TNT 2008, Oviedo

How are nanoparticle interactions and assemblies different from molecular and colloidal assemblies

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Surface-area-to-volume scaling effects: skin depths and proximity lengths

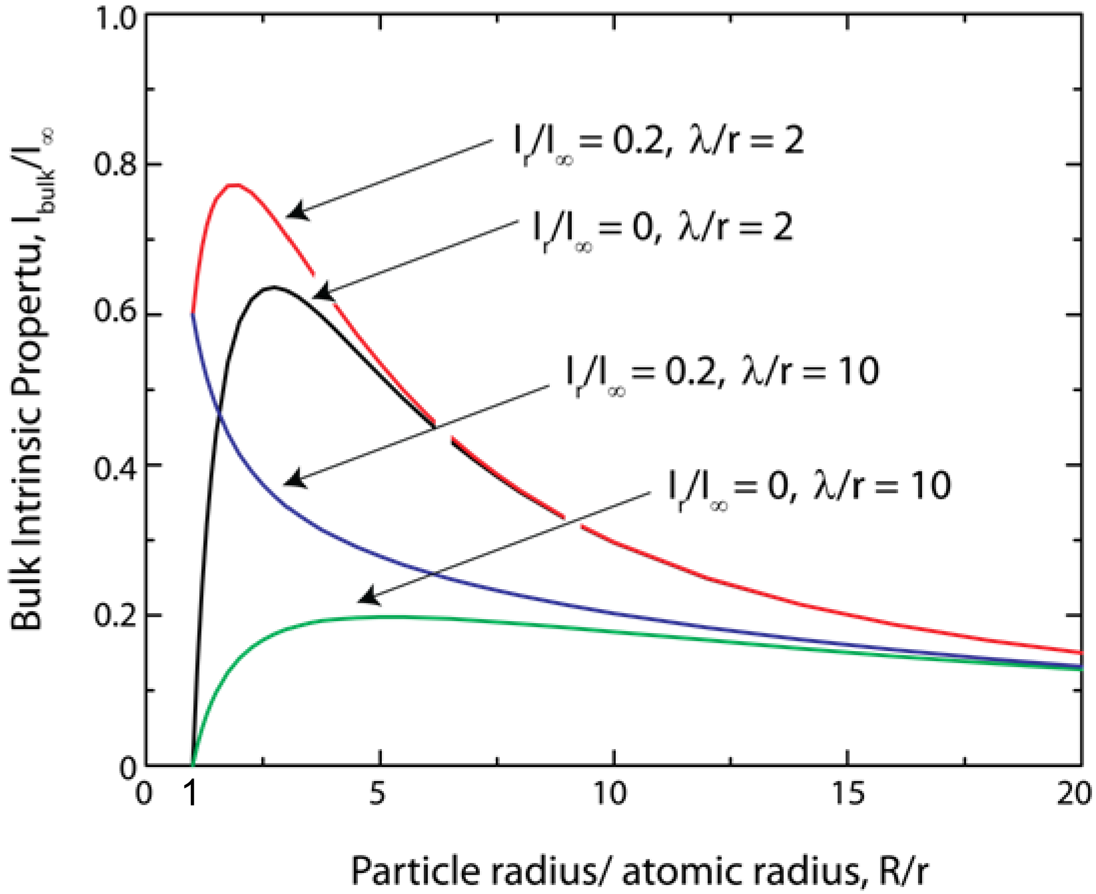
Many properties are not 'additive'. For example, AC conductivity, mechanical strength, melting temperatures, chemical activity, magnetic and opto-electronic properties are often determined within a finite surface layer, attaining their maximum value only after a certain critical 'skin-depth' or 'proximity length', λ, from the surface has been reached. The most common expression for such a property is: $I(x) = I_\infty - (I_\infty - I_r)e^{-(x-r)/\lambda}$.
where x is the distance from the surface, and r is the atomic or molecular size.

Table 1 Skin depths and proximity lengths, λ, of some common material properties.

Property	λ	Equations for particles (or thin films) of radius (film thickness) R
Cohesive energy, latent heat*	0.3 – 2 nm	$E_r = E_{bulk}(1-\lambda/R)$
Surface tension*	0.3–5 nm	Tolman equation: $\gamma_r = r\gamma_{bulk}/(R+\lambda)$
Melting point depression of metals*	1–3 nm	$T_r = T_{bulk}(1-\lambda/R)$
Vapour pressure	0.3–10 nm	Kelvin equation: λ depends on the relative humidity or vapour pressure.
Chemical reactivity		
Covalent bonds	0.5 nm	-
Electron transfer	0.7–1.0 nm	'Harpooning effect'
Opto-electronic properties†		
a.c. conductivity (metals)	~1 μm at 1 GHz	$\lambda \propto 1/\sqrt{\text{frequency}}$
d.c. (conducting polymers)	~Two molecules	-
Bandgap energy	2–30 nm	-

*The first three properties are intimately related and interdependent.
†Detailed discussion of electronic and optical properties is outside the scope of this review.

Review article by Min *et al.*, **nature materials** (2008) 7, 527.

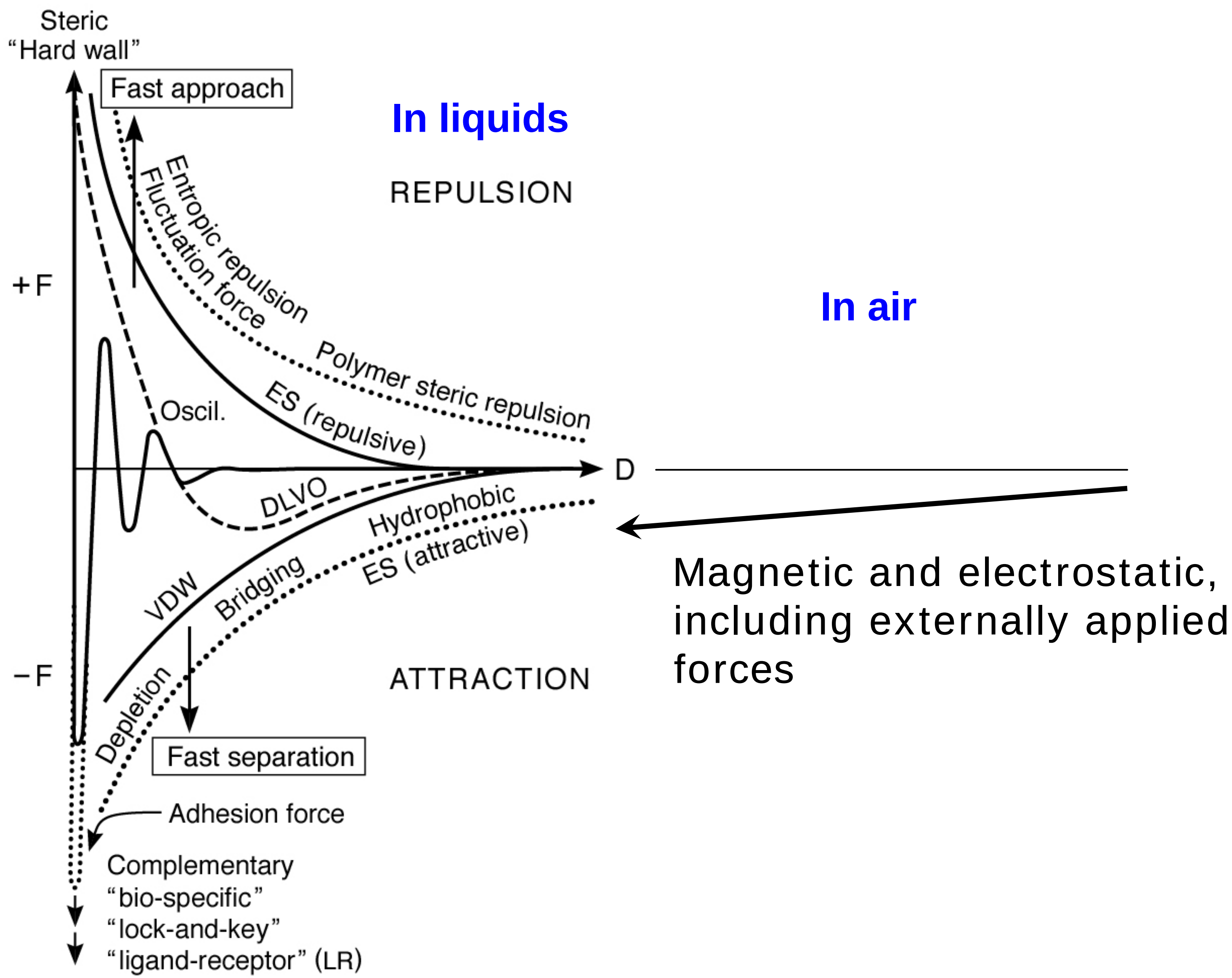


For a nano-structured material composed of nanoparticles of radius *R*, putting *x*=*R*, the bulk intrinsic property of the material is therefore

