Patchy depletion interactions

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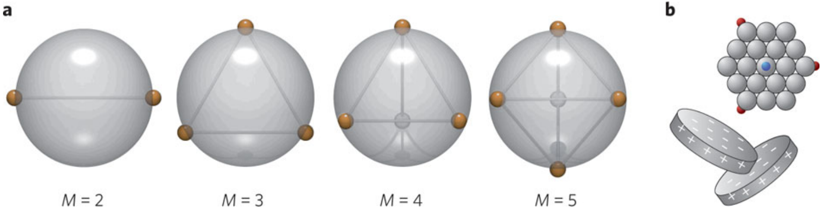
Summary

- Shape and Depletion
- Directional depletion in Cut-Spheres
- Key-Lock depletion interaction
- A gallery of shapes
- Conclusions

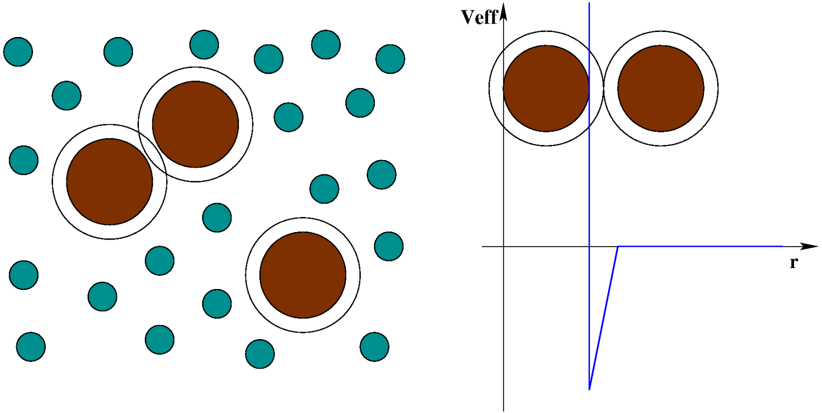
Which kind of patchyness?



Boltzman envisioned chemical attraction between particles as contact between their sensitive regions, that is, attractive patchy interactions
L. Boltzmann, Lectures on gas theory, Dover, New York 1995
A patchy particle is a patterned particle with at least one well-defined patch through which the particle can experience a strongly anisotropic, highly directional interaction with other particles or surfaces
Z. Zhang, S. C. Glotzer, Nano Lett. 2004, 4, 1407

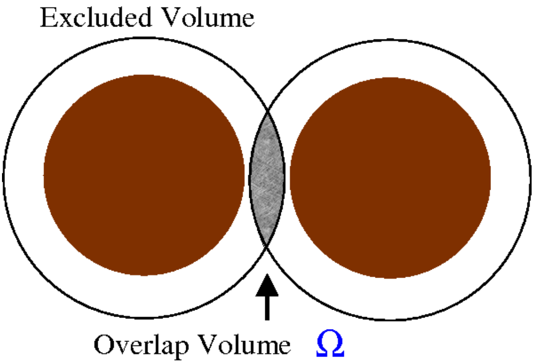
The Primitive Model for Water was expanded to to as the Sticky Hard-Sphere model to include an arbitrary number of patches
J. Kolafa, I. Nezbeda, Mol. Phys. 1987, 61, 161
Network glasses region in the patchy particle phase diagram
F. Sciortino, Eur. Phys. J. B 2008, 64, 505
Empty liquids, Equilibrium Gels
Bianchi et al, Phys. Rev. Lett. 2006, 97, 168301
Ruzicka et al, Nat. Mat. 2011, 10, 56

Depletion Interactions



- Colloidal Suspensions
- Driven Granulars
- *In-vivo* Proteins ? (*crowded molecular environments*)

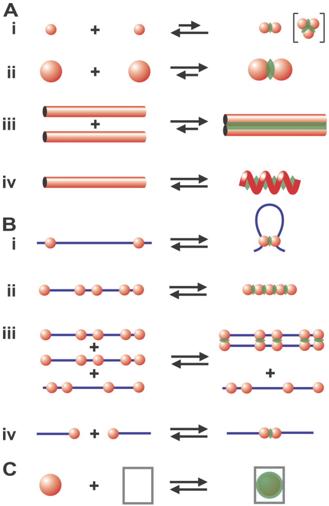
Excluded Volume



Interaction strenght $\Delta F \sim f\,\Omega \sim \phi\Omega$

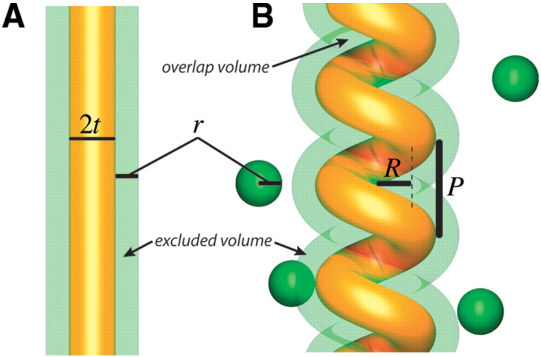
(free energy per volume $f \sim \phi$ at low density)

