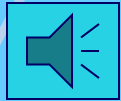


Audio test:



Kohezní a táhnutí NPs

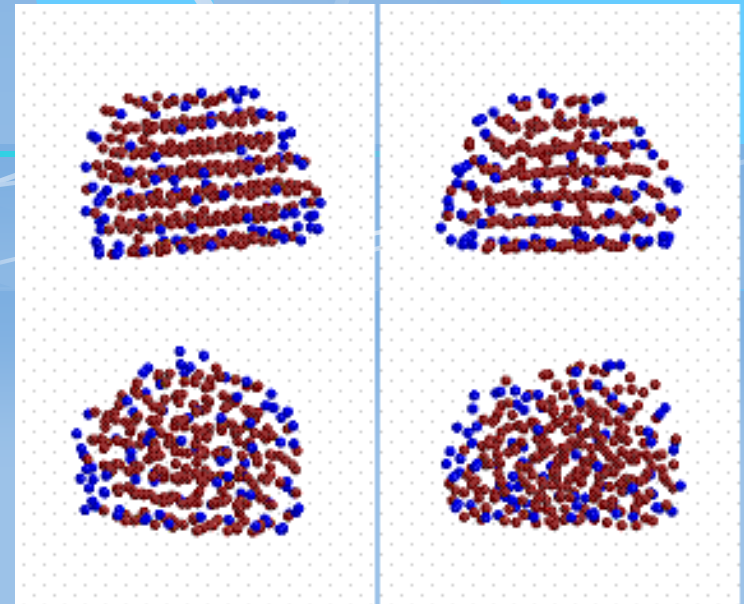
Start



Brno, PS 2012

Přednášející: doc. Jiří Sopoušek E-mail:
sopousek@mail.muni.cz, tel.: 549497138

Ofice: UKB A12/M231



Kohezní energie bulku

Kohezní energie je rozdíl energie atomů vázaných v pevné látce a energie jednotlivých atomů v plynné fázi

$$E_c = E_{\text{tot}}(A, g) + E_{\text{tot}}(B, g) - E_{\text{tot}}(AB, s) > 0$$

Závisí na charakteru vazby:

Iontová vazba - elektrostatické síly mezi ionty, lokalizované elektrony, vysoká vazebná energie.

Kovalentní vazba - sdílení valenčních elektronů mezi sousedními atomy, orientované vazby, vysoké až střední energie vazeb.

Kovová vazba - sdílení malého množství elektronů všemi atomy krystalu, volné elektrony, nízká vazebná energie

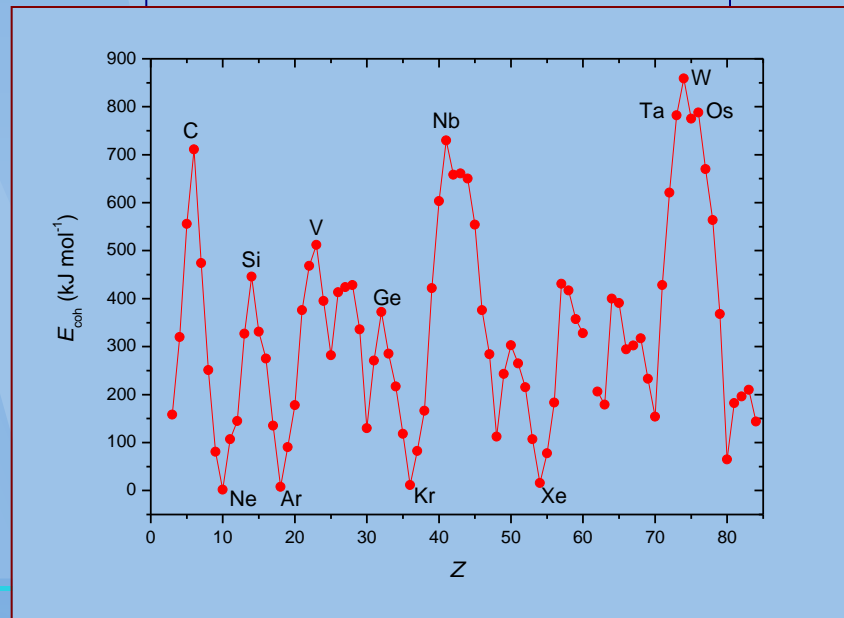
Slabé vazby - van der Waalsovy síly (dipól-ion, dipól-dipól, indukované dipóly), H-vazby

Víceatomové molekuly v plynné fázi:

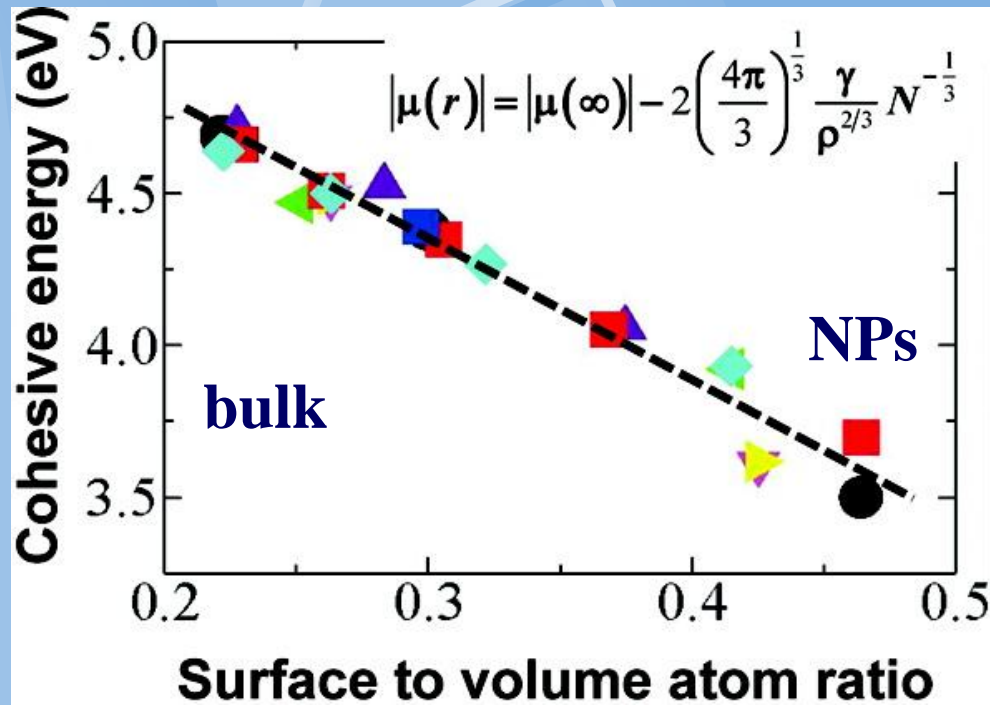
$$E_c = \frac{1}{2} E_{\text{tot}}(A_2, g) - E_{\text{tot}}(A, s)$$

Čisté kovy

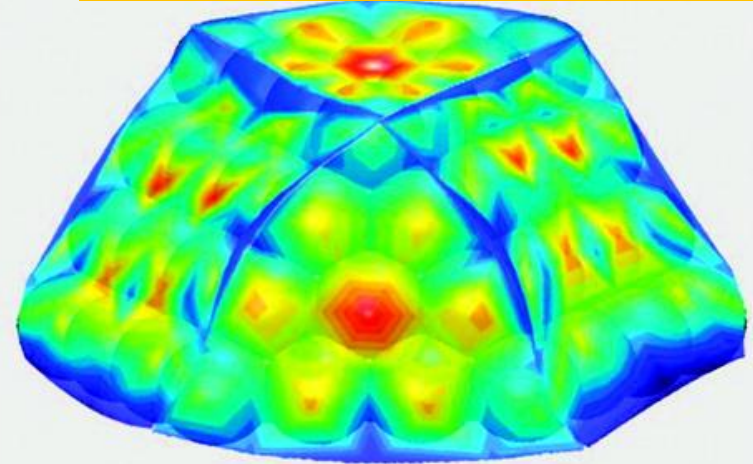
$$E_c = E_{\text{tot}}(A, g) - E_{\text{tot}}(A, s)$$



Kohezivní energie NPs



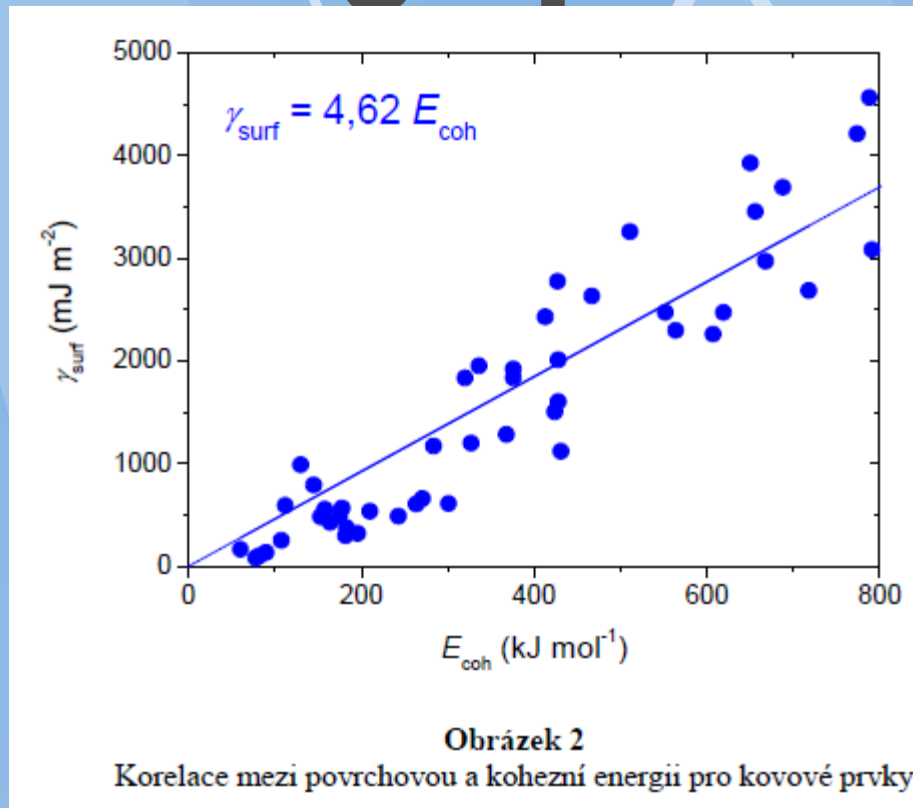
Kohezní energie není všude stejná (ab-initio výpočet):



Kohezivní energie nanočástic různých tvarů a velikosti jako funkce podílu povrchu k objemu.

