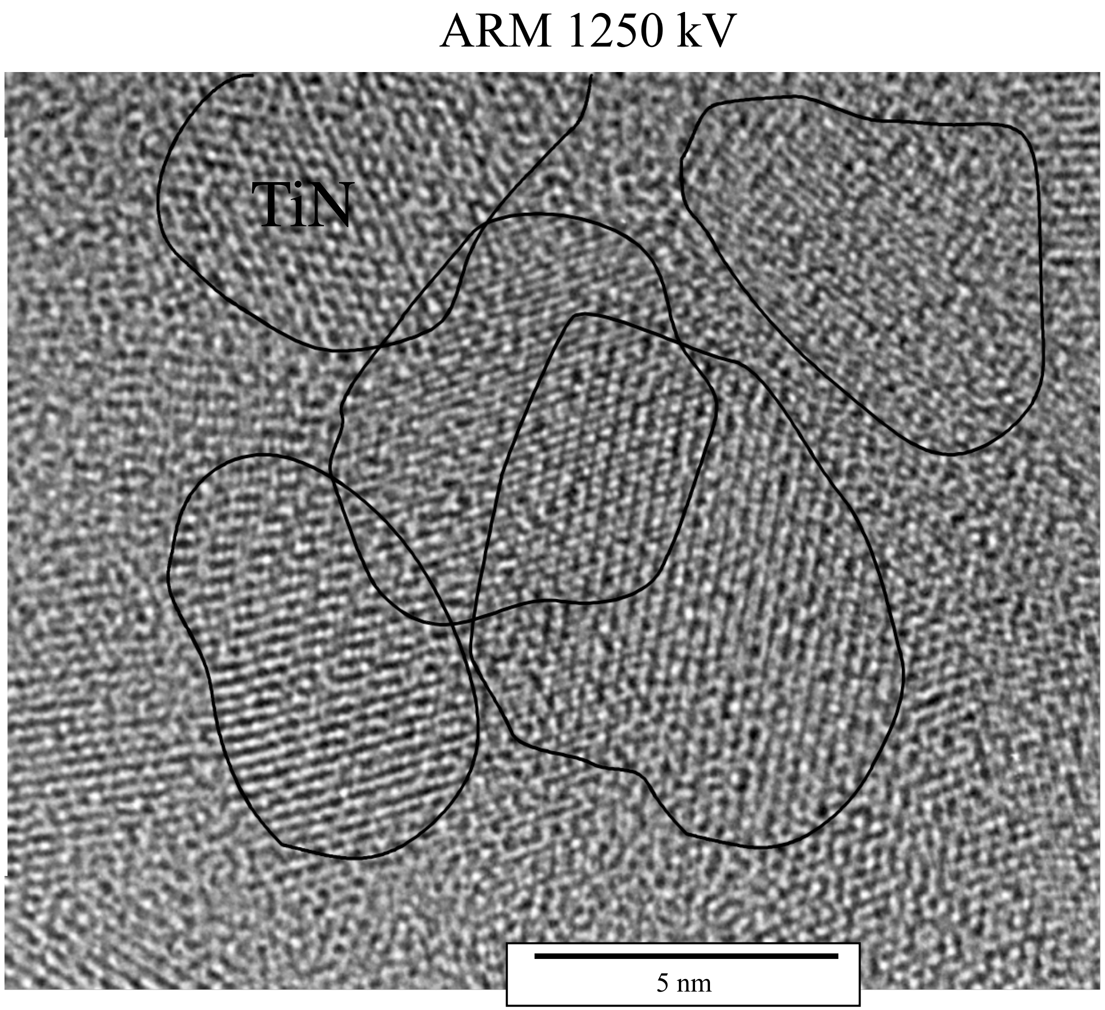
„Damscene steel“
Wieland der Schmied (Mimung)

SMALL IS STRONG!

stained-glass windows with Au particles (Freiburger Münster)



NANOCOMPOSITES FOR HIGH PERFORMANCE



small (nano)crystals have high strength!

