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Health consequences of nanoparticles and migration of nanoparticles from packaging to food

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Overview

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3. General properties of NPs
4. Interactions of NPs with biopolymers and living systems
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1. INTRODUCTION

Nanostructure science and technology - a broad and interdisciplinary area of research

Nanotechnology - the most promising technologies of the edge of the centuries.

Number of applications - electronic components, clothes, paints, house-cleaning products, varnishes, environmental remediation technology, energy capture and storage technology, military technology, medical and cosmetic products, agriculture and food

NMs - applied worldwide

Safety, implications on human and environmental health and potential risks - under discussion

Opinions - from “completely harmless and safe” to “extremely hazardous”.

Conflicting results about the nanotoxicity are due to the lack of standardized physico-chemical characterisation of various types of nanoparticles and even different manufactures or batches of the same engineered nanoparticle

Nanoscale - having one or more dimensions of the order of 100 nm or less

Size of pores in human body - about 200 nm $\Rightarrow$ additional toxicity of NMs

Soluble and biodegradable NMs – toxicity as the bulk counterparts

Biopersistent NPs – may accumulate

Physicochemical properties of NPs – structure vs. properties

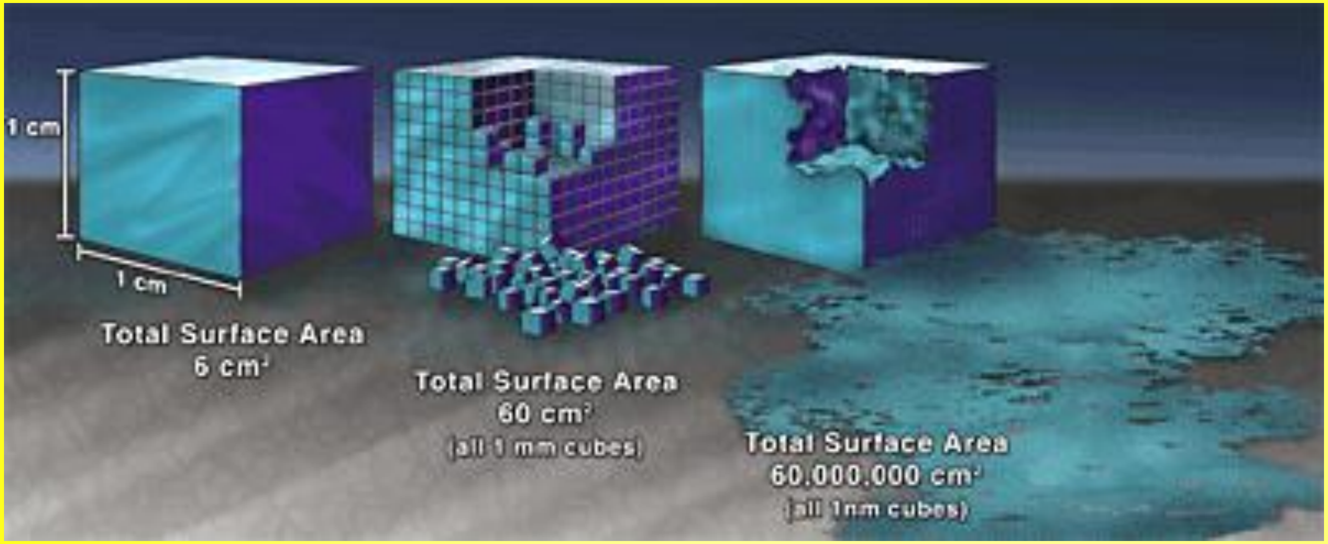
Information on relevant physicochemical properties of NPs:

- essential for proper risk assessment

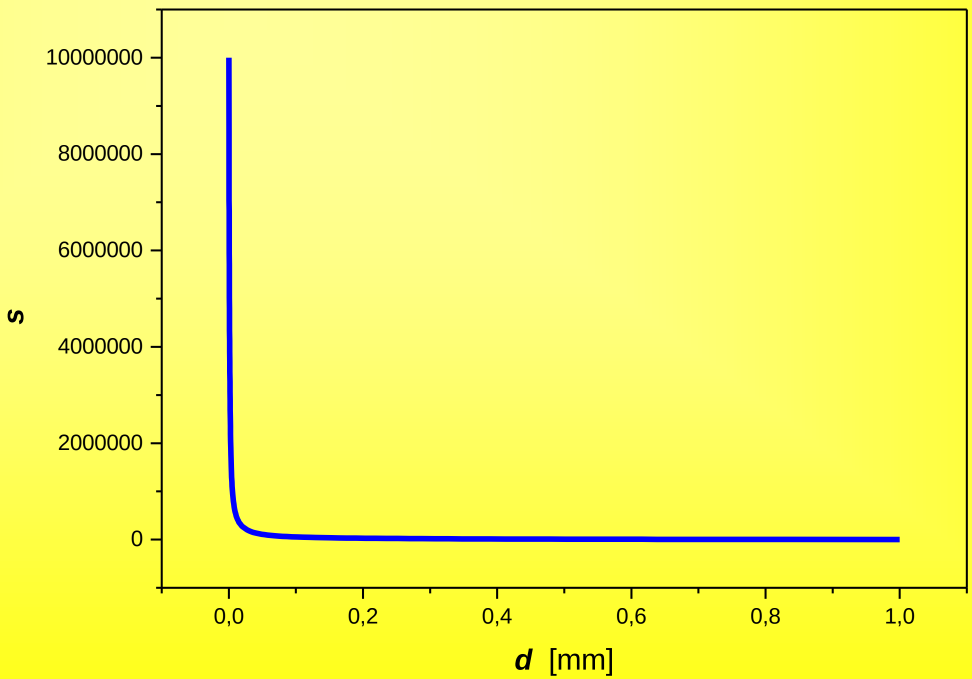
- necessary for the dose assessment

- necessary for the predictability of the interaction of NPs with biological matrices.