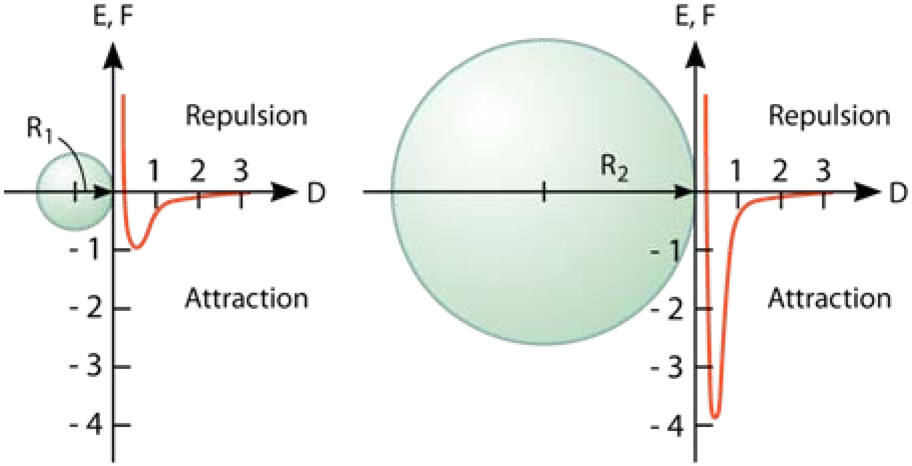
$$I_{\text{bulk}} = 4\pi R^2 I(R) \times (\text{particle density}) \approx 4\pi R^2 \left[I_\infty - (I_\infty - I_r) e^{-(R-r)/\lambda} \right] / \tfrac{4}{3}\pi R^3.$$

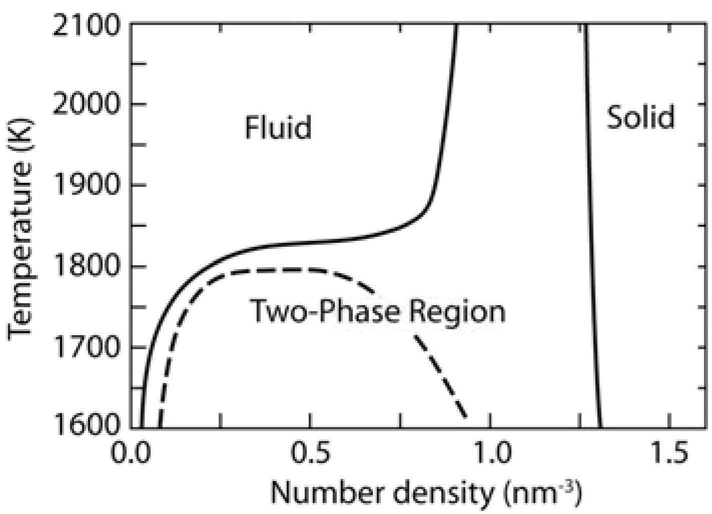
The figure shows plots of I_{bulk} for various values of I_r/I_∞ *vs* the normalized skin depth, λ/r. Note how the bulk properties of nano-structured materials can peak at a particular radius *R* of their constituent nanoparticles even though the properties of the individual nano-particles do not peak at any particular size.

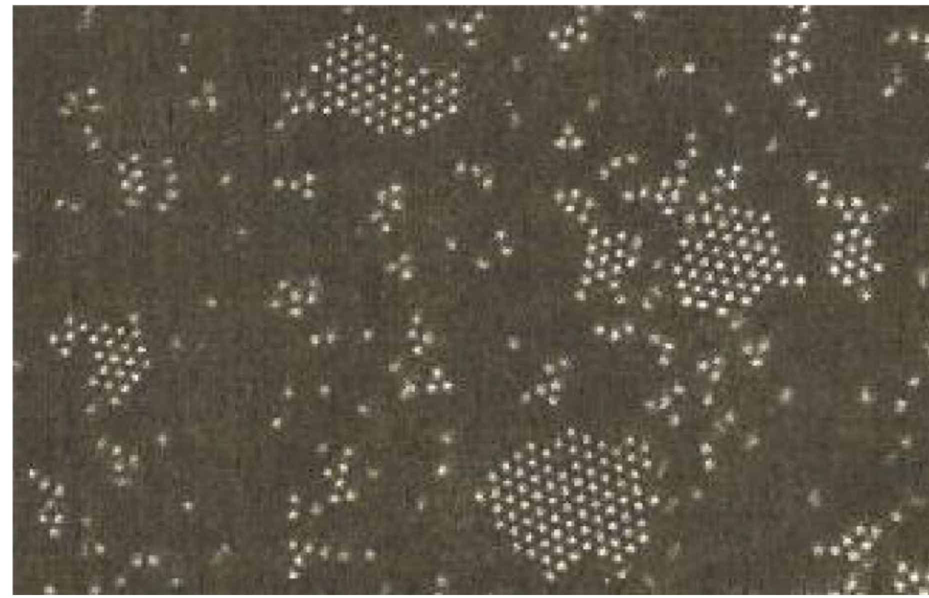
Different intermolecular and interparticle forces, some short-ranged, some long-ranged.