SIZE EFFECTS IN MATERIALS - CLASSIFICATION

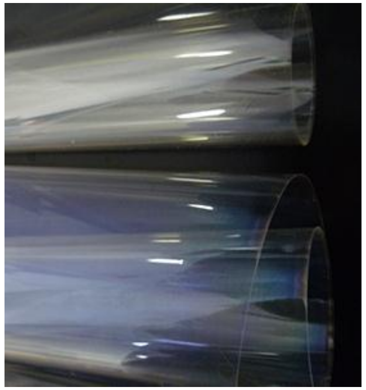
1. surface/ volume	2. size matching	3. quantum effects	4. bio interaction
→ scaling effects	→ light interaction (λ)	→ emission/absorption	→ cell behavior
→ curvature effects	→ free mean path(e,ph)	→ band gap engineering	→ medical surfaces

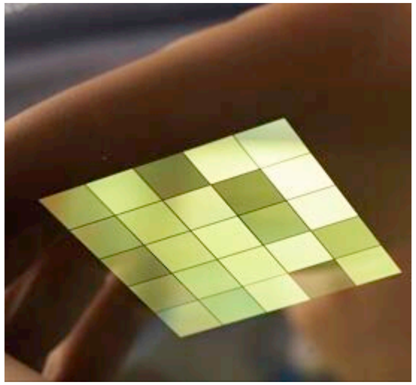
nanochemistry/ nanomechanics
new batteries
adhesion devices
nanofilters
cosmetics, lacquers

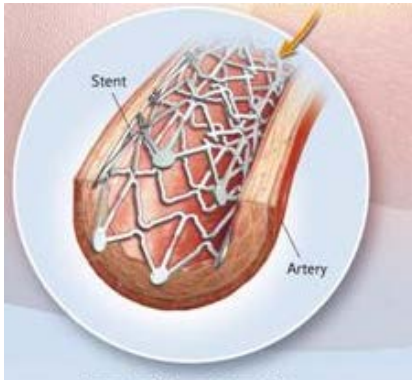
nano-optics
light management
anti-reflection
new lenses
heat insulation
electrosorption

nanoelectronics
efficient lighting
new memories
better solar cells
new magnets
self-cleaning

nano-bio
implant engineering
diagnostics
cancer therapy
nanotoxicity
sustainability