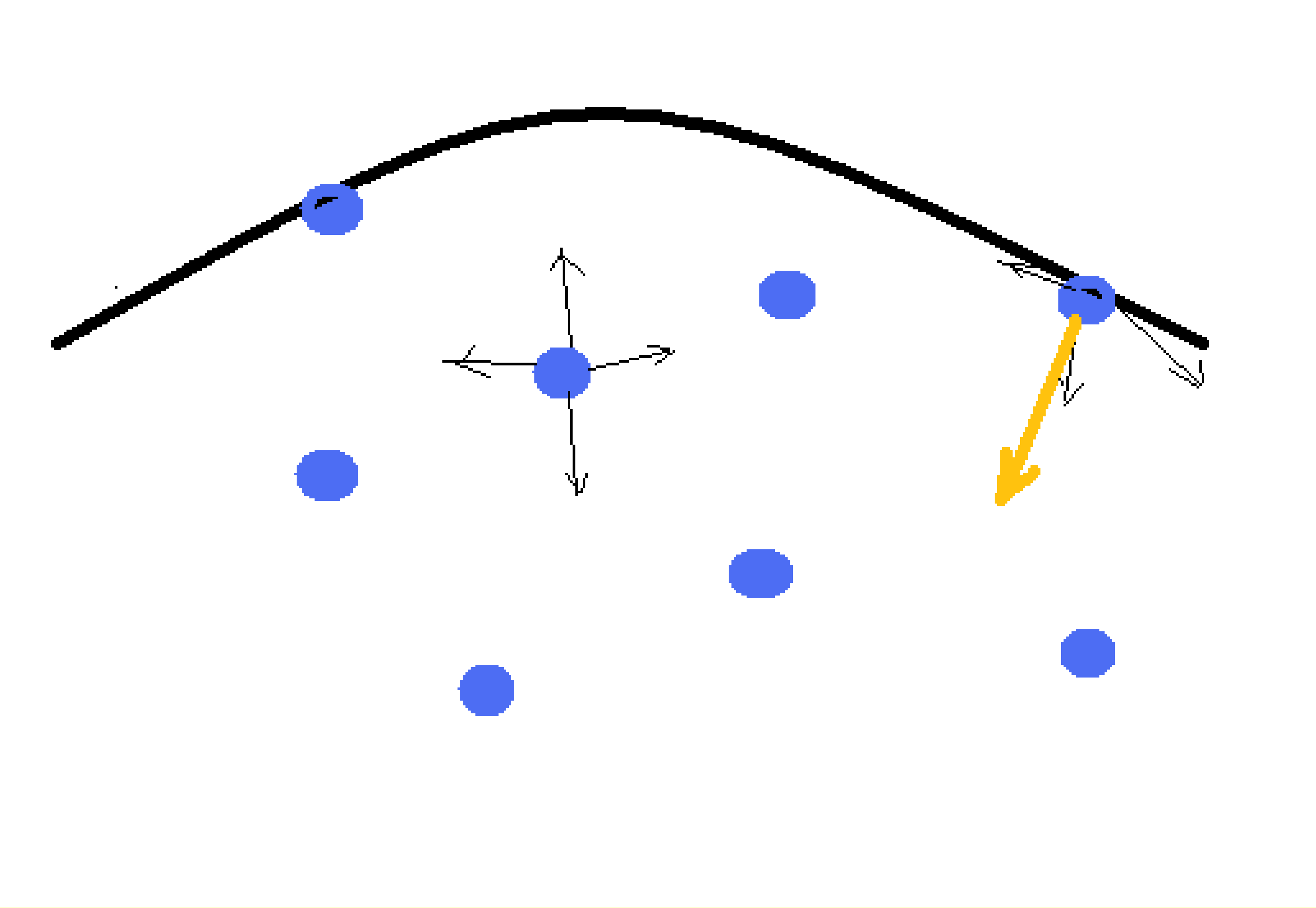
2. Surface free energy and consequences



$$s = \frac{S}{V} \propto \frac{1}{d}$$



Surface energy



Atoms/molecules on a solid surface miss the nearest neighbours above the surface - **unsatisfied bonds exposed to the surface**.

Surface atoms /molecules convey an extra potential energy = **surface free energy**

Due to the huge surface energy, NMs are **thermodynamically unstable** or metastable and exert **high chemical activity**.

Properties of NPs differ from those of the bulk material

Two principal factors cause the properties of nanomaterials to differ significantly from bulk materials, i.e. the **great relative surface area** and **quantum effects**.

The principal parameters of nanoparticles:

- size
- shape (including aspect ratios where appropriate)
- morphological sub-structure of the substance
- composition
- solubility
- surface area per unit mass
- surface layer composition (especially important if this differs from the composition of bulk material)
- surface charge
- particle morphology - extremely important. For example, not only rutile and anatase nanoparticles of TiO_2 are known, but also nanorods, nanotubes, nanowires and other nanoparticle forms are reported. Each nanoform will interact with the surrounding matrix in a different way.

3. General properties of NPs

3.1. ***Relaxation of the surface energy***

Nanomaterials are inherently unstable and highly reactive due to huge surface free energy

Ways of reducing the surface energy:

- agglomeration/aggregation
- adsorption
- ageing

These processes may take some time $\Rightarrow$ properties of nanoparticles may change during ageing due to the changes in surface structure and composition.

3.2. Nanoparticles and crystallization

Recrystallization - Kelvin equation: the saturation solubility increases with decreasing radius of the particle $\Rightarrow$ small NPs dissolve and recrystallize giving bigger particles.

Nanoparticles can act as nuclei for the **heterogeneous crystallization**. The crystallization can be induced and facilitated by impurities, i.e. nanoparticles, acting as foreign surfaces.

3.3.Catalysis

High surface energy and abundance of structural defects result in catalytic effects, mainly for inorganic NPs.

Many transition metal oxides are selective oxidation catalysts. In addition, these materials tend to produce free radicals.

Acidic solids such as silica-aluminas are excellent for catalyzing reactions of the carbocation type which are initiated by protons.

The possible catalytic influence of NPs, mainly for the oxidation reactions, should always be taken into account.

NANOPARTICLES IN FOOD

Biopersistent micro- and nanoparticles commonly found in food:

-silicon dioxide (SiO_2, E551),

-magnesium oxide (MgO, E530)

-titanium dioxide anatase (TiO_2, E171).

-The antimicrobial properties of nanosilver are known and such properties have recently been discovered for nano-zinc oxide and magnesium oxide

4. INTERACTIONS OF NANOPARTICLES WITH A LIVING SYSTEM

To understand the mechanisms of **nanoparticle toxicity -** information on the response of living systems to NPs is needed.

NPs can interact with all functional groups in biopolymers via physical, polar or chemical adsorption.

Ionic crystal nanoparticles have been observed to **accumulate protein layers**.

Many biomolecules consist of long folded macromolecular chains. Here, nanoparticles, of a few nm in size, may intrude into the complex folded structures and can bring about, for example, **DNA damage**.