Missing phases (phase transitions) in nanoparticle assemblies

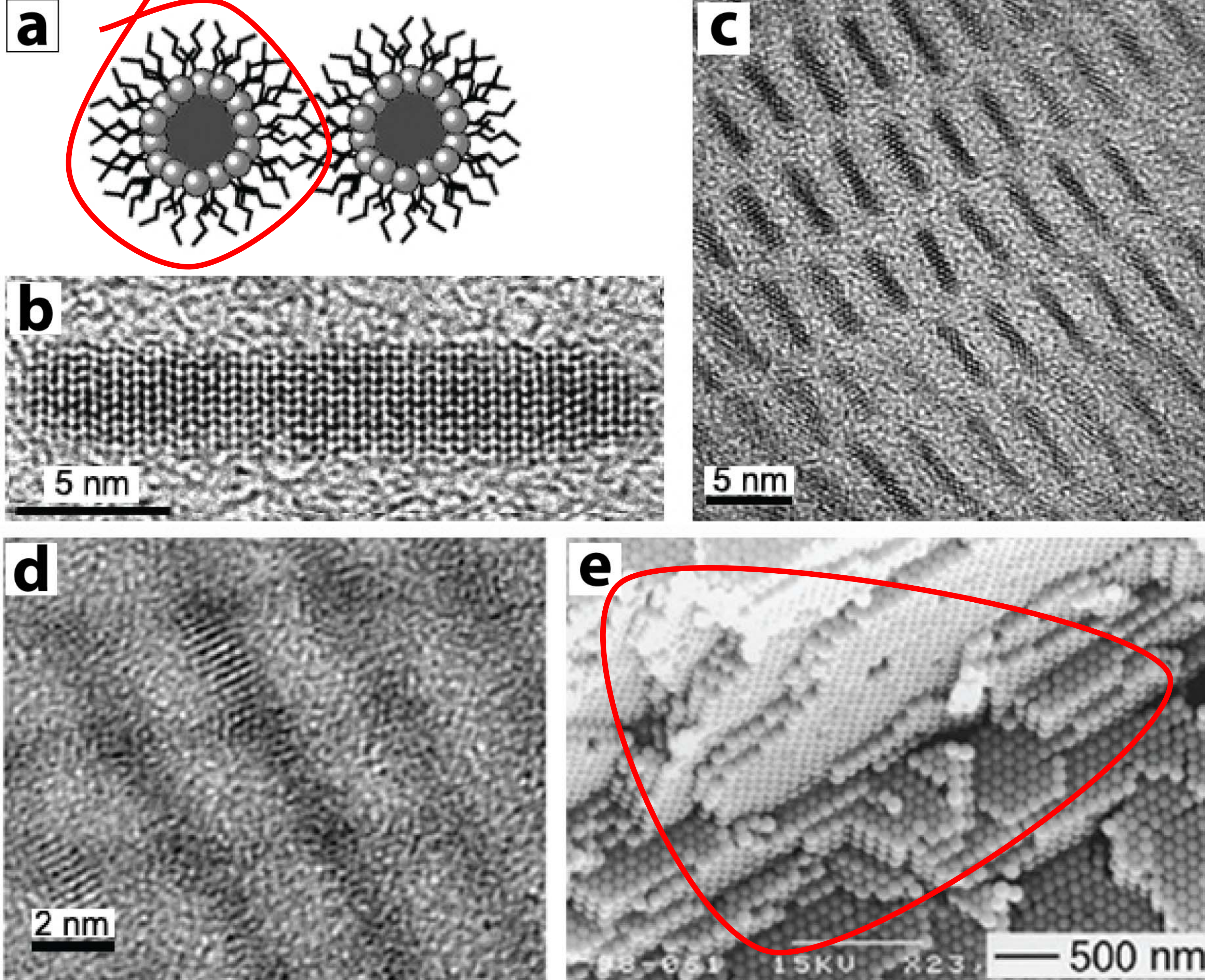


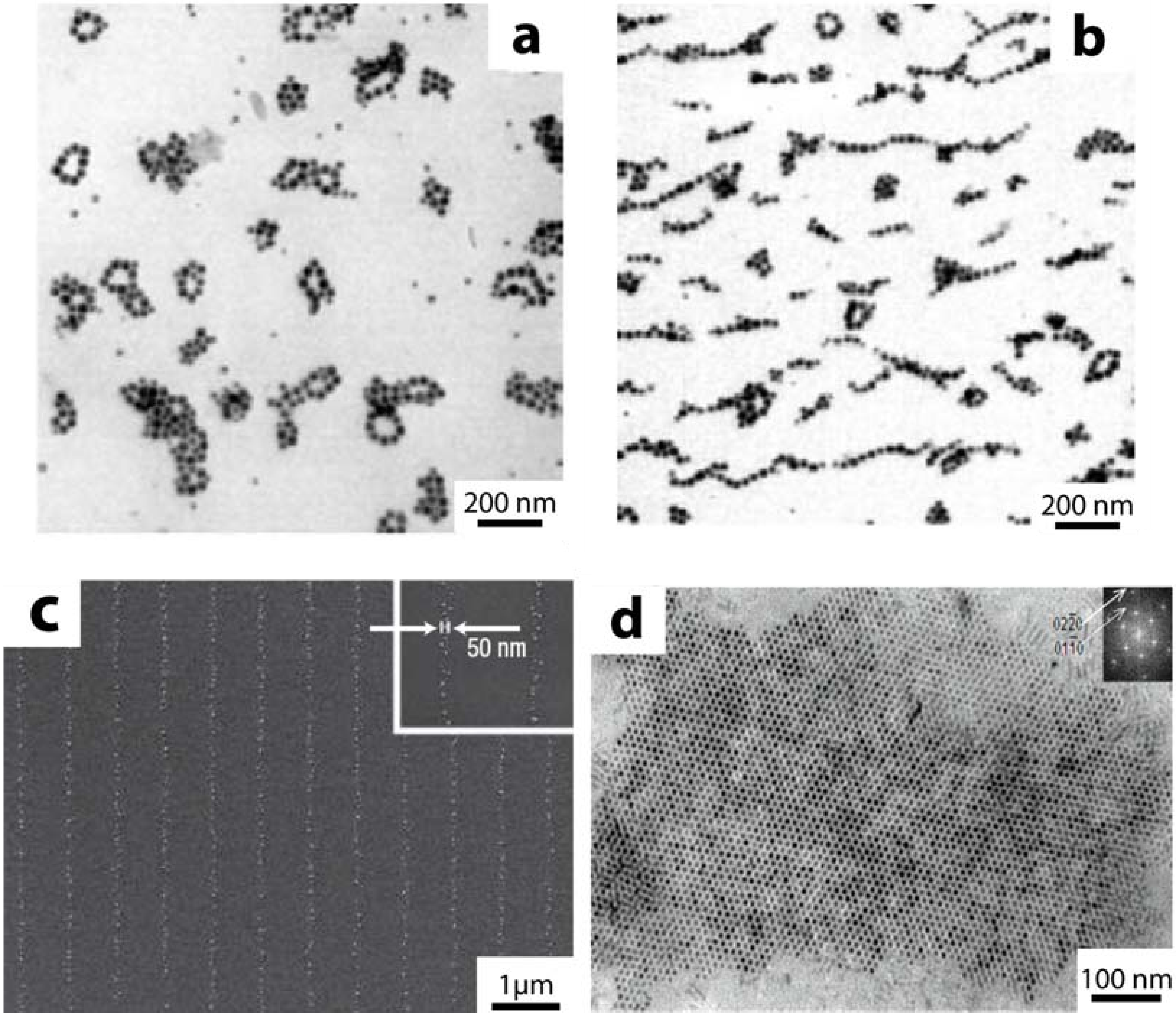




Self- and directed-assembly

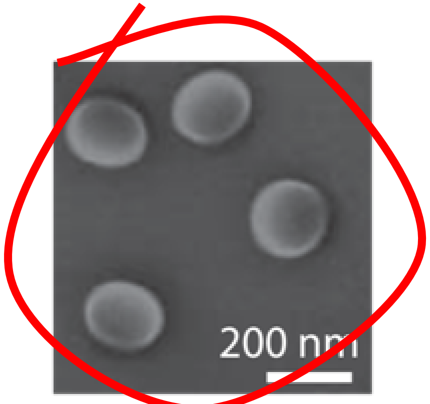
nature materials (2008) 7, 527.

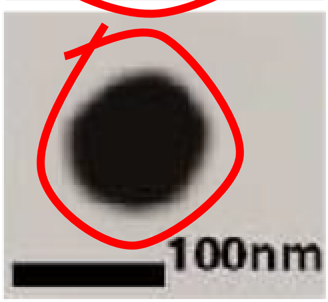

a
b
5 nm
c
5 nm
d
2 nm
e
500 nm



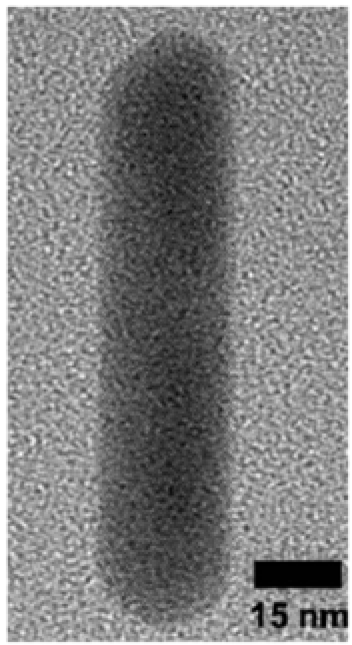
a
200 nm
b
200 nm
c
50 nm
1μm
d
02$\bar{2}$0
01$\bar{1}$0
100 nm