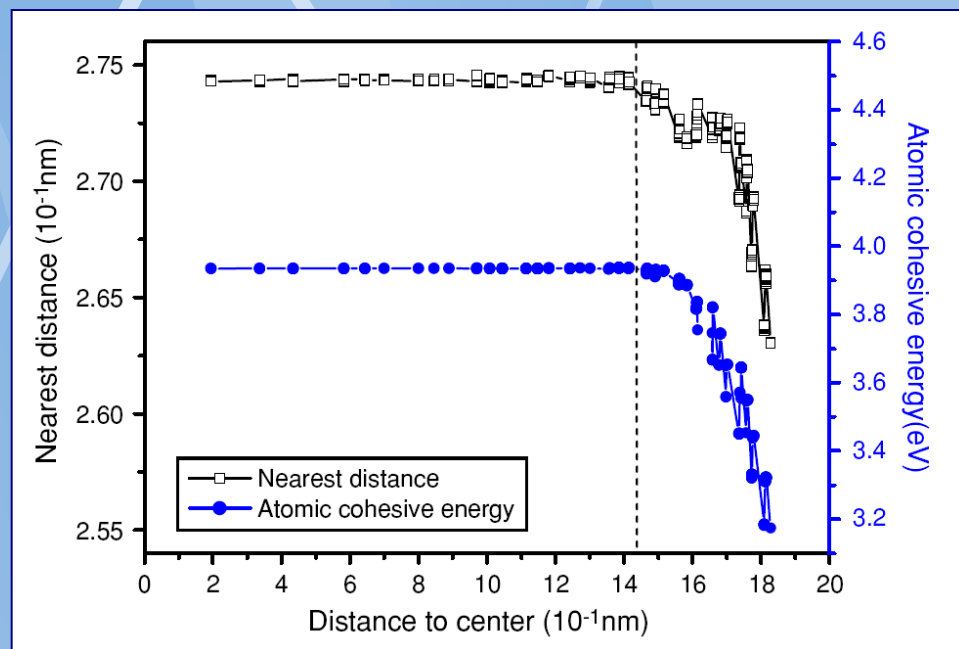
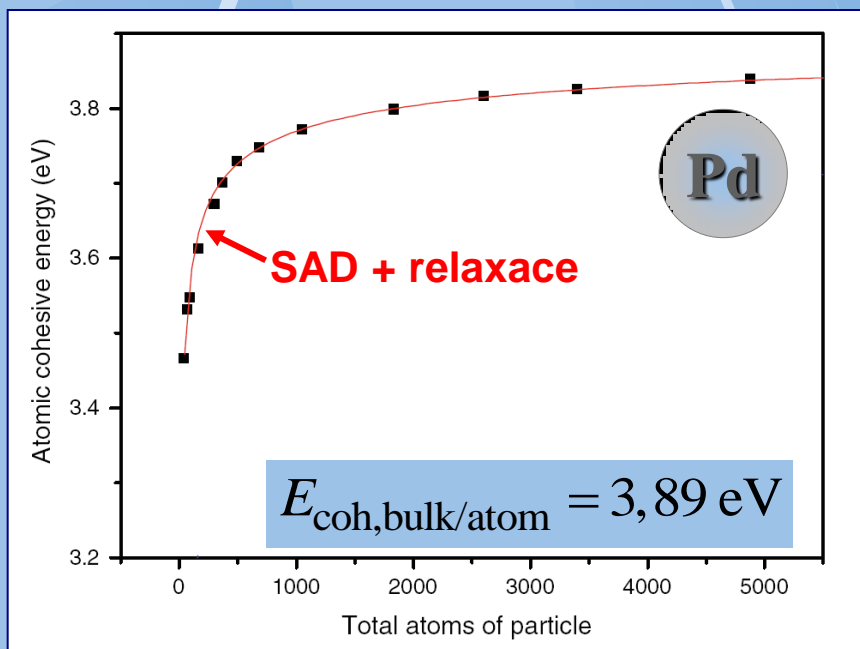
Místa náchylná k adsorpci kyslíku.

Korelace mezi povrchovou a kohezní energií pro bulk



Kohezní energie povrchu NPs

Povrchové atomy jsou vázány menším počtem kratších a pevnějších vazeb – kohezní energie $E_{\text{coh,surf/atom}} < E_{\text{c,bulk/atom}}$



$$N_{\text{at}} = 1830, \quad r_{\text{np}} = 1,84 \text{ nm}$$

Nanoscale Res Lett (2009) 4:269–273
 DOI 10.1007/s11671-008-9236-z

NANO EXPRESS

Structure of Unsupported Small Palladium Nanoparticles

Weihong Qi · Baiyun Huang · Mingpu Wang

Stlačitelnost

$$\kappa_T = \frac{1}{B_T} = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = \frac{1}{V} \left(\frac{\partial^2 F}{\partial V^2} \right)_T^{-1} = f(V, T) \quad \text{nebo} \quad f(p, T)$$

$$B_p = B_0 + B'p$$

$$\Delta p = p_{\text{in}} - p_{\text{out}} = \frac{2f}{r}$$

$$B_p = B_0 + B' \frac{2f}{r}$$

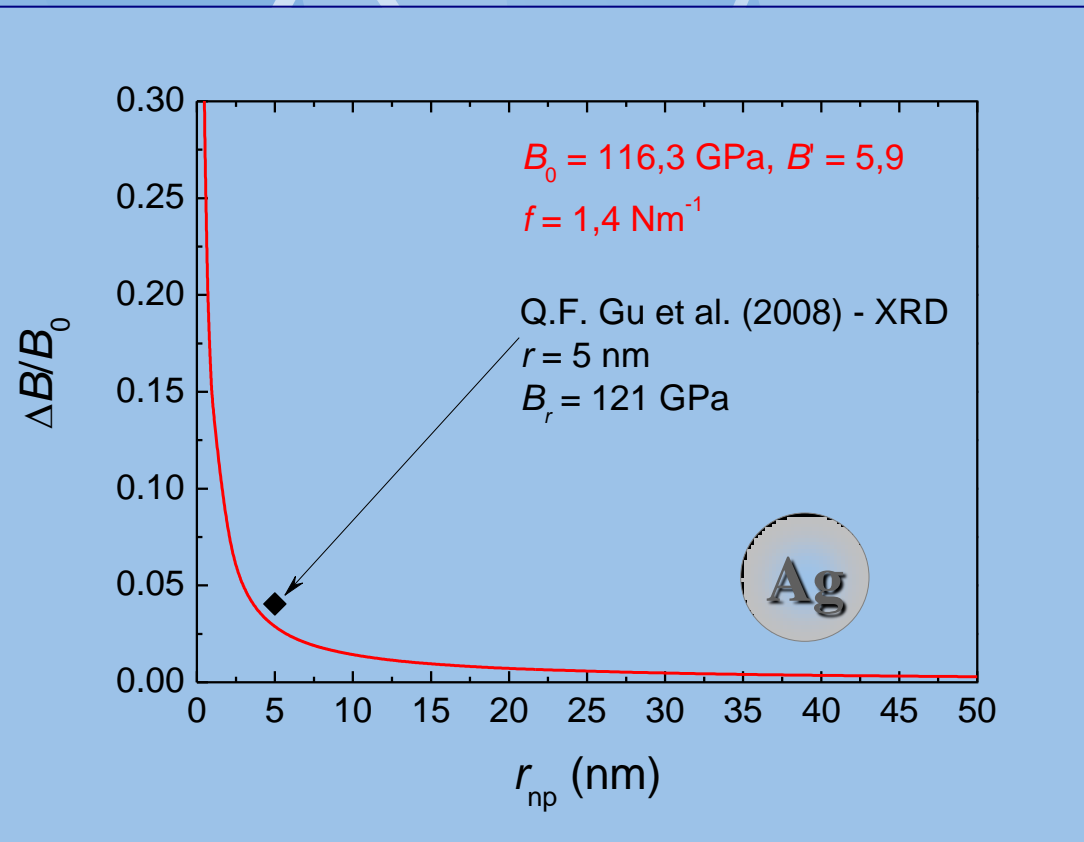
Postup stanovení B_0 a B'

Nanomateriál: r

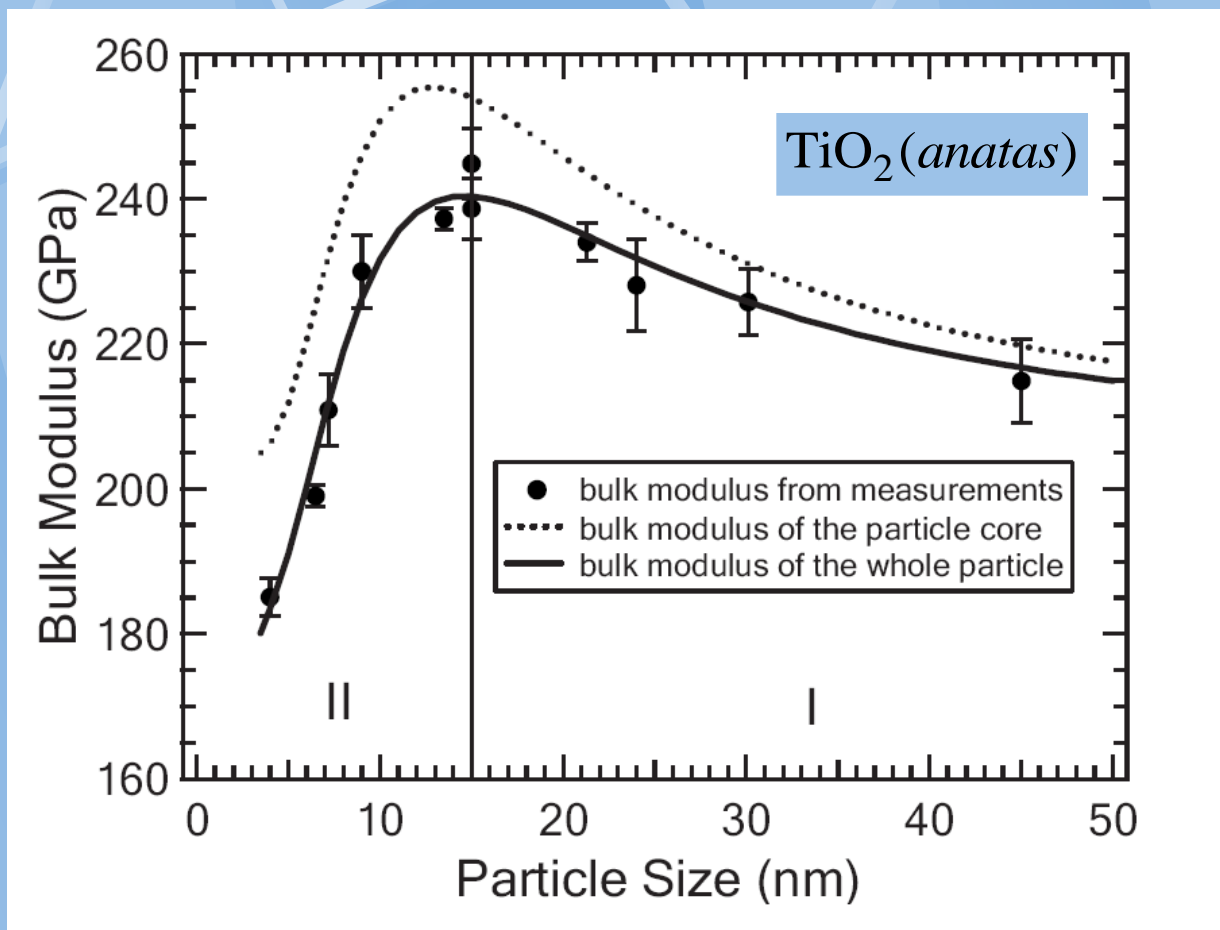
HP-XRD: $a(p) \rightarrow V(p)$

EOS: $V/V_0 = f(p) \rightarrow B_0, B'$

Závislost $B_0, B' = f(r)$



Stlačiteľnosť II



PHYSICAL REVIEW B 79, 125406 (2009)