Charged NPs in ionic solutions are **surrounded by an atmosphere of oppositely charged ions**.

When NPs move, **electrokinetic phenomena** can take place, such as the stream potential.

The electrokinetic phenomena can give rise to **potential differences in the body**.

Charge of NPs may play an important role in penetrating through pores, canals, etc. T**he fundamental membrane processes** of living cells, for example, generation of ion gradients, sensory transductance, conduction of impulses, and energy transduction, **are electrical in nature**. All these processes may be affected by the presence of charged NPs.

NPs are **oxidation catalysts**

Reactive oxygen species are formed inducing **oxidative stress** and inflammation.

A major consequence of oxidative stress is **damage to nucleic acid bases, membrane lipids, and proteins**, which in turn may contribute to development of various diseases.

A physico-chemical property omitted up to now is the **induced crystallization**.

This could be important for **enhanced deposition of urea acid, cholesterol or blood clotting**.

Nanoparticle-induced platelet aggregation and vascular thrombosis has been reported recently.

Nanoparticles are found to enhance the rate of protein fibrillation by decreasing the lag time for nucleation. Protein fibrillation is involved in many human diseases, including the Alzheimer and Creutzfeld-Jacob disease

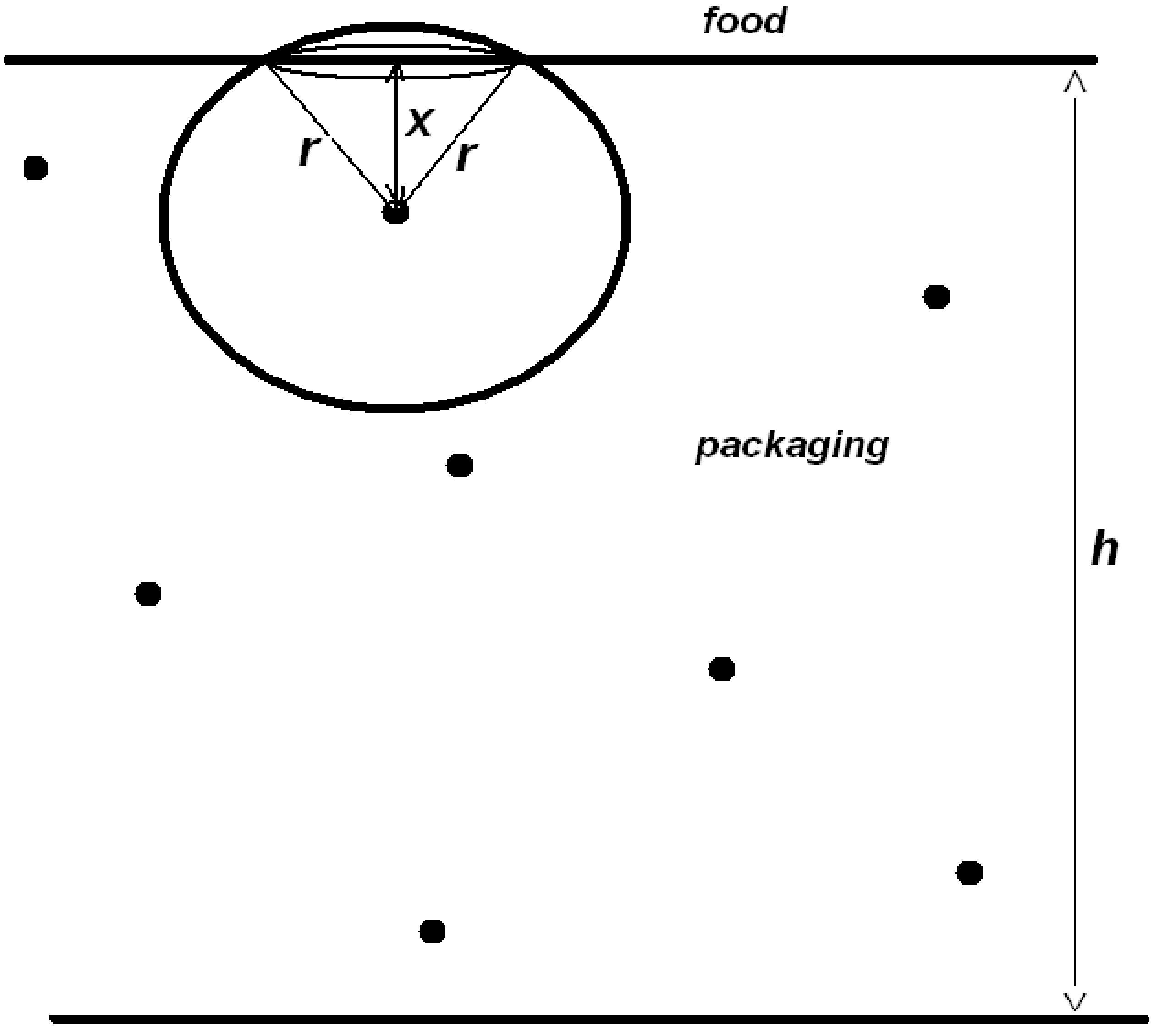
5. Migration of nanoparticles from packaging to food