1-component nanoparticles, simple shapes, hard or soft

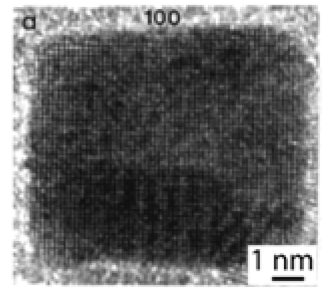




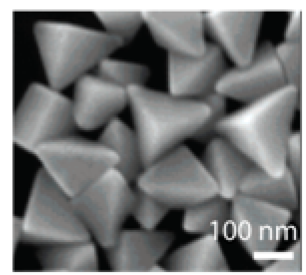
Spheres



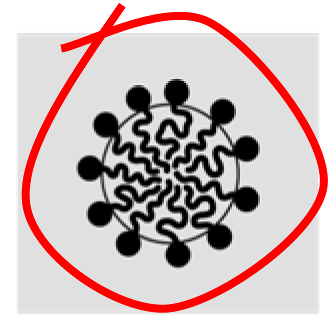
Rod



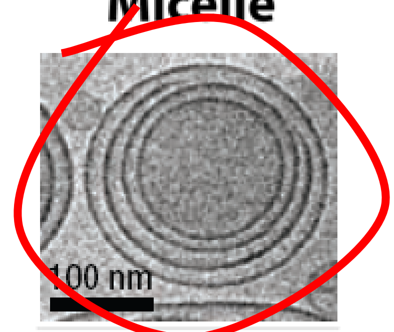
Cube



Bipyramids

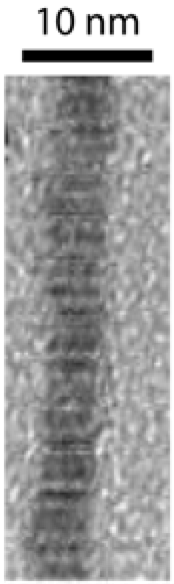


Micelle

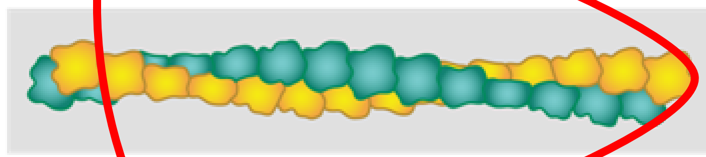


Vesicle

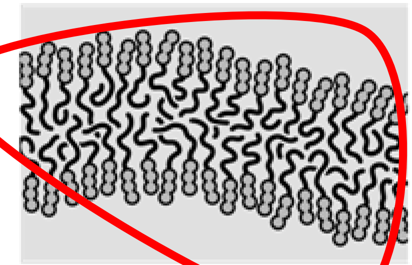
1-component, with at least one dimension in the nano-regime



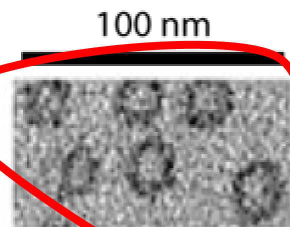
Wire

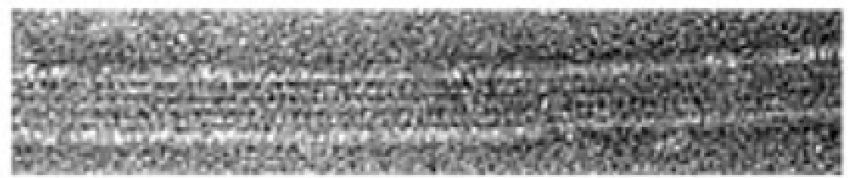


Actin



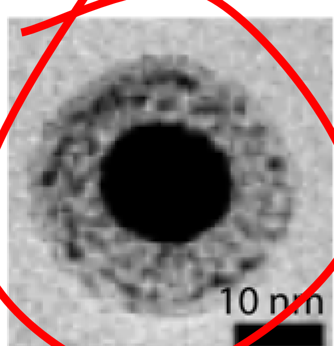
Bilayer



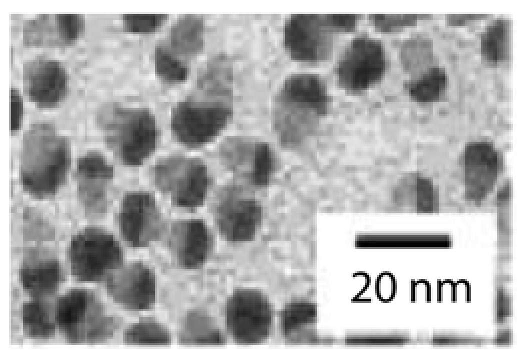


Microtubules

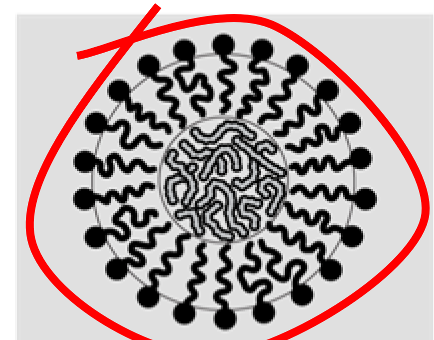
2 or more components (core-shell structures, etc.)



Core-shell
(egg)