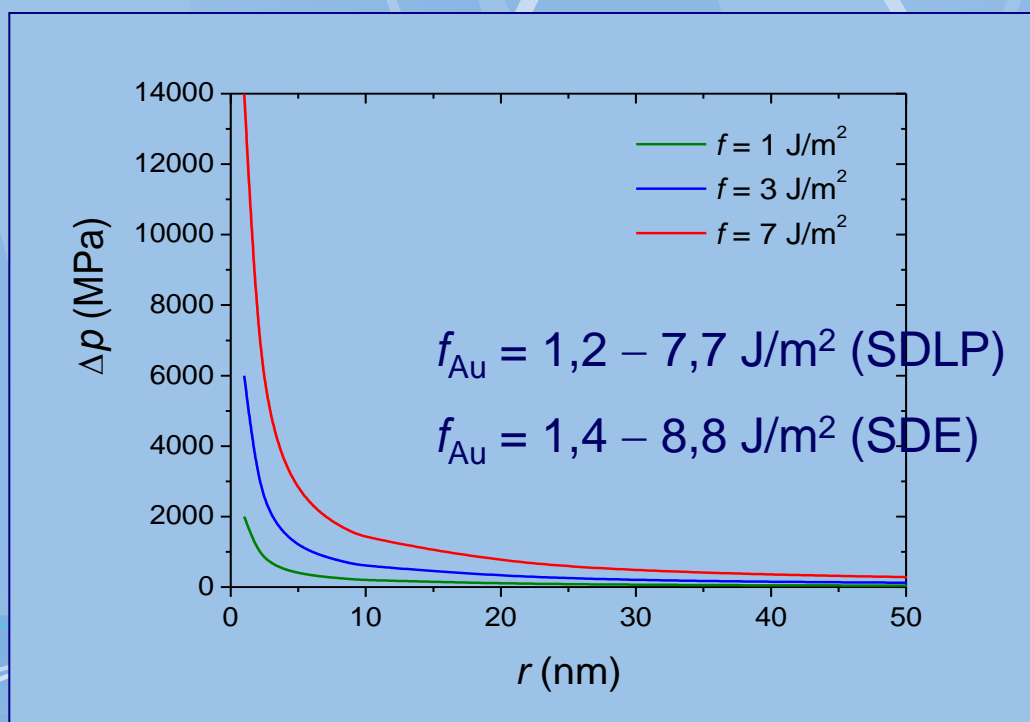
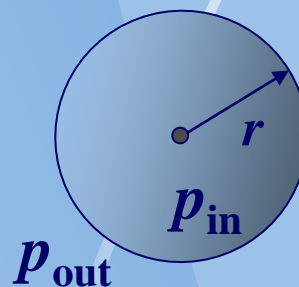
Size-dependent elasticity of nanocrystalline titania

Bin Chen,^{1,*} Hengzhong Zhang,¹ K. A. Dunphy-Guzman,^{1,2} D. Spagnoli,¹ M. B. Kruger,³ D. V. S. Muthu,^{3,4} M. Kunz,⁵ Sirine Fakra,⁵ J. Z. Hu,⁶ Q. Z. Guo,⁶ and Jillian F. Banfield¹

Tlak par nad NPs

Youngova-Laplaceova rovnice (1805)

$$\Delta p = p_{\text{in}} - p_{\text{out}} = \frac{2f}{r}$$



Elastická deformace

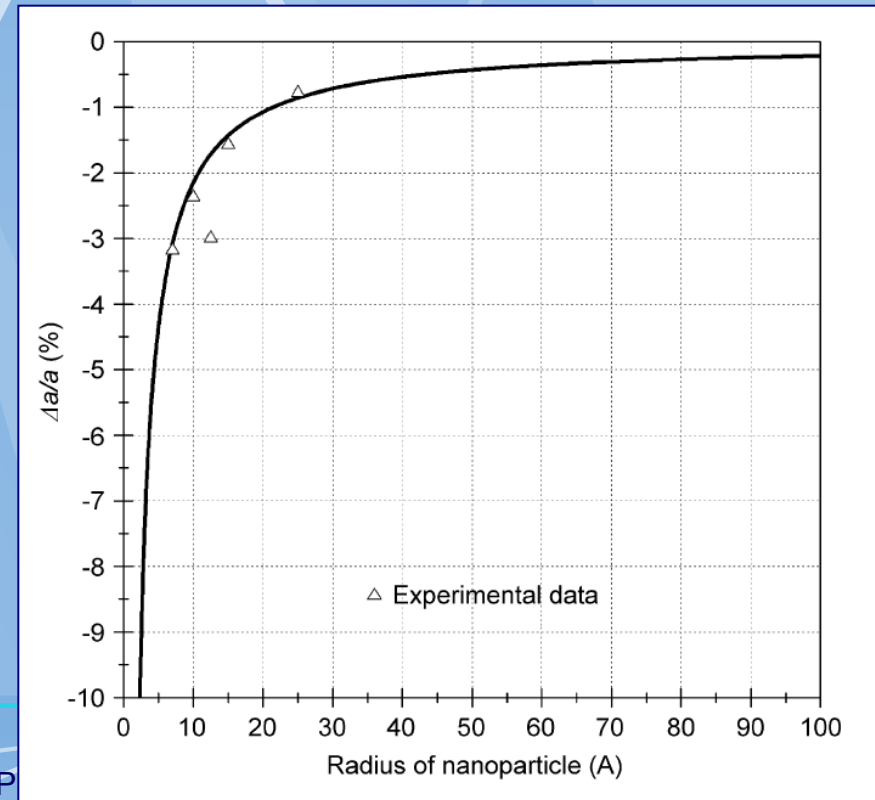
EDIST (elastic deformation induced by the surface tension)

Závislost f na velikosti nanočástice

Tvarový faktor α pro nekulaté nanočástice

$$\gamma(r) = \frac{\gamma_0}{1 + 2\delta/r}$$

$$\frac{\Delta a}{a} = - \frac{2\beta f / 3}{2\delta + r + \sqrt{r^2 + 4\delta(r + \delta - 4\beta f / 3)}}$$



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ScienceDirect

Journal of Physics and Chemistry of Solids 68 (2007) 530–535

JOURNAL OF
PHYSICS AND CHEMISTRY
OF SOLIDS

www.elsevier.com/locate/jpcs

Lattice contractions of a nanoparticle due to the surface tension:
A model of elasticity

Zaixing Huang^{a,*}, Peter Thomson^b, Shenglin Di^c

ce P

Vliv velikosti na teplotu tání/tuhnutí nanočástic

J.J. Thomson (1888)

Applications of Dynamics to Physics and Chemistry
... Effect of surface tension on the freezing point

P. Pawlow (1909)

Melting point dependence on the surface energy of a solid body

M. Takagi (1954)

Electron-diffraction study of liquid-solid transition of thin metal films

K.K. Nanda (2009)

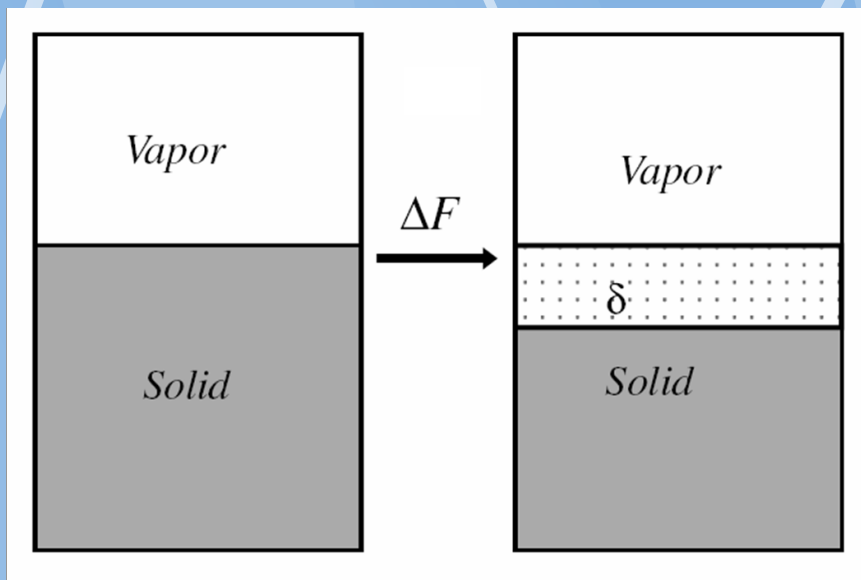
Size-dependent melting of nanoparticles: Hundred yers of thermodynamic model

Chem. Listy 105, 174–185 (2011)

TEPLOTA TÁNÍ NANOČÁSTIC

Proč závisí teplota tání na velikosti ?