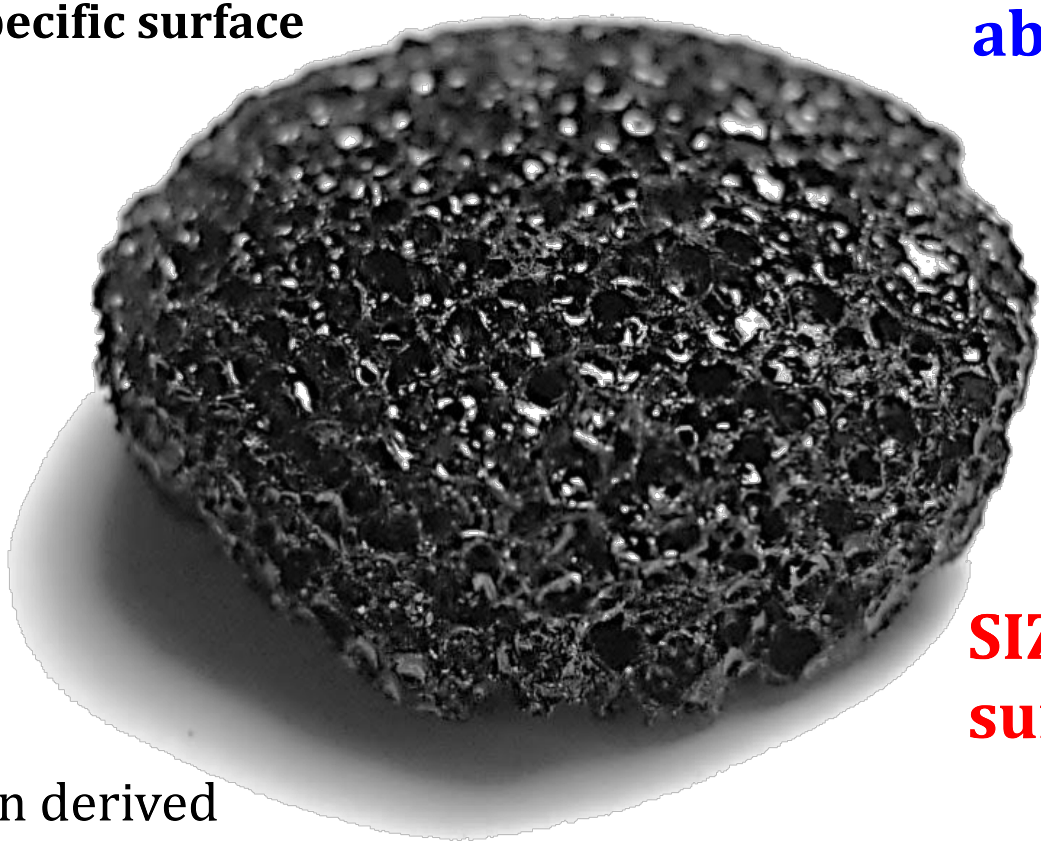






ENERGY STORAGE : SUPERCAP ELECTRODES

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



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

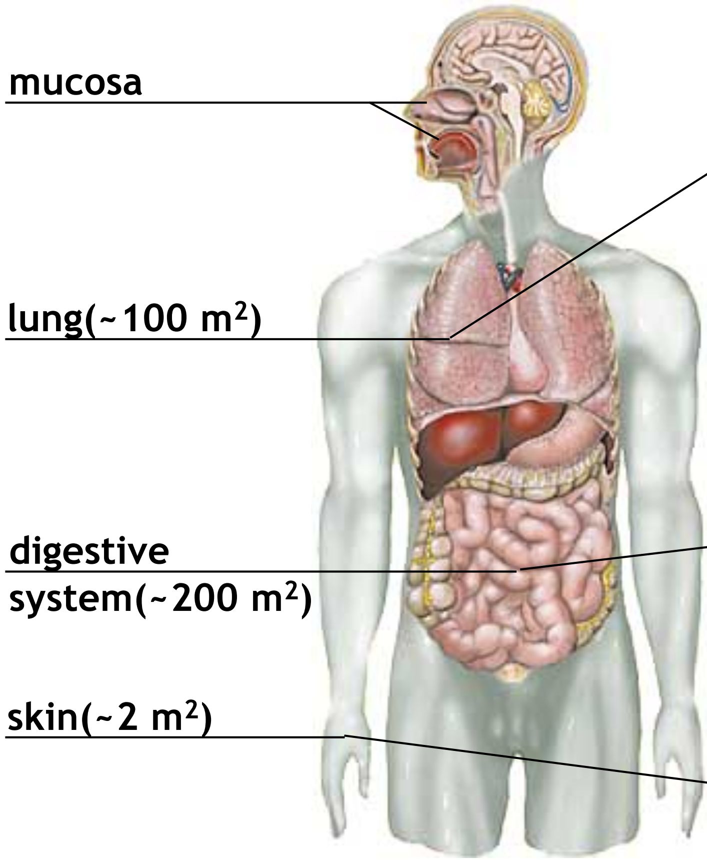
SIZE EFFECT 2: absolute pore size = ca. size of electrolyte ion

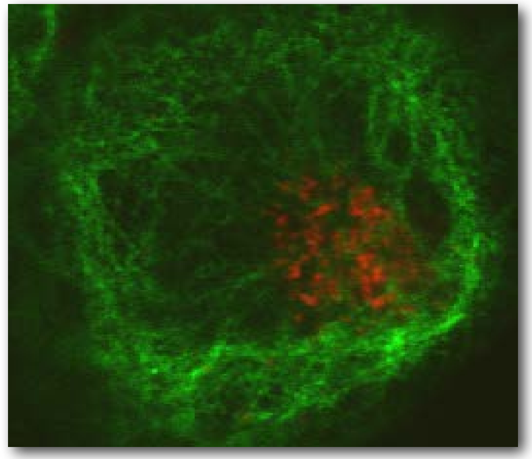
SIZE EFFECT 1: surface/volume ~ 1 / charact. size