Stokes-Einstein relation: $$D = \frac{k_B T}{6\pi\eta a}$$

The average distance, *r*, travelled by particles: $$r = 2\left(\frac{Dt}{\pi}\right)^{1/2} = \left(\frac{2k_B Tt}{3\pi^2\eta a}\right)^{1/2}$$

Williams-Landel-Ferry equation for polymer melts: $$\eta \;\; T \;\; = \eta \;\; T_g \;\; \exp\left[-\frac{C_1 \;\; T - T_g}{C_2 + T - T_g}\right]$$

The ability of NPs to migrate from the packaging to food, i.e. the migratability (*m*): $$m = \frac{n}{Sc_0} = \frac{1}{4}\left(\frac{2k_B Tt}{3\pi^2\eta a}\right)^{1/2} = \left(\frac{k_B Tt}{24\pi^2\eta a}\right)^{1/2}$$


food
x
r
r
packaging
h

Polymer	***m*** [m] 25 °C 1 month	***m*** [m] 25 °C 1 year	***m*** [m] 4 °C 1 month	***m*** [m] 4 °C 1 year	***m*** [m] –18 °C 1 month	***m*** [m] –18 °C 1 year
LDPE	3.7×10^{-7}	1.3×10^{-6}	2.5×10^{-7}	8.9×10^{-7}	1.9×10^{-7}	6.7×10^{-7}
HDPE	2.6×10^{-7}	9.2×10^{-7}	1.5×10^{-7}	5.3×10^{-7}	6.9×10^{-8}	2.4×10^{-7}
PP	1.5×10^{-7}	5.2×10^{-7}	5.1×10^{-8}	1.8×10^{-7}	8.0×10^{-9}	2.8×10^{-8}
PET	$< 3.0 \times 10^{-9}$	$< 1.0 \times 10^{-8}$	$< 2.9 \times 10^{-9}$	$< 1.0 \times 10^{-8}$	$< 2.8 \times 10^{-9}$	$< 9.7 \times 10^{-9}$
PS	$< 2.1 \times 10^{-9}$	$< 7.4 \times 10^{-9}$	$< 2.0 \times 10^{-9}$	$< 7.1 \times 10^{-9}$	$< 2.0 \times 10^{-9}$	$< 6.8 \times 10^{-9}$

Migration of NPs from packaging to food will be detected mainly in the case of:

- very small NPs with the radius in the order of 1 nm
- from the polymer matrices that have a relatively low dynamic viscosity,
- from the polymer matrices that do not interact with the NPs.
- These conditions could be met for nanocomposites of silver with polyolefines (LDPE, HDPE, PP).
- For bigger NPs that are bound in polymer matrices with relatively high dynamic viscosity, the migration will not be detectable.
- This corresponds to nanosilver composites with PET and PS, and surface-modified montmorillonite embedded in various polymer matrices.

Conclusions

1. Nanomaterials – may enter unusual sites in the body

2. Biopersistent nanomaterials may accumulate

3. On the molecular level, the interaction of NPs with biopolymers, water and ions can be expected

4. **Information on physicochemical properties** inevitable to understand the mechanism of toxicity

Publications:

1. Šimon P. & Joner E., *Journal of Food and Nutrition Research* **47** (2008) 51-59: Conceivable interactions of biopersistent nanoparticles with food matrix and living systems following from their physicochemical properties.

2. Šimon P., Chaudhry Q. & Bakoš D., *Journal of Food and Nutrition Research* 47 (2008) 105-113: Migration of engineered nanoparticles from polymer packaging to food – a physicochemical view.

Thank you for your attention!

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