1. Povrchové tání objemového materiálu



$$\gamma_{sl} + \gamma_{lg} < \gamma_{sg}$$

2. Velký poměr povrch/objem

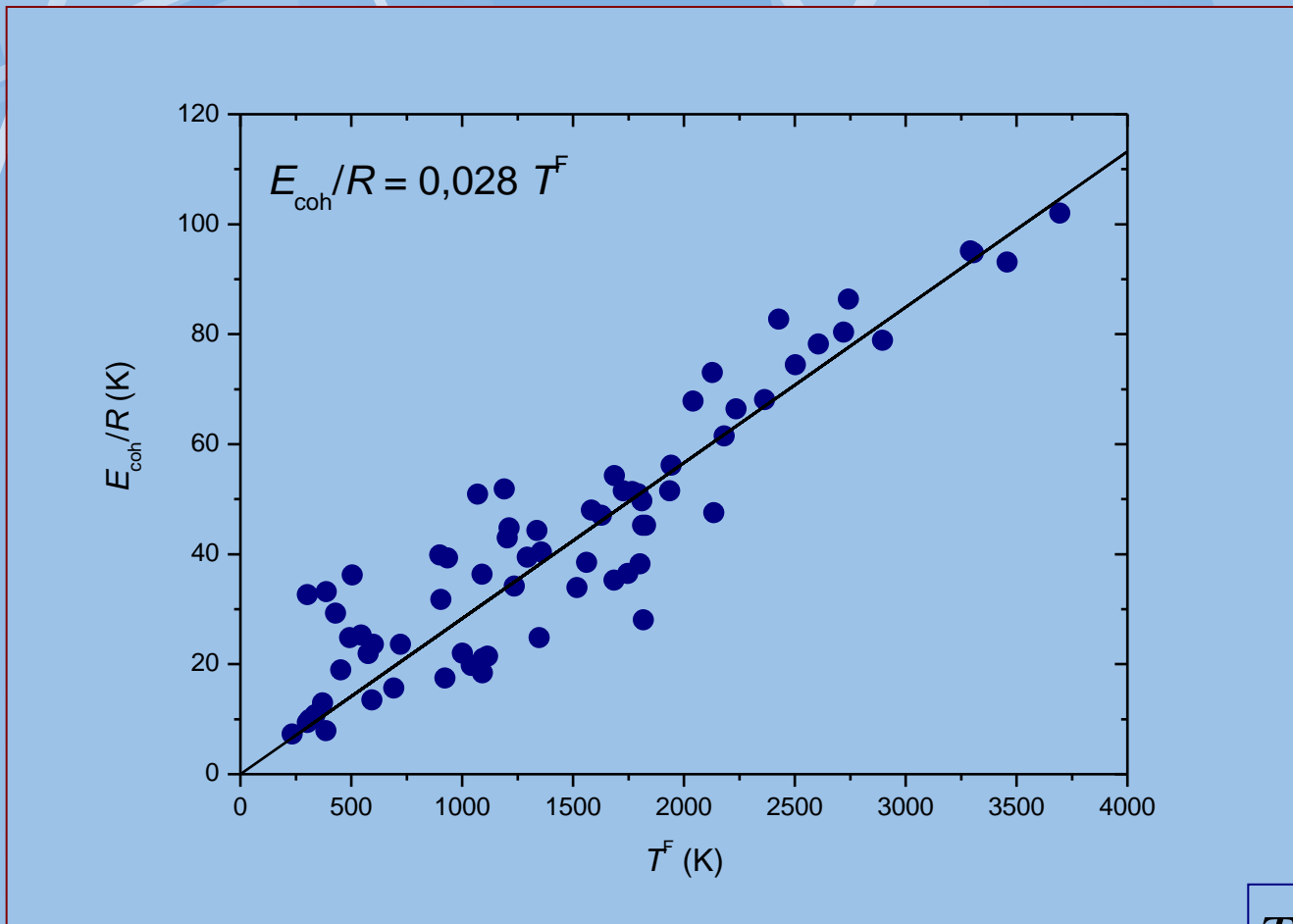
Experimentální metody

- Kalorimetrie (DSC, nano-DSC)
- Elektronová mikroskopie (ED, DF, BF)
- Vysokoteplotní XRD
- Speciální metody

Teoretické modely

- Korelace T^F a E_c
- Lindemannovo kritérium ($\text{msd}_{\text{surf}} > \text{msd}_{\text{bulk}}$)
- Rovnováha (solid)-(liquid)
- Molekulární simulace
- *Ab-initio* výpočty

Teplota tání, stejně jako kohezní energie, je mírou pevnosti vazby



$$\frac{T_r^F}{T_\infty^F} \approx \frac{E_{c,r}}{E_{c,\infty}}$$

C.H. Li et al. / Journal of Physics and Chemistry of Solids 64 (2003) 201–212

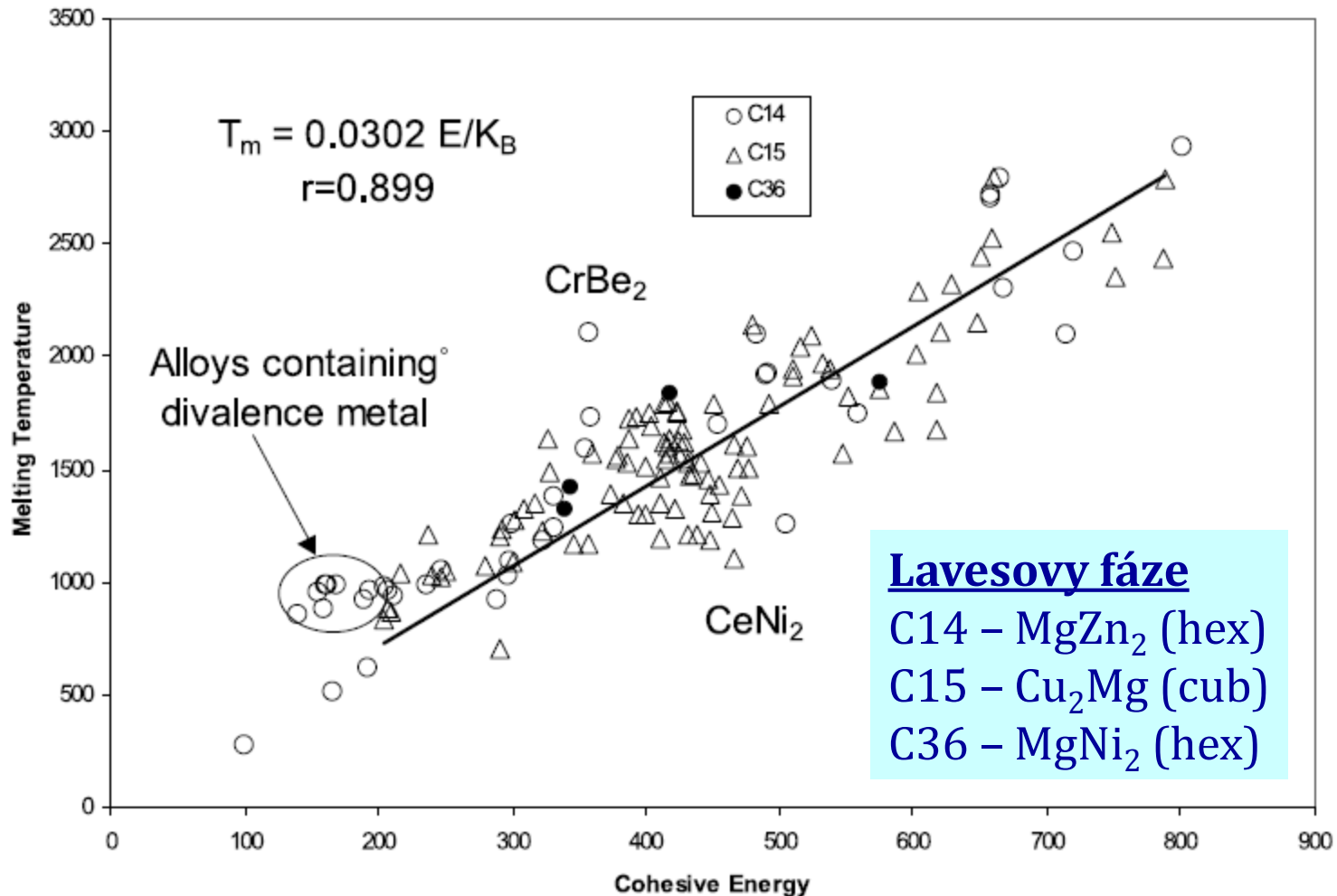


Fig. 4. Melting temperature vs. cohesive energy for Laves phases.

Teplota tání nanočástic I - Bond energy



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Physica B 368 (2005) 46–50

PHYSICA B

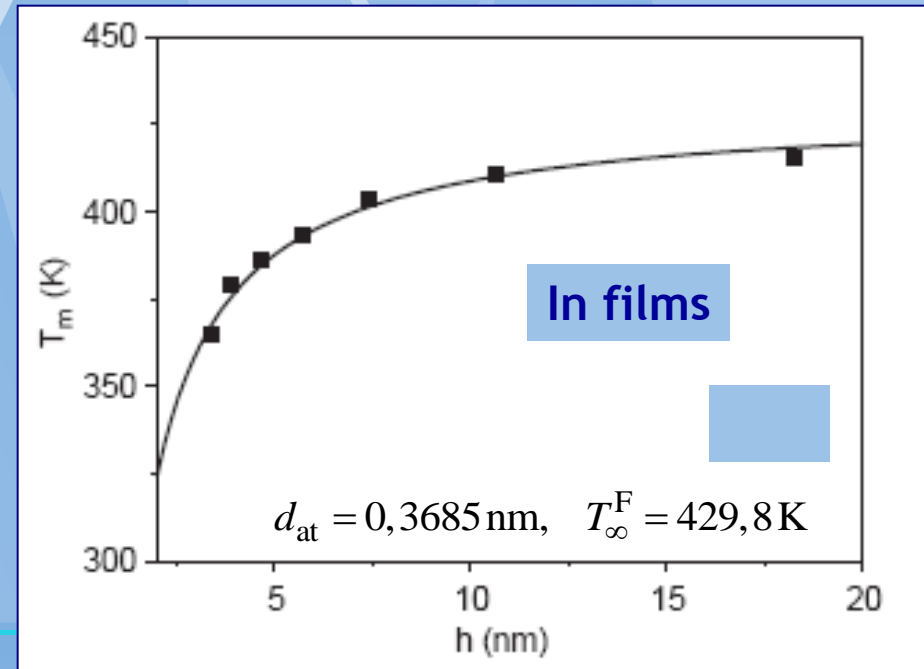
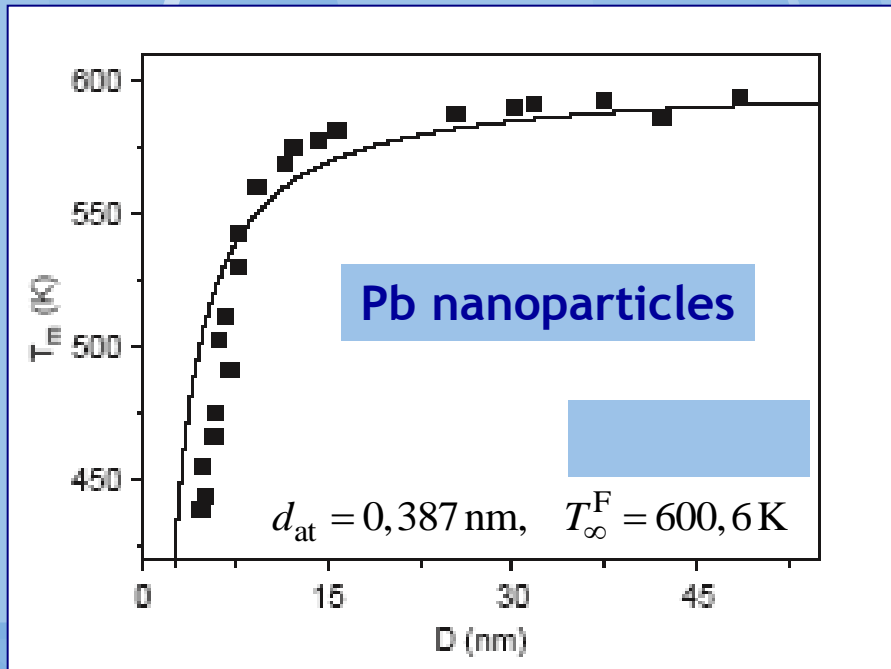
www.elsevier.com/locate/physb