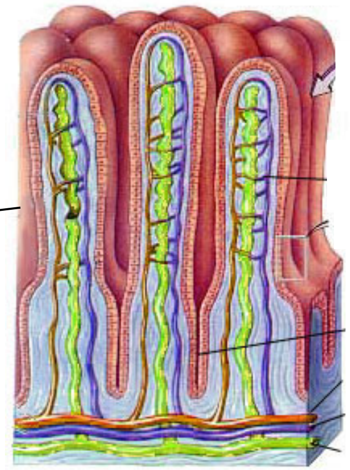
V. Presser, INM

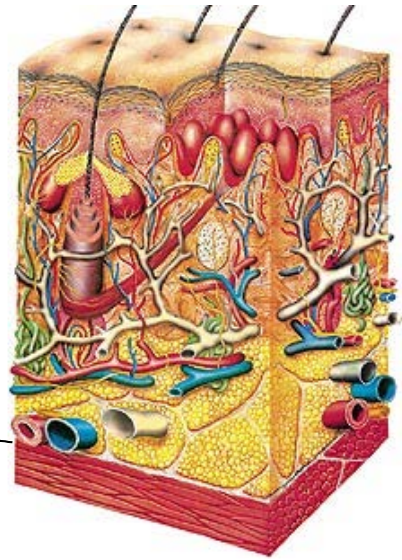
POTENTIAL HAZARDS DUE TO NANO-OBJECTS

see A. Kraegeloh



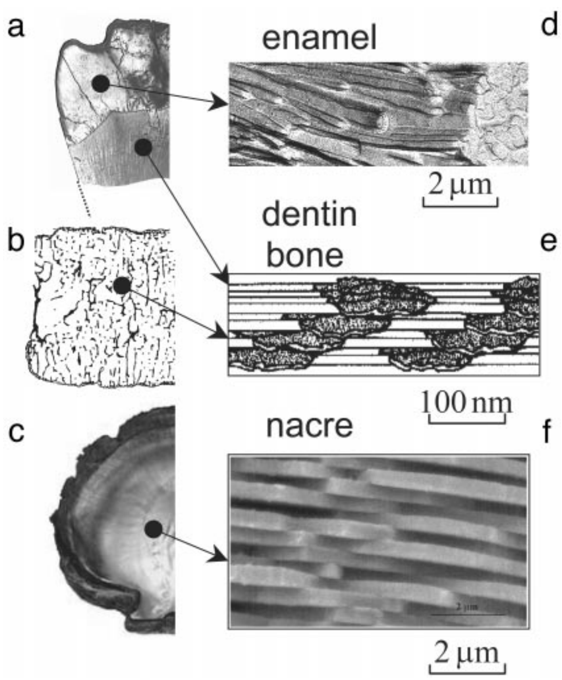


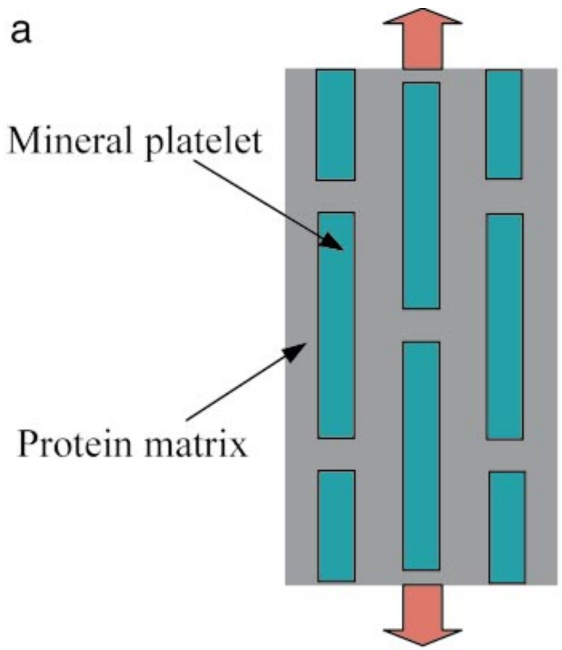




ELASTICITY, STRENGTH AND FRACTURE: SMALL = STRONG!

ELASTICITY: no size effect
PLASTICITY: smaller objects are stronger
FRACTURE: small fail later