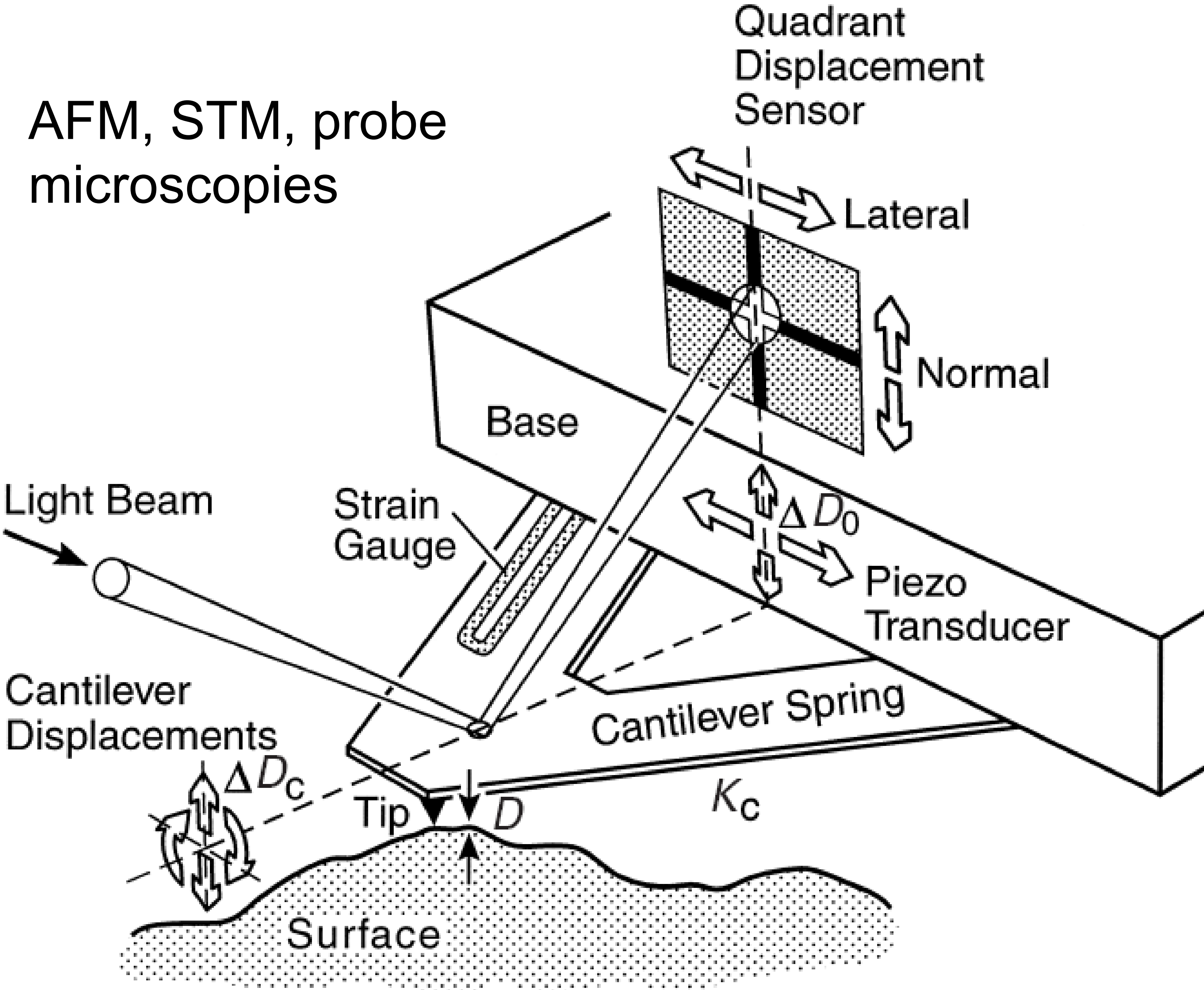


Acorns



Microemulsion droplet
(swollen micelle)

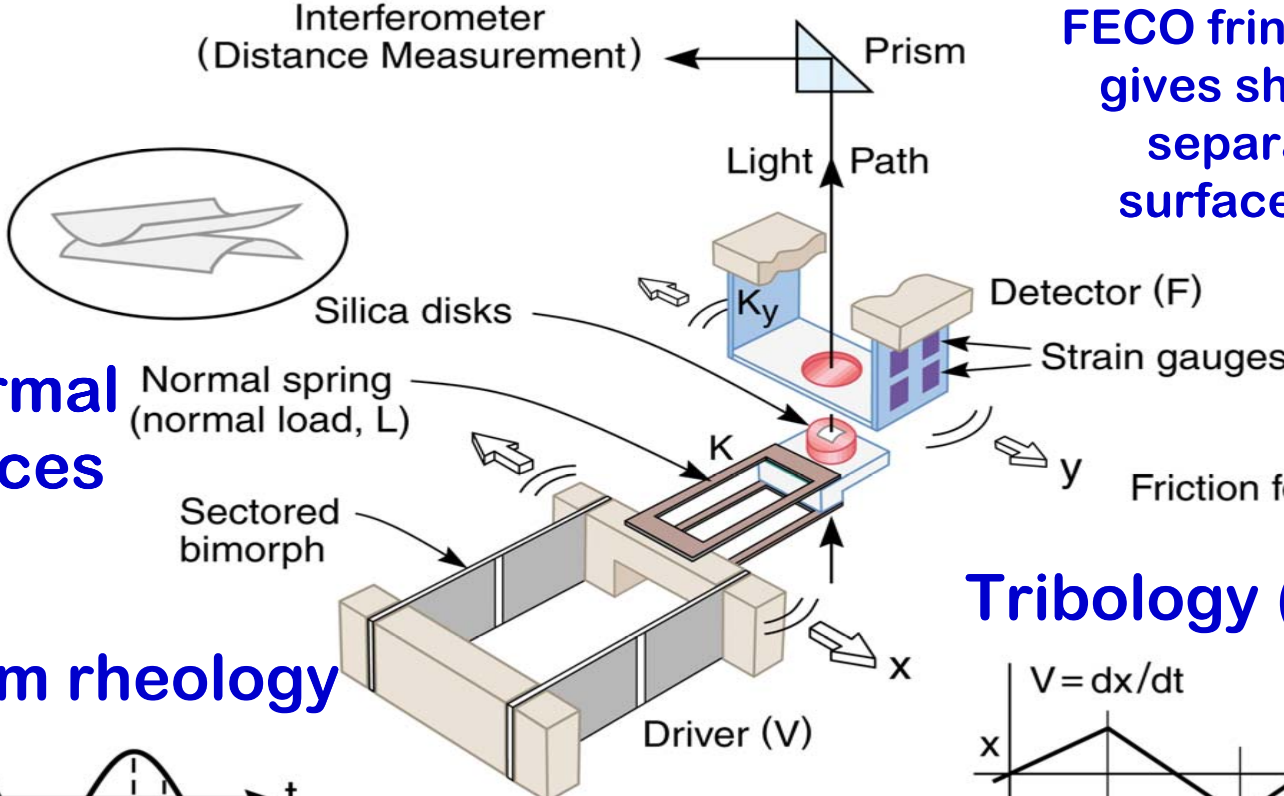
AFM, STM, probe microscopies



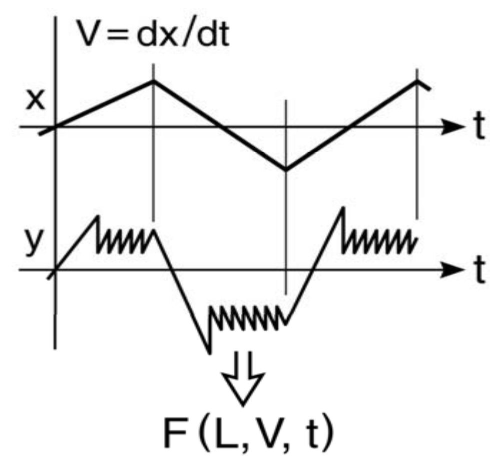
Surface Forces Apparatus (SFA)

FECO fringe pattern gives shapes and separation of surfaces to ~1Å

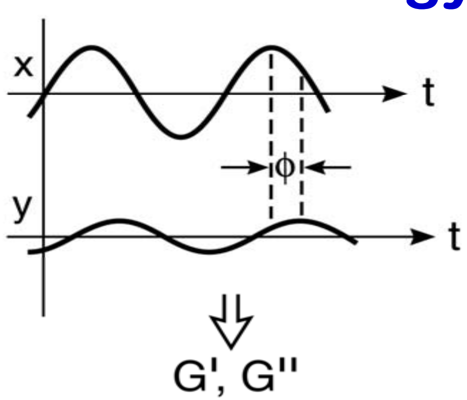
Normal forces



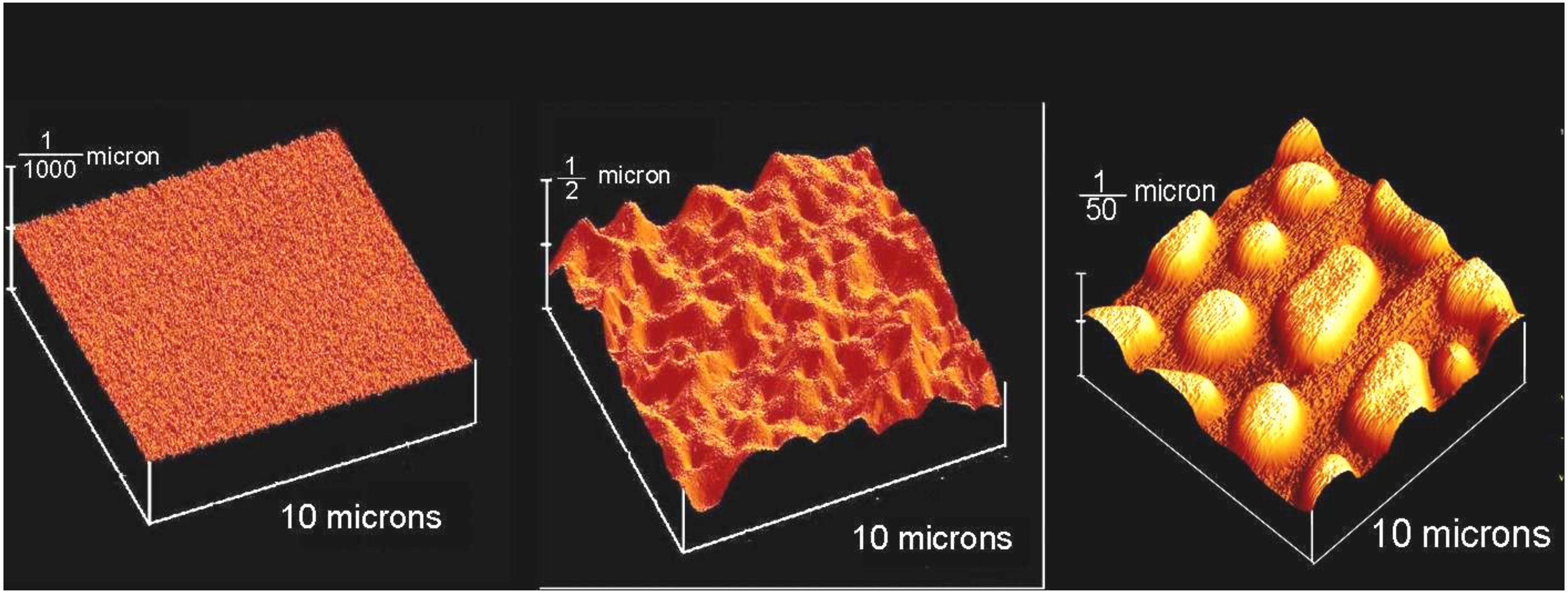
Tribology (friction)