Size effect on melting temperature of nanosolids

W.H. Qi*

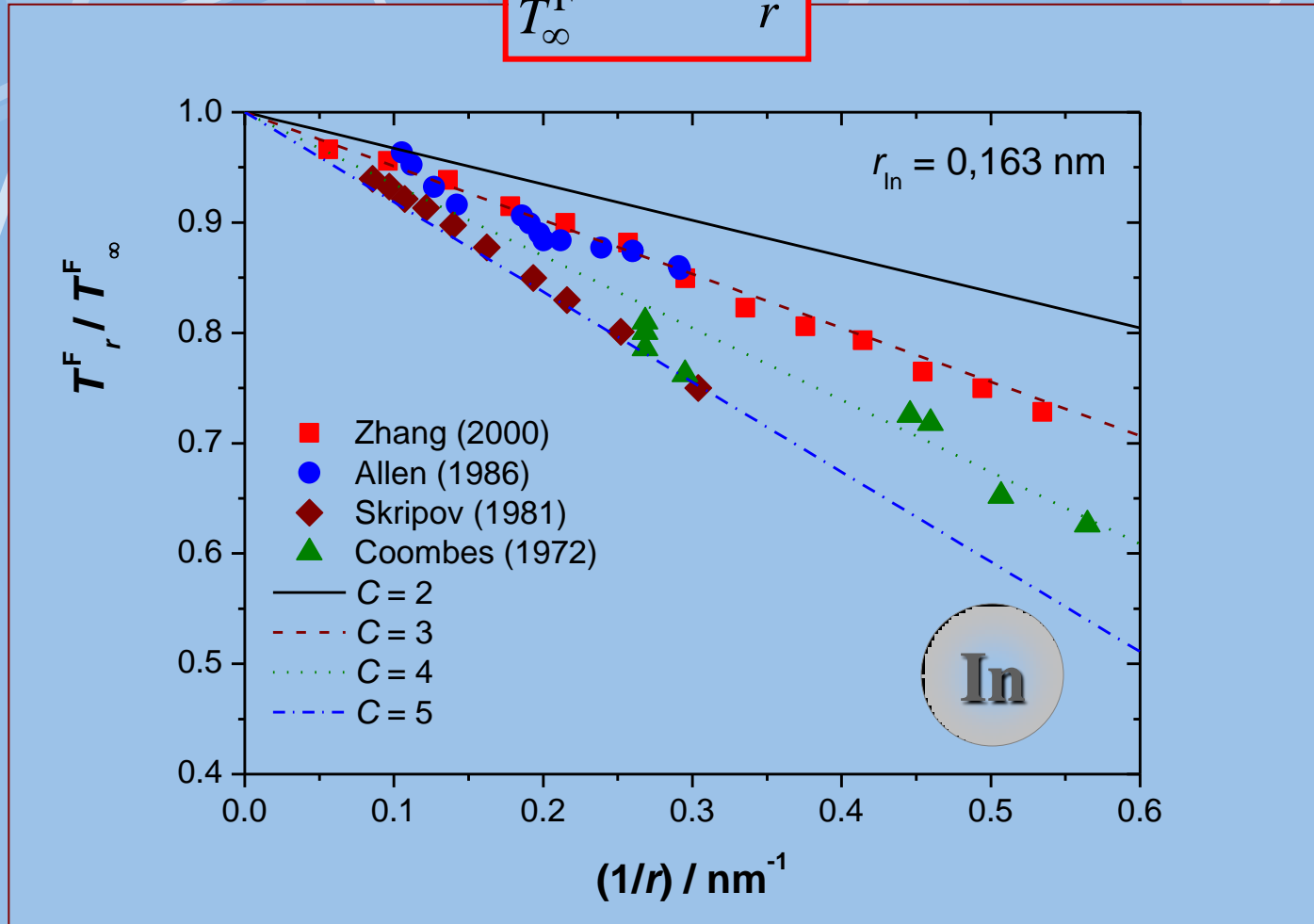
$$T_r^F = T_\infty^F \left(1 - \frac{d_{at}}{r} \right)$$

$$T_h^F = T_\infty^F \left(1 - \frac{2d_{at}}{3h} \right)$$



Teplota tání nanočástic I

$$\frac{T_r^F}{T_\infty^F} = 1 - C \frac{r_{at}}{r}$$



Teplota sublimace nanočástic

Physics Letters A 372 (2008) 6930–6934

Contents lists available at ScienceDirect



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Physics Letters A

www.elsevier.com/locate/pla

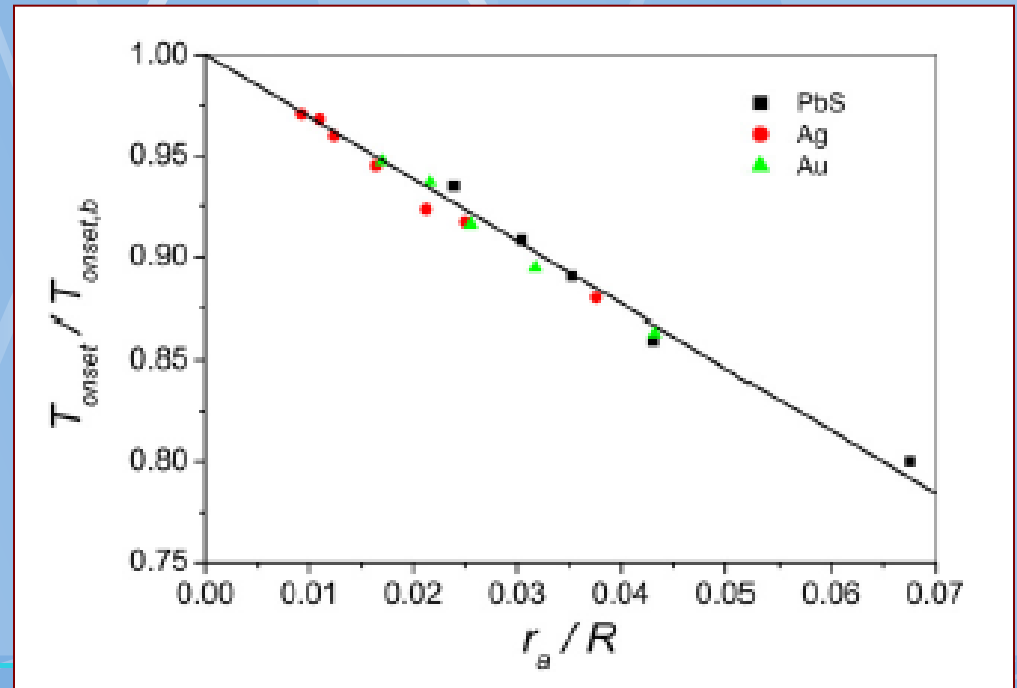


A universal relation for the cohesive energy of nanoparticles

S.C. Vanithakumari, K.K. Nanda*

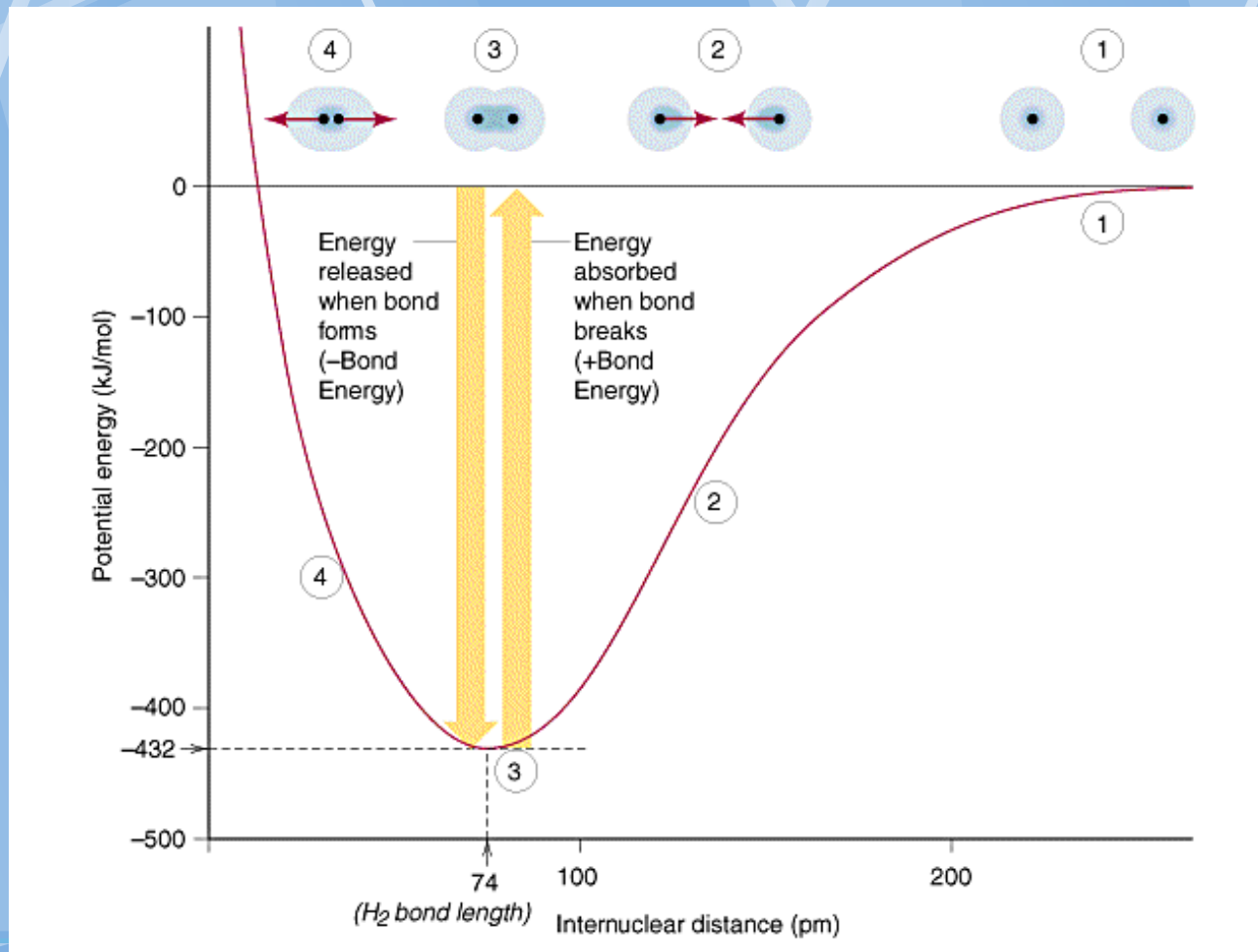
Materials Research Centre, Indian Institute of Science, Bangalore 560012, India

$$\frac{E_{c,r}}{E_{c,\infty}} = \frac{T_r^{\text{subl}}}{T_\infty^{\text{subl}}} = 1 - C \frac{r_{at}}{r}$$