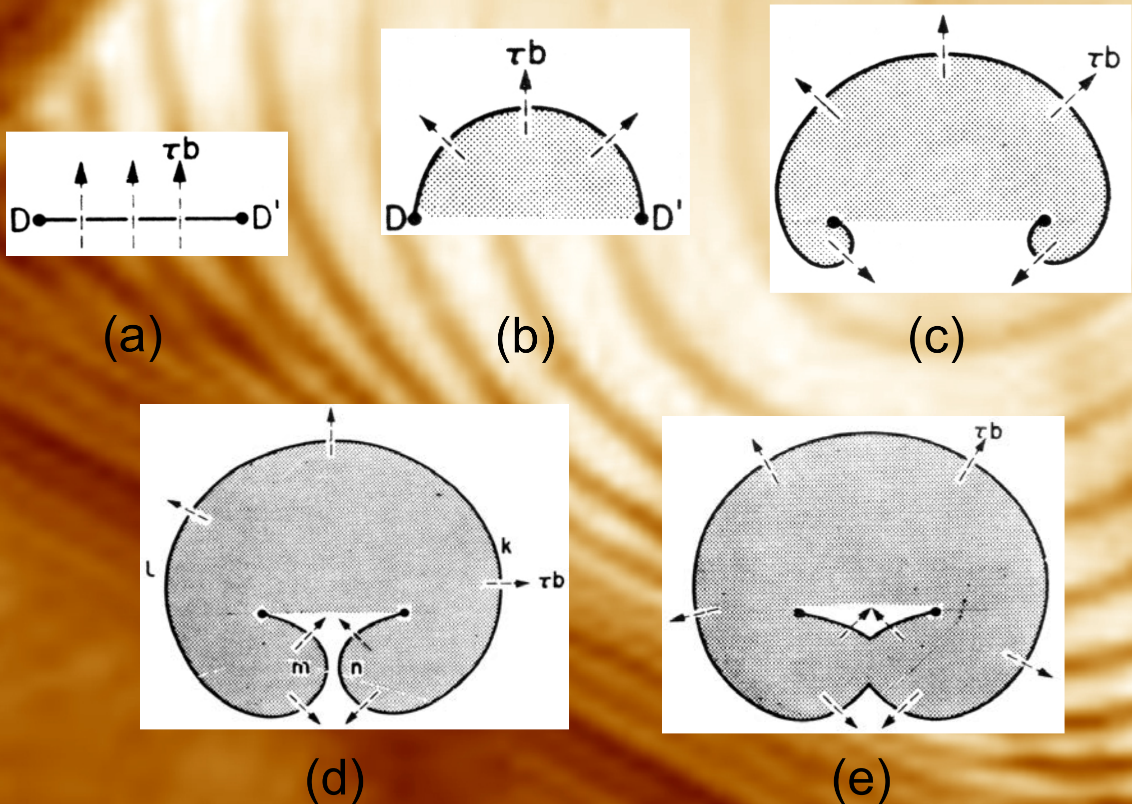




size must be below a characteristic length (γ surface energy, E Young's modulus, σ_{th} theoretical strength):

$$L < L_{crit} \approx \pi \frac{\gamma E}{\sigma_{th}^2}$$

Plastic Strength



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

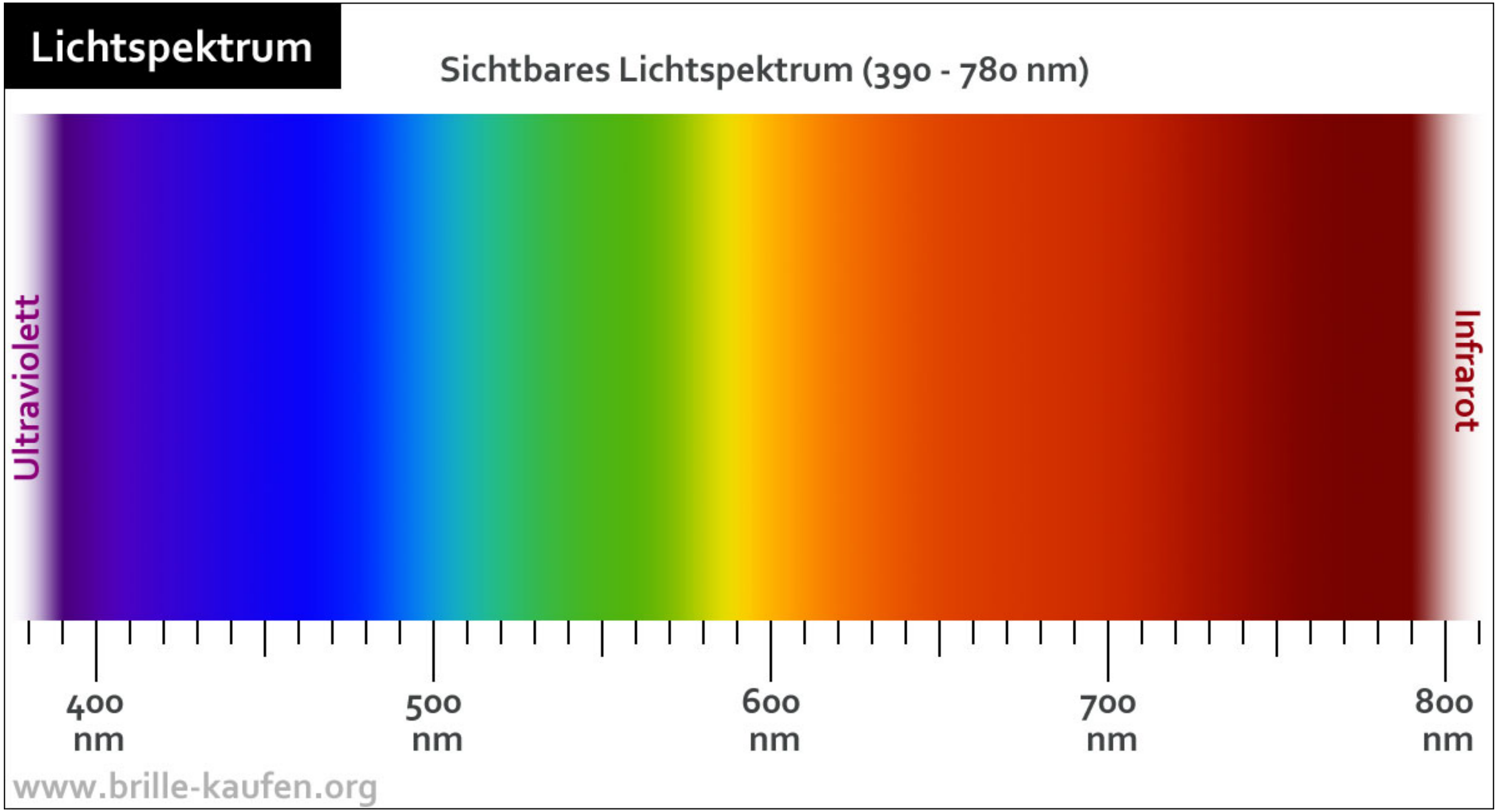
dislocations need space to move and multiply