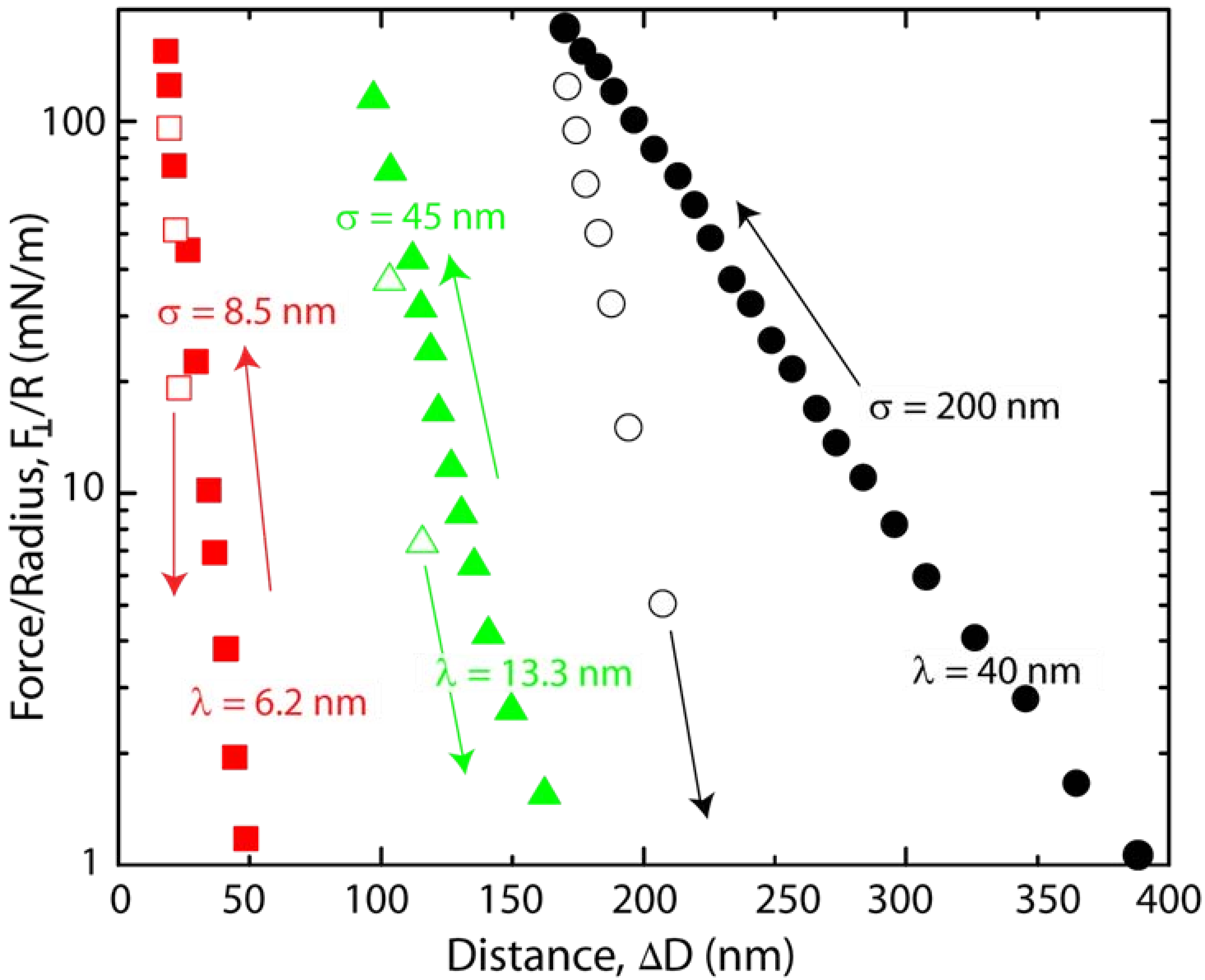
Thin-film rheology



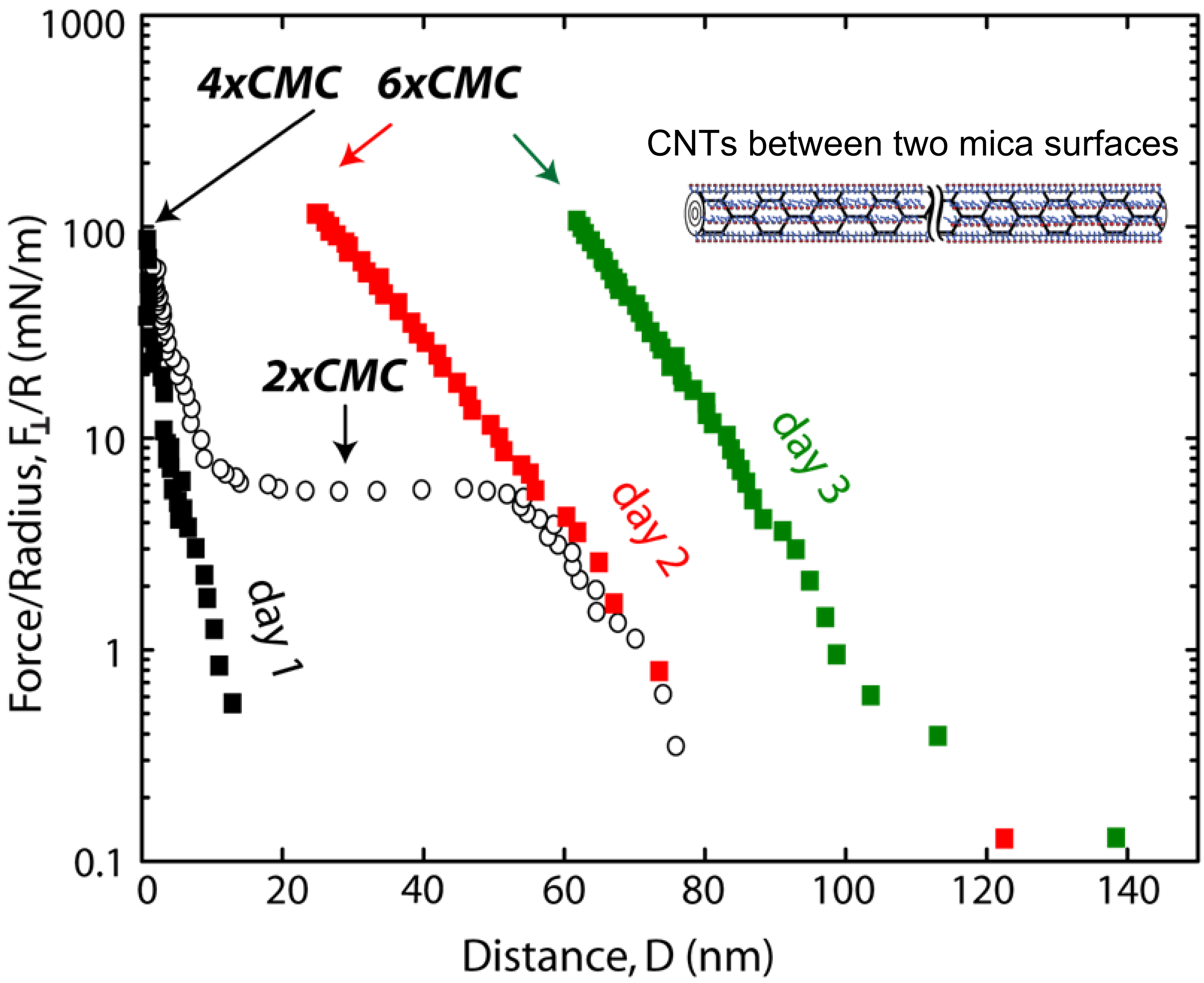
Various types of randomly rough, patterned and nanoparticle-coated surfaces studied by SFA