Aktivační energie difúze

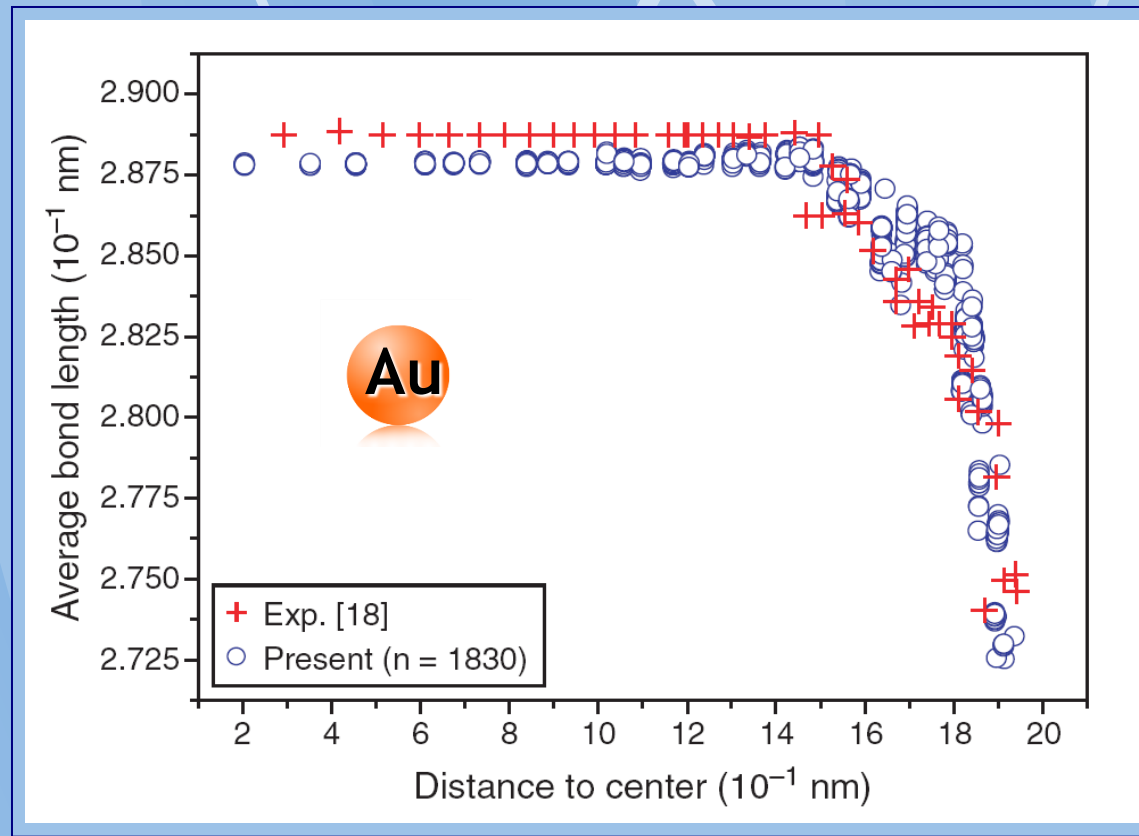
Kohezní energie vs. vazebná energie

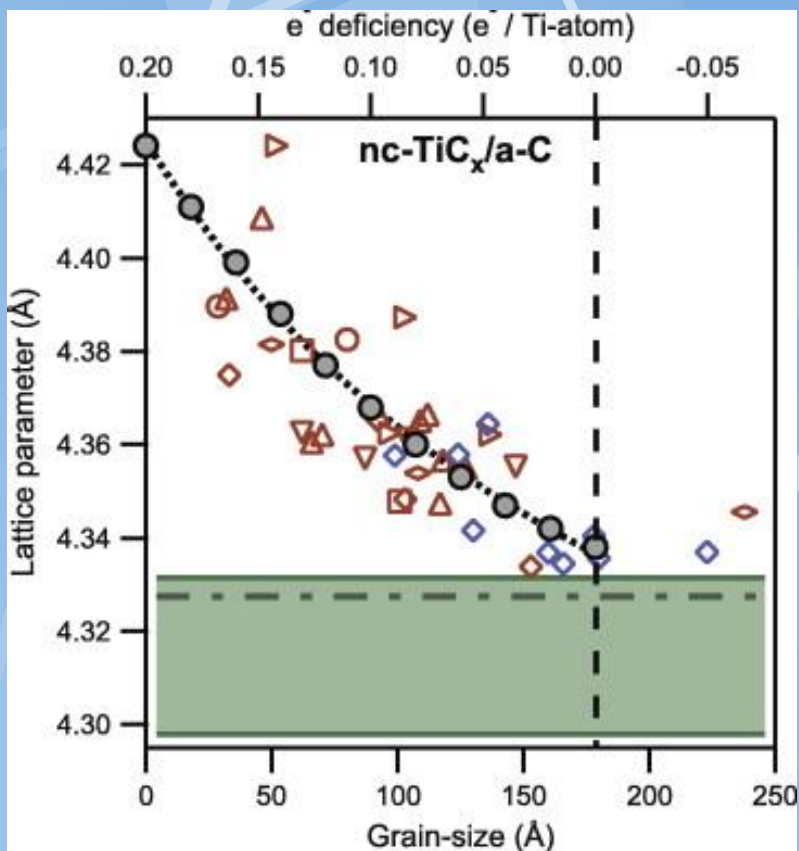


Vlastnosti spojené s povrchem NPs

Povrchová komprese nanočástic

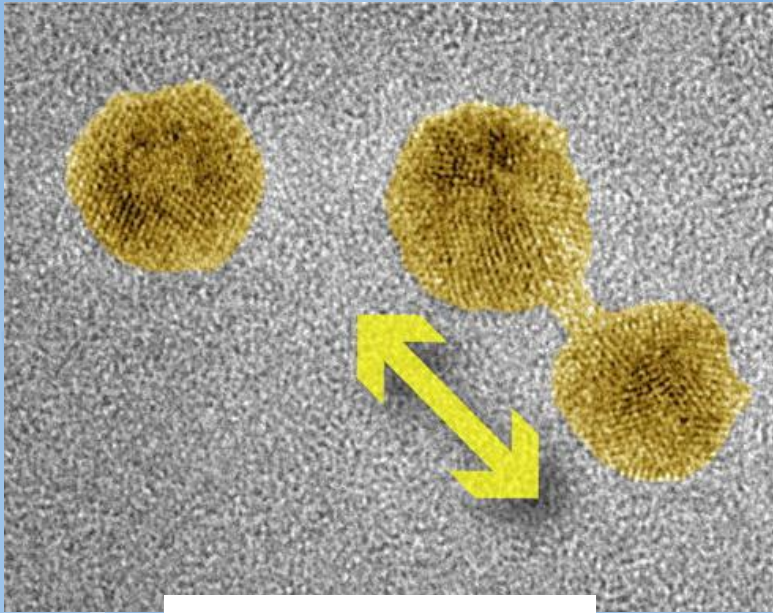
Povrchová komprese NPs



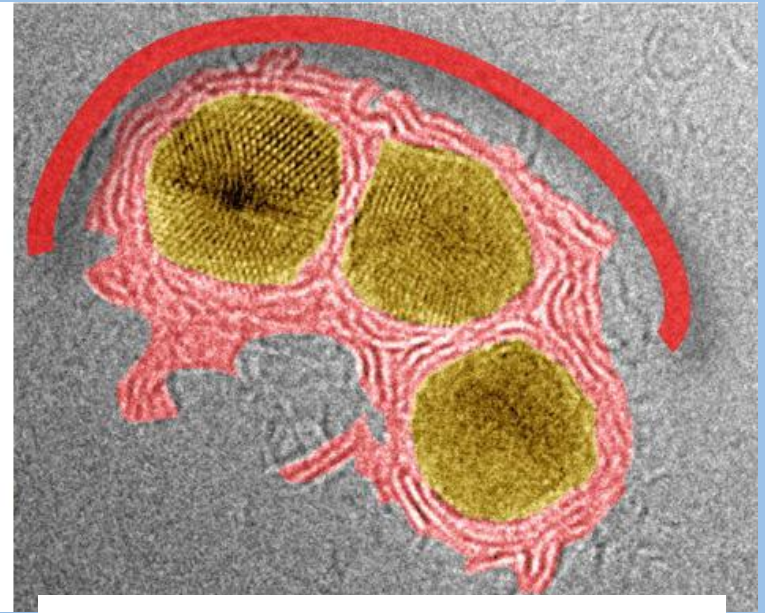


Nanocomposit (TiC_x v amorfním C)

Povrch nanočástic kovů



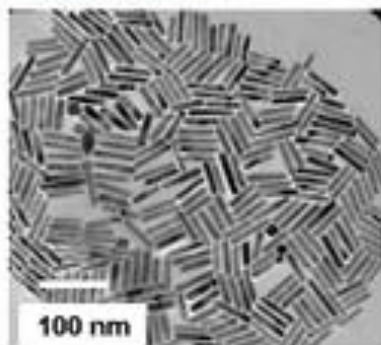
Agregace Au



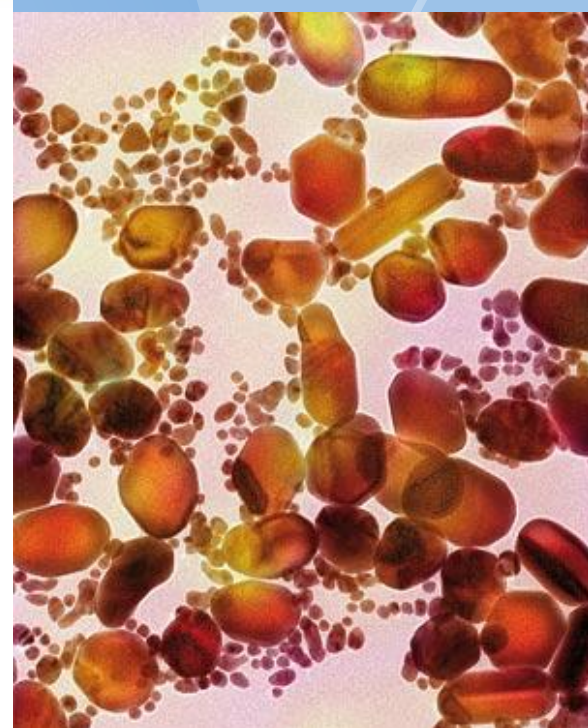
**Stabilizace Au
přítomností jiných
látek (polymer
protective shell).**

Stabilizace např. Přírodními oxidy, PAL, chemická vazba na org. látky, karbonizace, ...povrchový náboj (zetapotenciál).