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

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

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

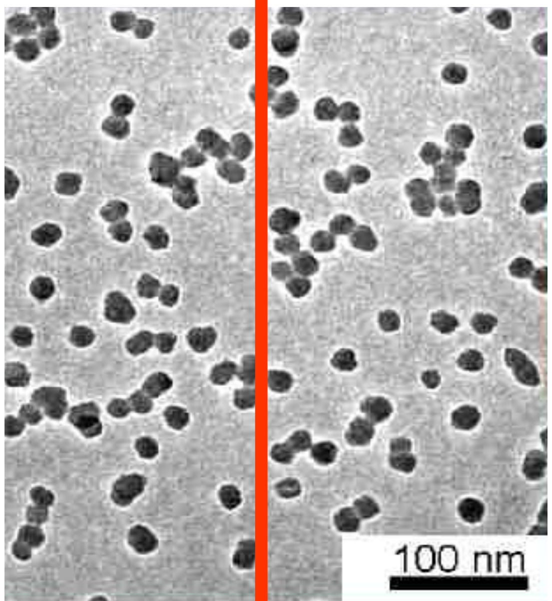
SPEKTRUM DES SICHTBAREN LICHTS

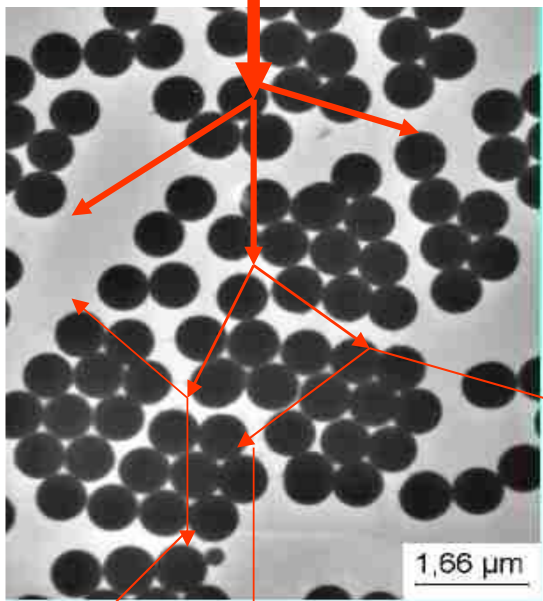


HIGH TRANSPARENCY VIA SMALL PARTICLE SIZE

no light scattering

light scattering





Scattering theory:
Lord Rayleigh 1870
(John Strutt)