M. Benz et al., *J. Phys. Chem. B* (2006) 110, 11884.

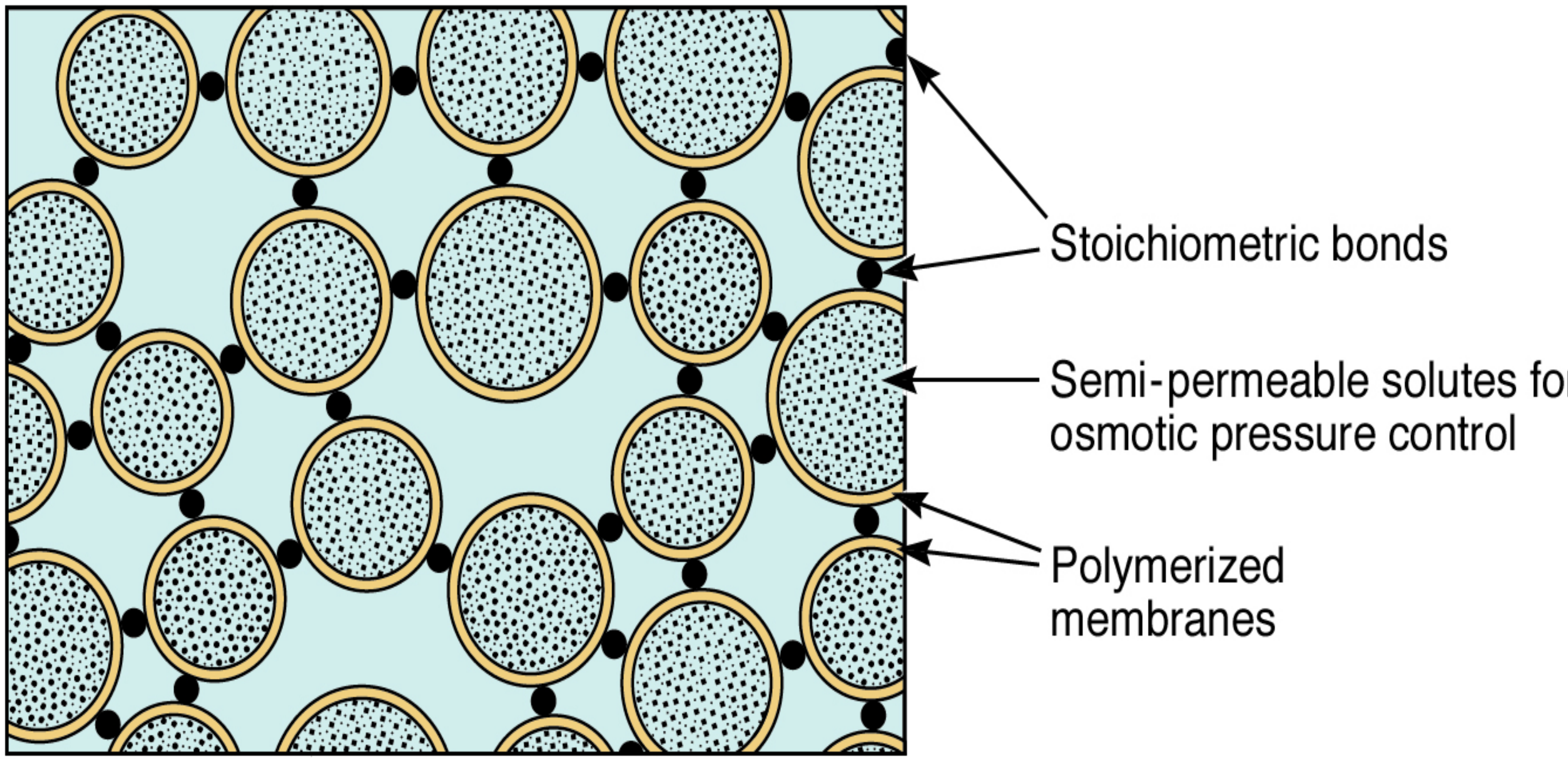


Force/Radius, $F_\perp/R$ (mN/m)
Distance, ΔD (nm)
σ = 8.5 nm
λ = 6.2 nm
σ = 45 nm
λ = 13.3 nm
σ = 200 nm
λ = 40 nm