Stabilita, růst a agregace nanočástic



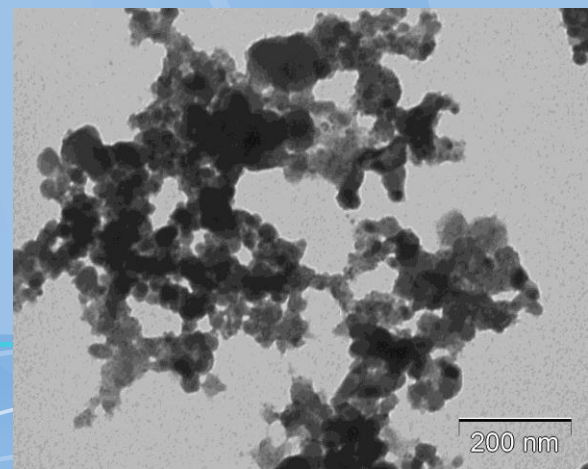
Gold nanorods



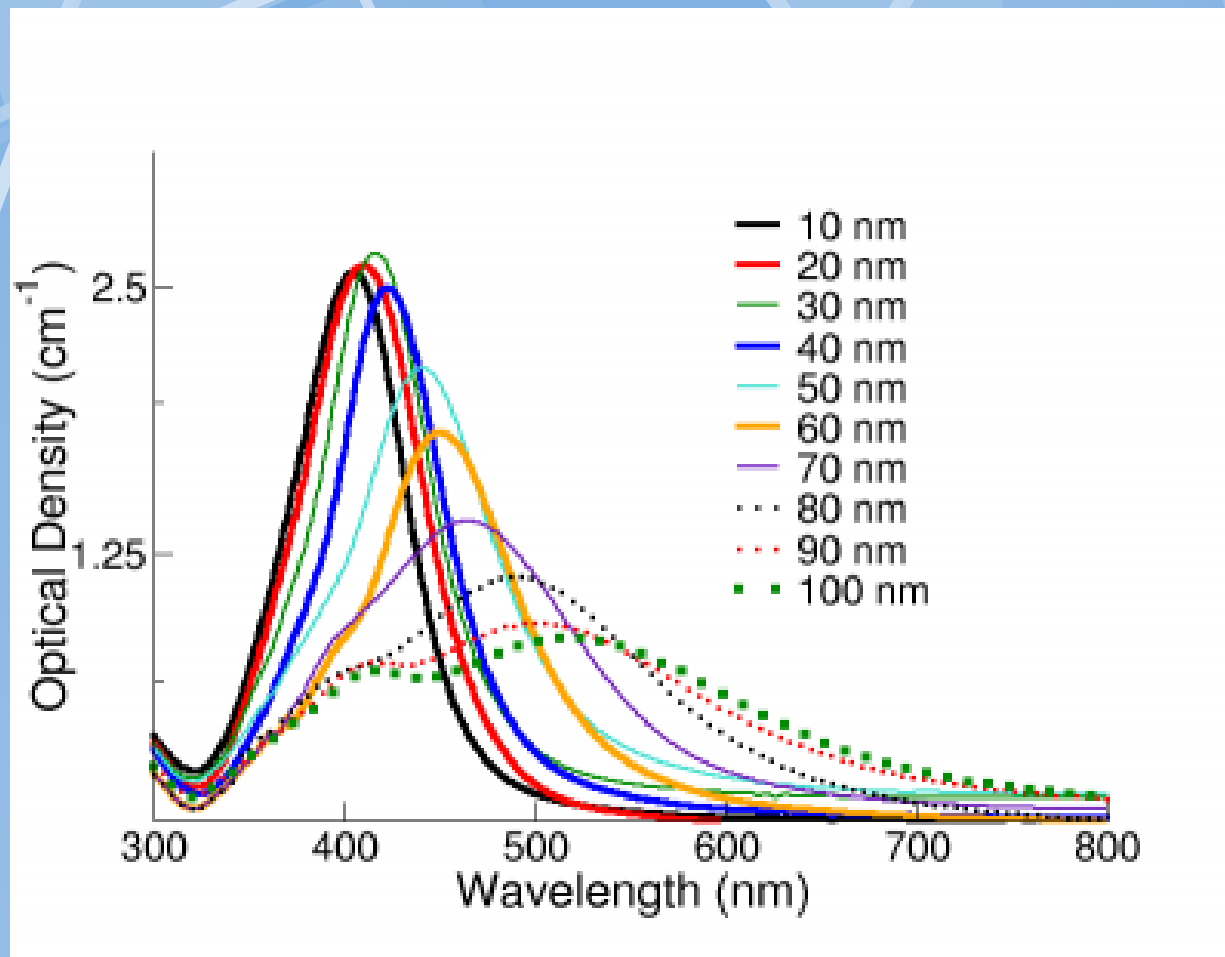
Au nano

Různé formy Au nanočástic.

Agregace Sn3.5wt%Ag →



Spektrální vlastnosti



Ag-NPs

Funkcionalizace povrchové vrstvy NPs

Vlastnosti funkčního povrchu

Ochrana jádra před agregací a nežádoucími reakcemi:

-oxidy, surfaktanty,
karbonizované
povrchové vrstvy, ...

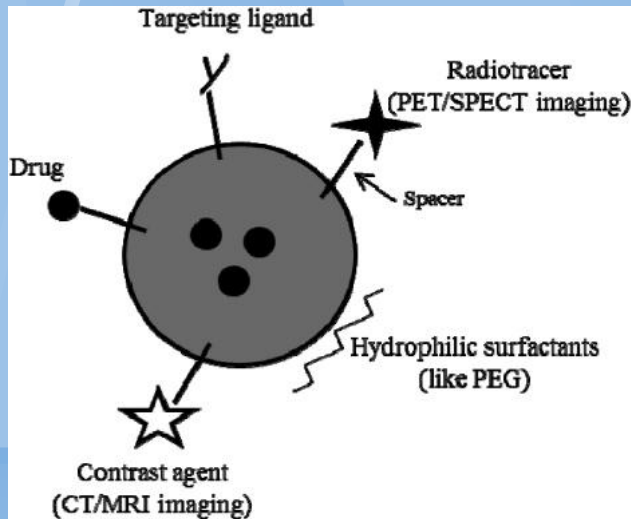
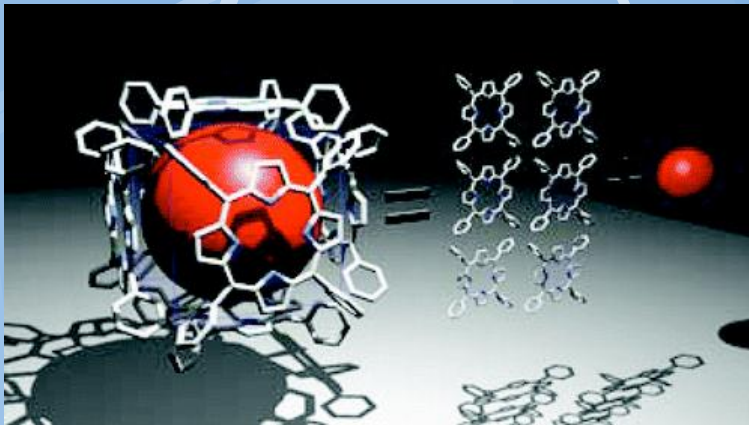
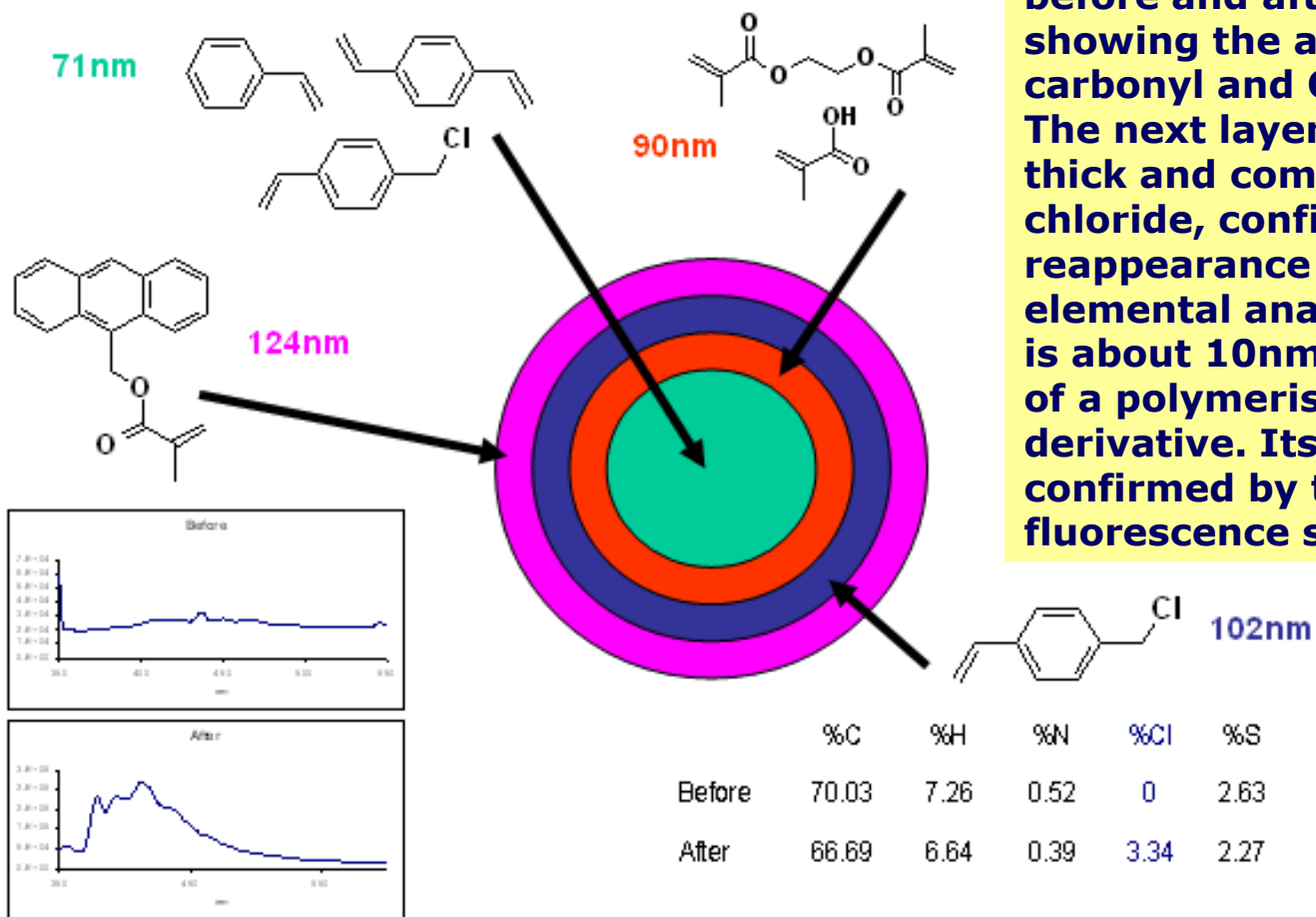
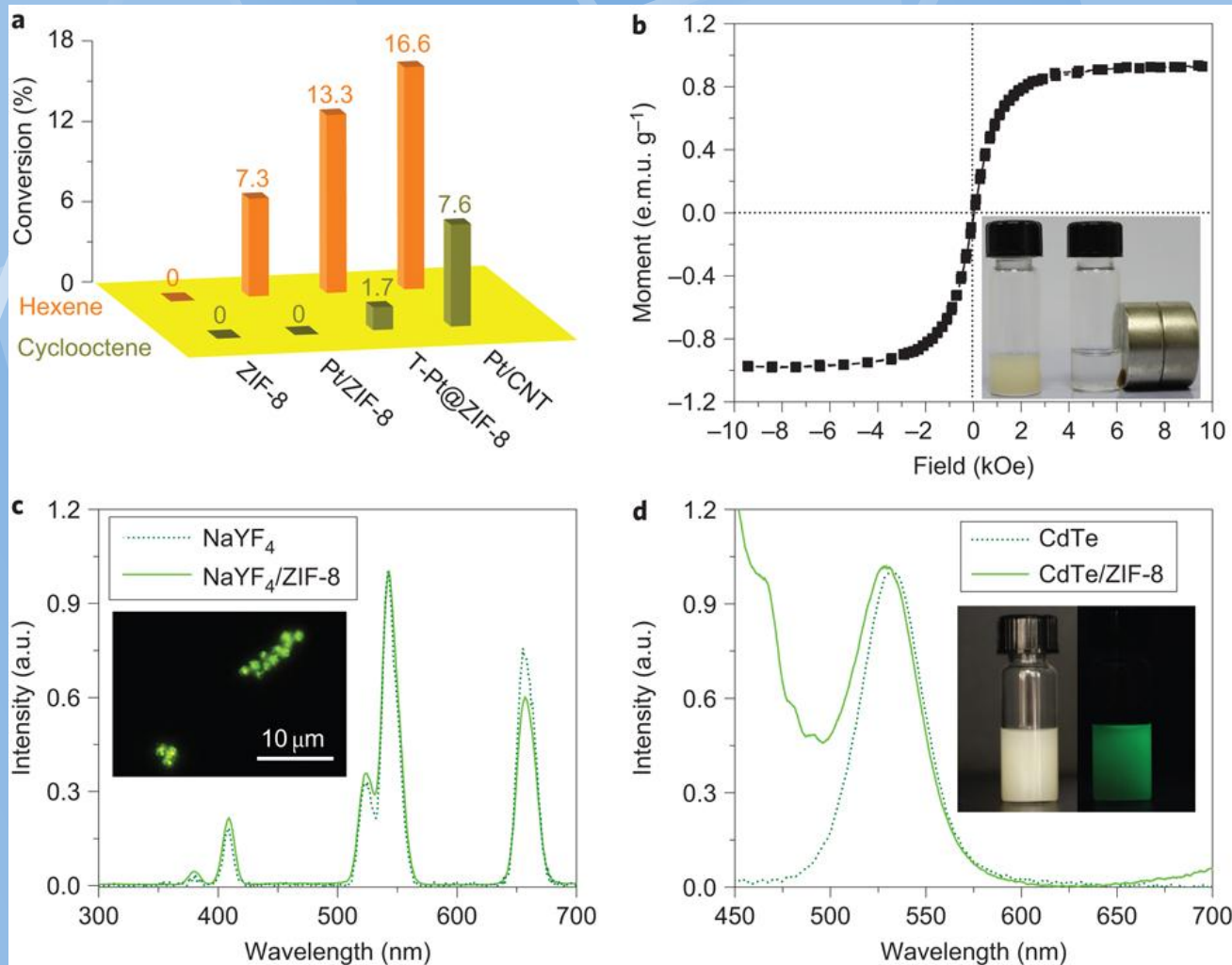