Nobel Prize 1904
(discovery of Ar gas)

highly transparent

cloudy

C. Becker-Willinger

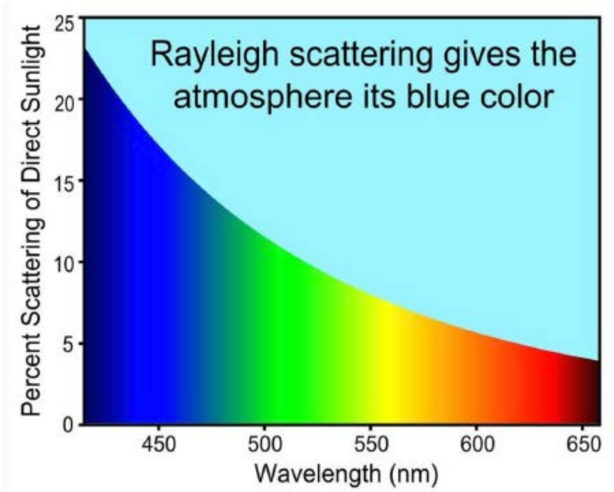
NANOPARTICLES CAN MODIFY OPTICAL PROPERTIES

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

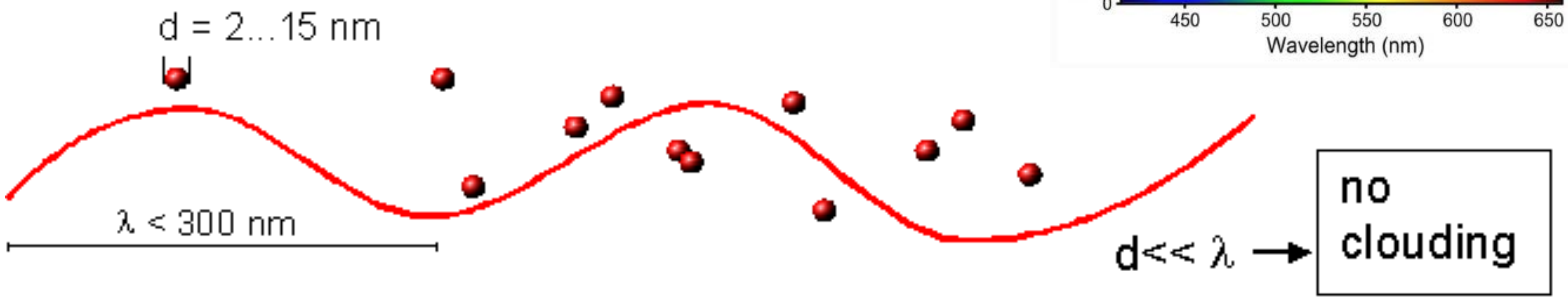
n ... refractive index of composite
n_1...refractive index of matrix
n_2...refractive index of particle
c....vol% particles

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

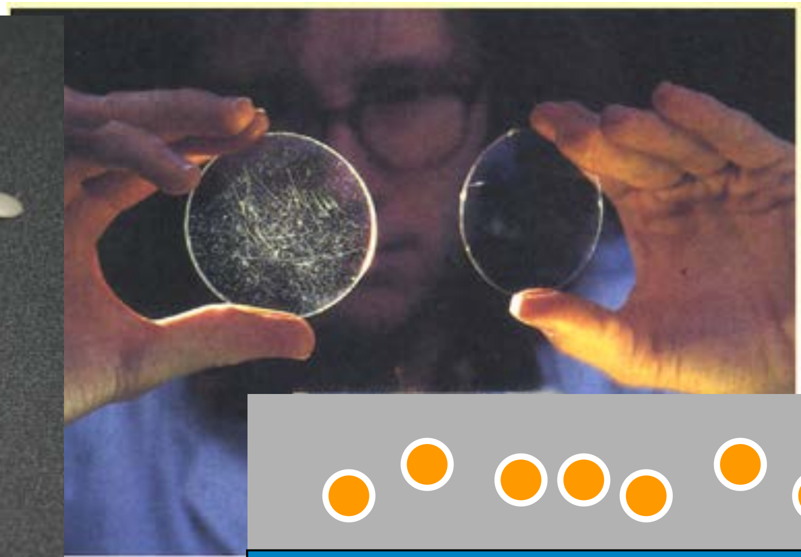
I_{sc}...scattered intensity
I_o...initial intensity
D...particle diameter
λ...wavelength (λ_0/n_1)