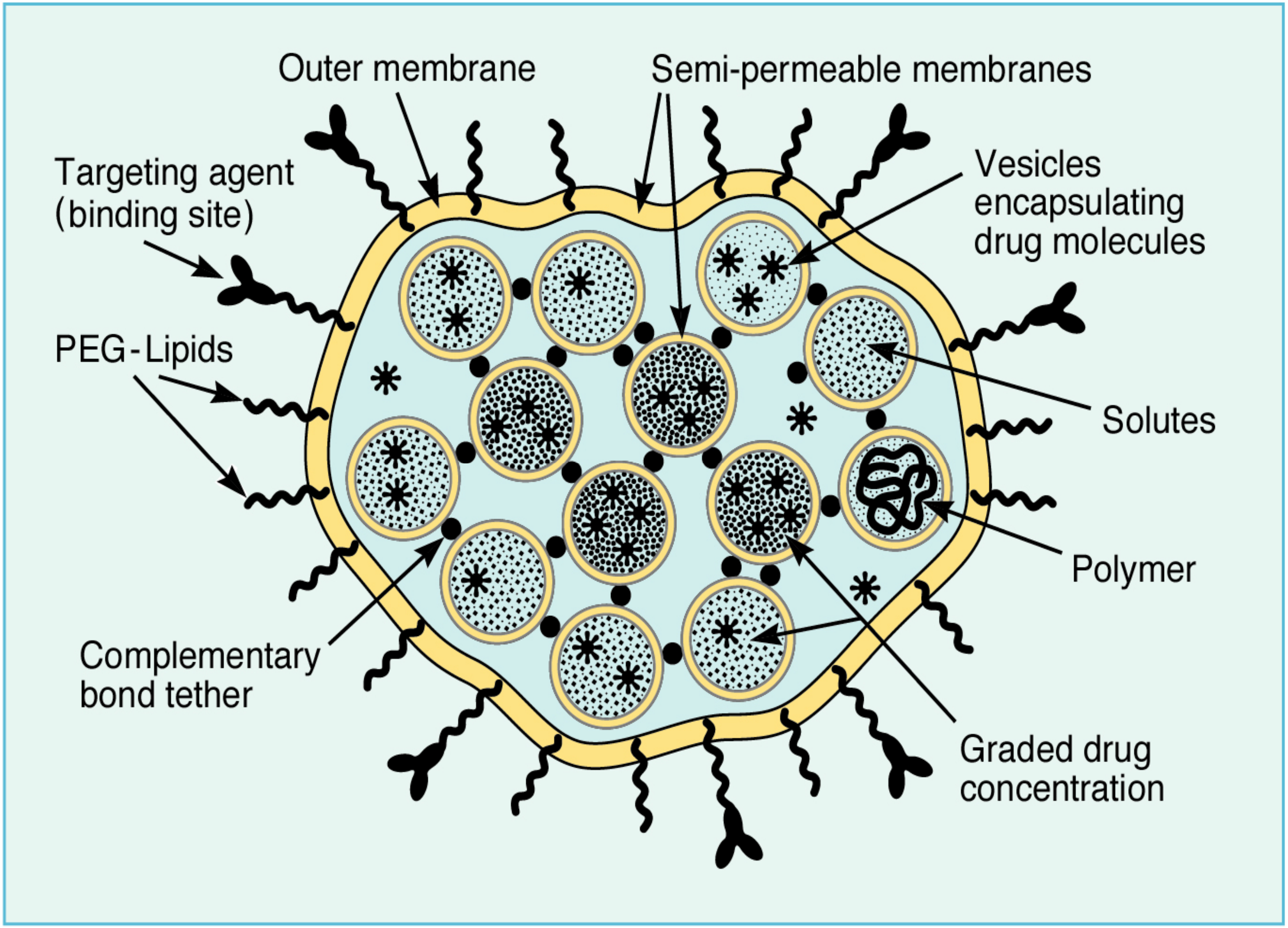


4xCMC
6xCMC
CNTs between two mica surfaces
2xCMC
day 1
day 2
day 3
1000
100
10
1
0.1
0
20
40
60
80
100
120
140
Force/Radius, $F_{\perp}/R$ (mN/m)
Distance, D (nm)

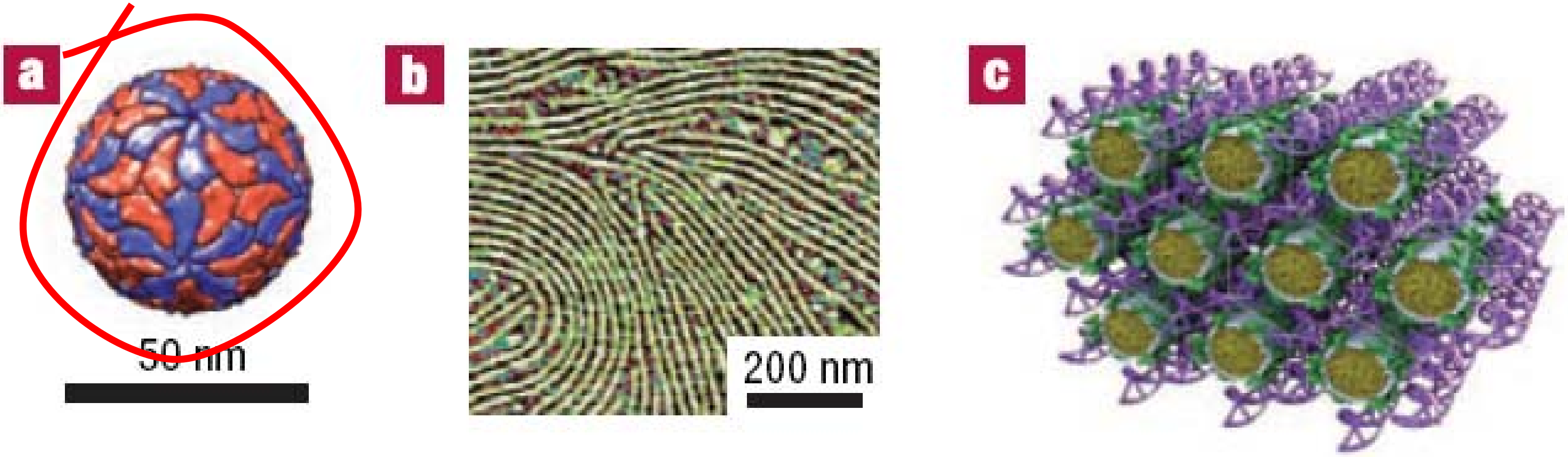
Engineered nano-structured materials
[smart, adaptable, switchable, responsive, ….]



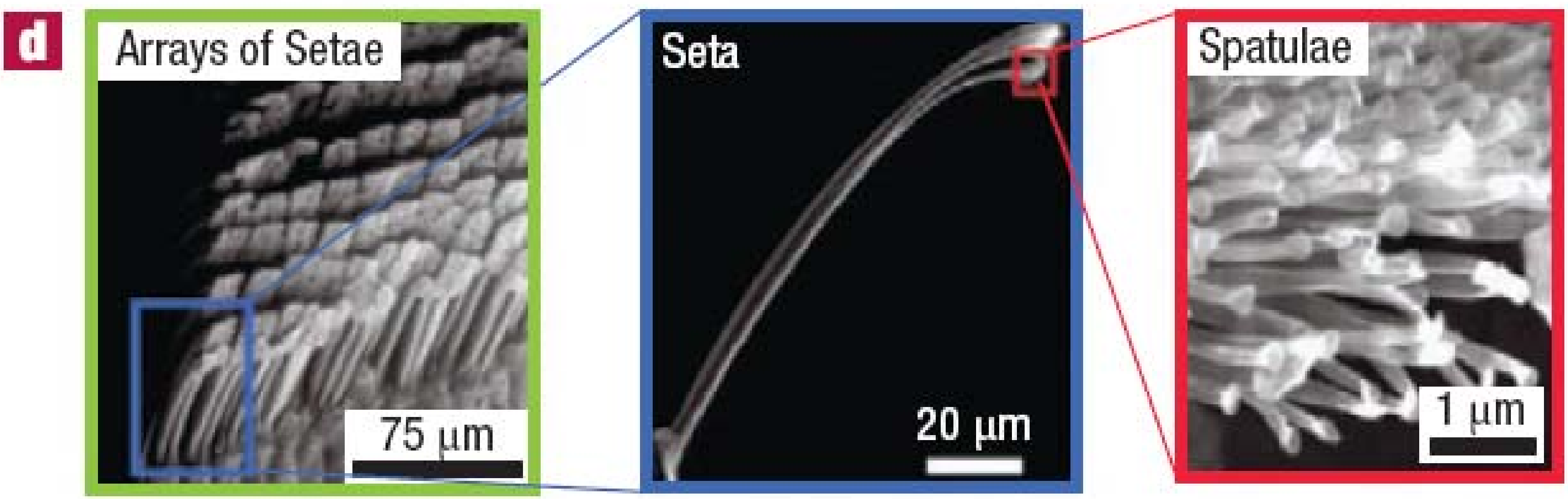
Bioengineered soft, cell-like structures



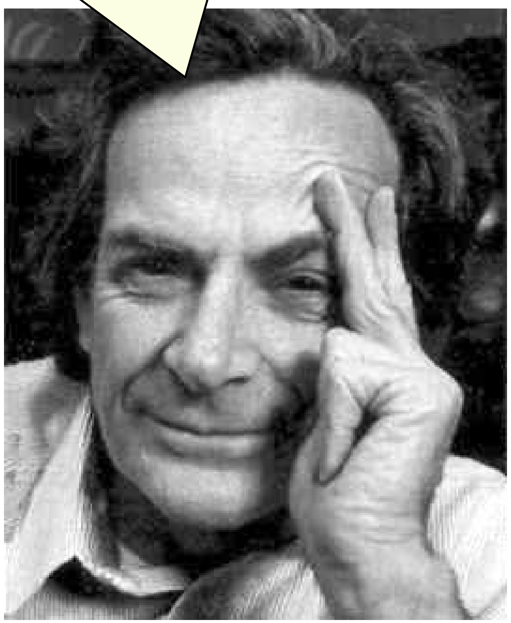
Biological nanostructures



The surfaces of gecko toes



There's plenty of room at the bottom.



Feynman (1959)

The bottom's full. But there's plenty of room in the middle.