Figure 2. *Multi-functionalized NPs.* Graphical representation of multifunctional NP for molecular imaging (functionalized with contrast agents for CT/MRI, with radiotracer for PET/SPECT), for drug delivery (functionalized with drug molecules incorporated within the core of NP or conjugated to the surface), for specific targeting (functionalized with specific ligands) and for stealth (hydrophilic surfactants). Spacer/linker molecules are also indicated

Multifunkční povrch

In the figure above, the core is based on styrene DVB. The first layer is approx. 10 nm thick, comprising EDMA and MAA. Its presence is confirmed by the before and after IR spectra, clearly showing the appearance of the carbonyl and OH stretch signals. The next layer was about 5 nm thick and composed of vinyl benzyl chloride, confirmed by the reappearance of chlorine in the elemental analysis. The final layer is about 10nm thick and composed of a polymerisable anthracene derivative. Its presence is clearly confirmed by the before and after fluorescence spectra.





a, Size-selective hydrogenation of *n*-hexene and *cis*-cyclooctene catalysed by Pt/ZIF-8 composite (3.3 nm Pt nanoparticles, Pt content 2%). Pure ZIF-8, T-Pt@ZIF-8 composite (Pt content 2%) and Pt/CNT (Pt content 5%) were used as controls. *b*, Field-dependent magnetization curve of 8 nm Fe₃O₄/ZIF-8 composite at room temperature (inset: photograph of the composite by applying a magnetic field (right) to its suspension (left)). *c*, Normalized photoluminescence spectra with excitation at 980 nm for lanthanide-doped NaYF₄ rods (50 nm × 310 nm) (dotted line) and the corresponding NaYF₄/ZIF-8 composite (solid line) in methanol (inset: photoluminescence microscope image of the NaYF₄/ZIF-8 hybrid crystals excited at 980 nm). *d*, Normalized photoluminescence spectra with excitation at 405 nm for CdTe nanoparticles and the corresponding CdTe/ZIF-8 composite in methanol (inset: photographs of the CdTe/ZIF-8 composite suspended in methanol illuminated with ambient light).

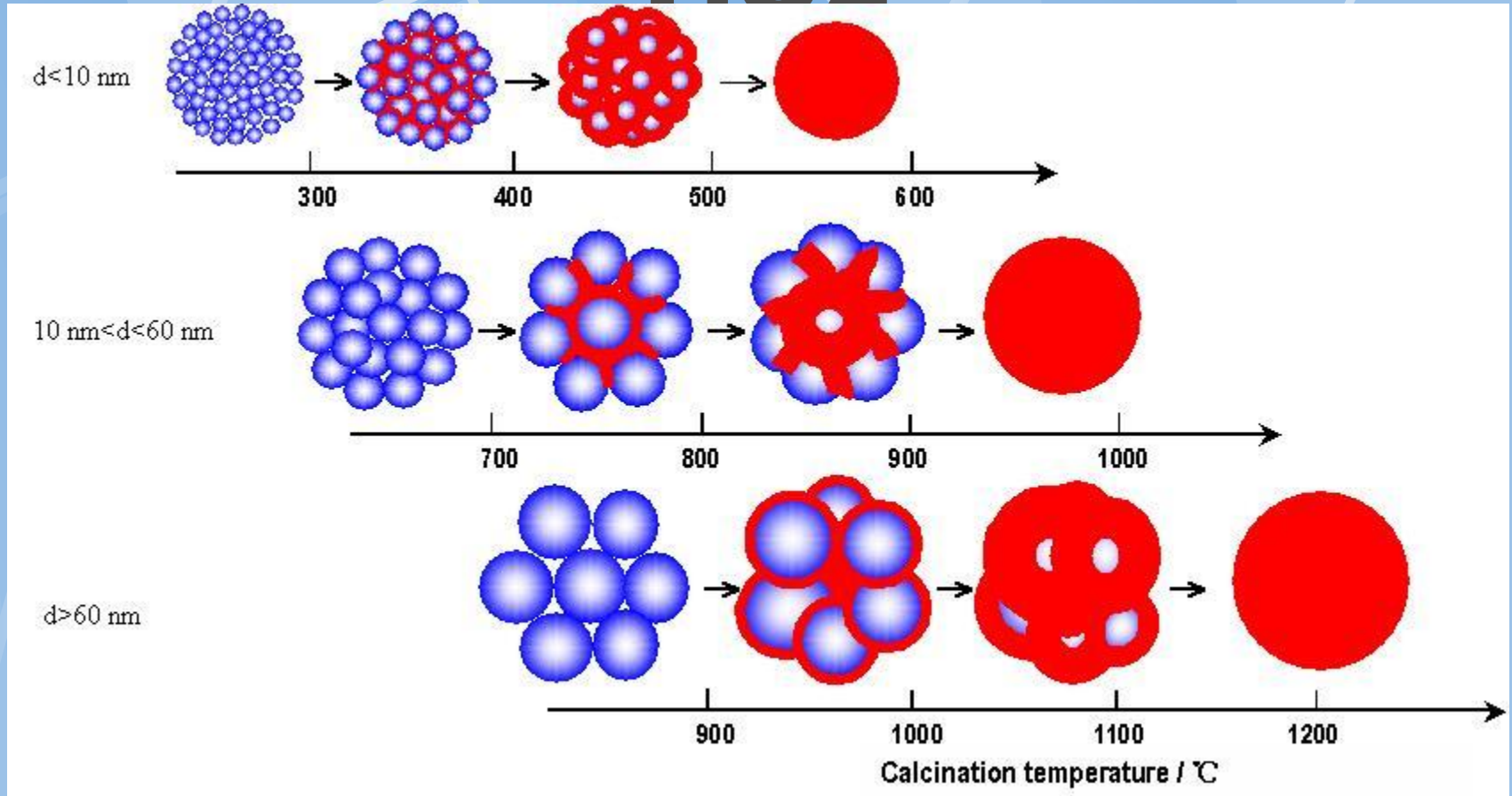
Diskuse



● Zjistit co dělají na pensylvánské Univ.:

- El. články s nano: <http://inhabitat.com/researchers-shine-light-on-gold-nanoparticles-to-produce-electricity/>

TiO₂



<http://dx.doi.org/10.1021/jp80801>

3k