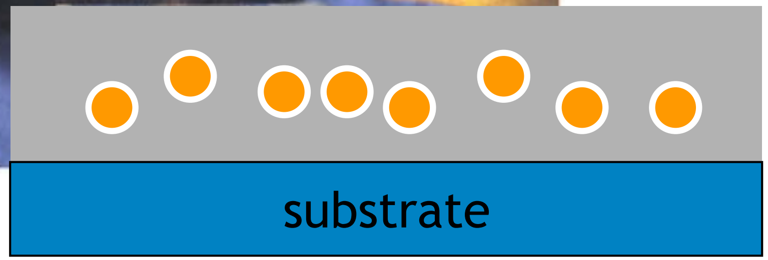


transparency: $D_{max} < 0.05\,\lambda$ (ca. 20 nm), no clusters



SCRATCH RESISTANT *AND* TRANSPARENT



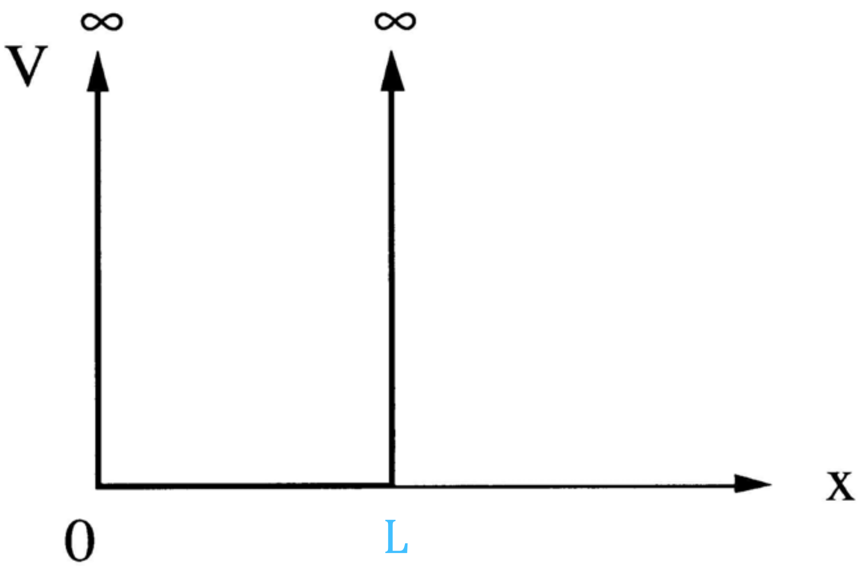


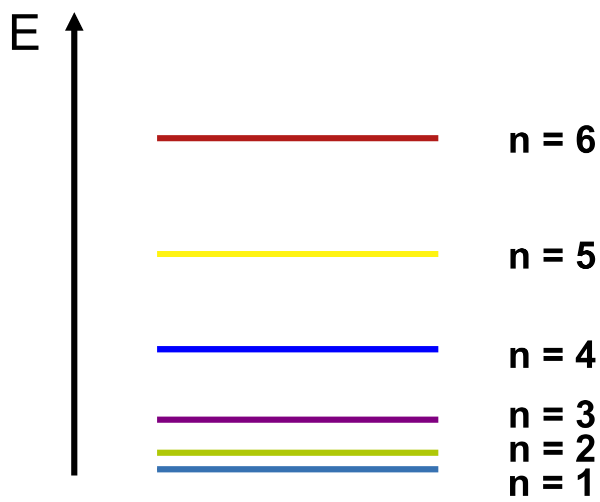
Nanomer® coating for plastic lenses

EU driver license

C. Becker-Willinger, INM

QUANTUM CONFINEMENT OF ELECTRONS IN AN INFINITE WELL OF SIZE L





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**)

ABSORPTION/EMISSION (PHOTON INTERACTION)

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

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

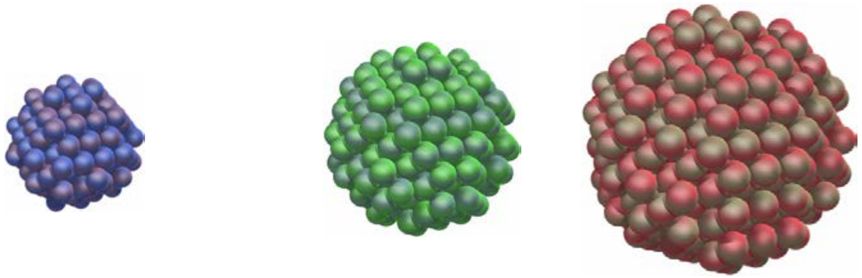
leads to emission/absorption: $\Delta E = h\nu = hc/\lambda$

$$\lambda \propto L^2$$

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

COLOR EFFECTS IN NANOPARTICLES

semi-conductors (quantum confinement) **metals (plasmon resonance)**



CdSe quantum dots [Niemeyer, 2005]

metallic nanoparticles [Wagner, 2007]

"blue shift" with smaller size

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?