Entropy driven genome organization?



nonspecific entropic forces could also drive biomolecular self-assembly
Davide Marenduzzo et al, Biophysical Journal 90, pp. 3712-3721, 2006

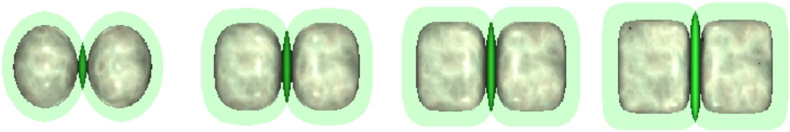
Shape can have dramatic effects



helix forming (Snir & Kamien, Science 307, pp. 1067, 2005)

Flatness enhances interaction

SuperEllipsoid: $\left(\frac{x}{a_z}\right)^{n_x} + \left(\frac{y}{a_y}\right)^{n_y} + \left(\frac{z}{a_x}\right)^{n_z} = 1$

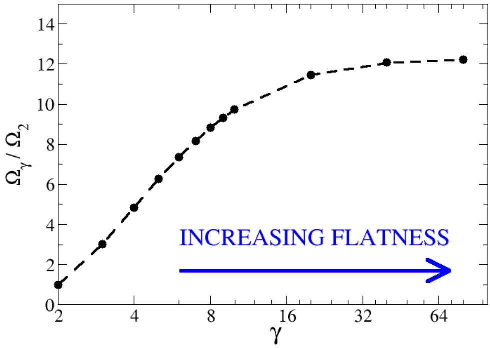


$\mathbf{n = 2}$ $\mathbf{n = 3}$ $\mathbf{n = 4}$ $\mathbf{n = 6}$

- increased strenght & induced directionality

Strength vs Flatness

At low depletant density, Ω_γ/Ω_2 extimates the ratio of the interaction strengths

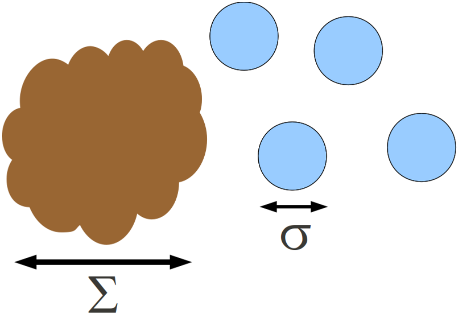


Ω_γ overlap volume of SuperEllipsoids

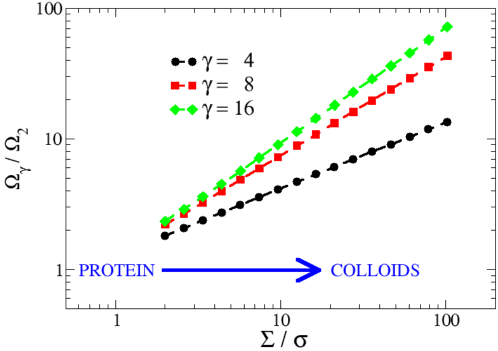
Ω_2 overlap volume of Spheres

Different scales

\# protein/nanoparticle limit $\Sigma/\sigma \sim 1$
\# colloidal limit $\Sigma/\sigma \gg 1$



Strength vs Depletant Size

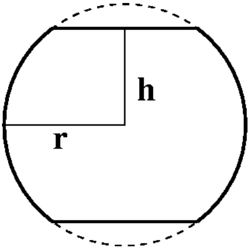


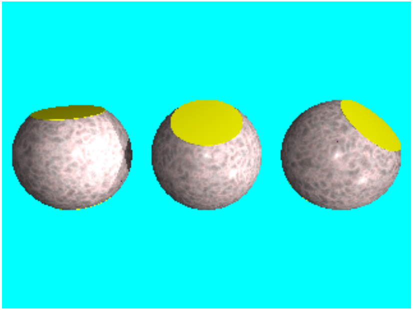
Σ size of depleted particles

σ size of the depletant

Case study 1 : Directional Binding

Cut Spheres

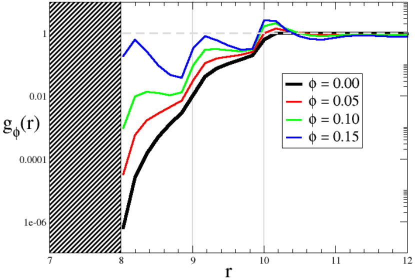




We study a template model that highlights the effect shape having:

- either zero curvature (flat faces)
- or constant curvature (spherical sides)

Monte Carlo Simulations

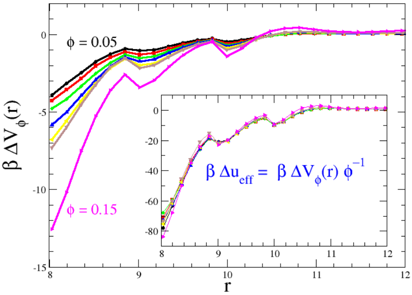


- $\phi = 0.05 \ldots 0.15$
- up to 10^4 solvent spheres
- 10 to 20 independent runs
- 10^{11} MC steps per run
- flat $\langle \cos\theta \rangle$
- $\langle \Delta r^2 \rangle \approx L$

Special thanks to Donald Blaak for the CS-CS overlap routine

MC: Scaling of the depletion interaction

$$g_\phi(r) = g_0(r) \exp[-\beta \Delta V_\phi(r)]$$

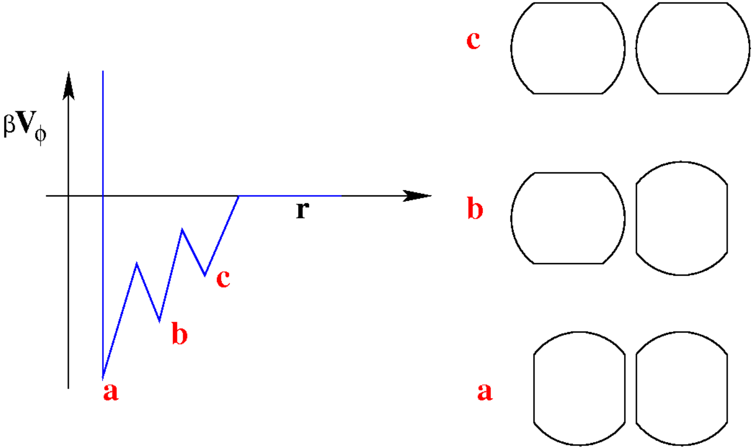


For small ϕ, the attractive interaction scales as $\Delta V_\phi \approx \phi \Delta u_{eff}$

The effective interaction mimics patchy-particles potentials -> toward “empty liquids”

E. Bianchi et al, Phys. Rev. Lett. 97, p. 168301, 2006

Effective Interaction



Geometry dictates the attractive interaction with three minima among cut spheres

Histogram Method for effective potentials

It is possible to find self-consistently a $\beta V_\phi(r)$ such that sampling moves with probability $\exp\left[\beta V_\phi(r)\right]$ the measured radial distribution function is flat

two-body interactions in the dilute limit:

$$g_\phi(r) \equiv_{def} \exp\left[-\beta V_\phi(r)\right]$$

F. Wang and D. P. Landau , Phys. Rev. Lett. 86, p. 2050 , 2001

Bootstrapping the Monte Carlo

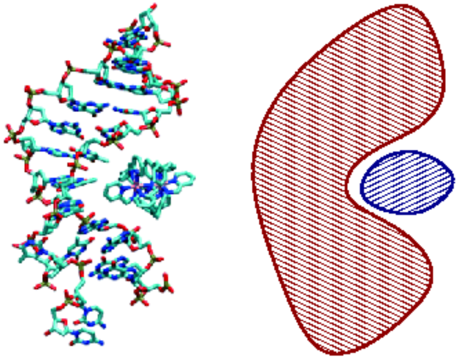
to calculate $\beta\,\Delta V_{\phi}^{eff}$ for $\phi = 0 < \phi_1 < \phi_2 < \ldots$

- calculate g_0 (simulation of two particles) and set $\beta\, V_0^{eff} = -\ln g_0$
- set $\beta\, V_0^{eff}$ as initial guess for $\beta\, V_{\phi_1}^{eff}$
- calculate g_{ϕ_1}
- set $(\phi_2/\phi_1)\ \beta\, V_{\phi_1}^{eff}$ as initial guess for $\beta\, V_{\phi_2}^{eff}$
- ....

$$\beta\,\Delta V_{\phi_i}^{eff} = \beta\, V_{\phi_i}^{eff} - \beta\, V_0^{eff}$$

Case study 2 : Key-Lock

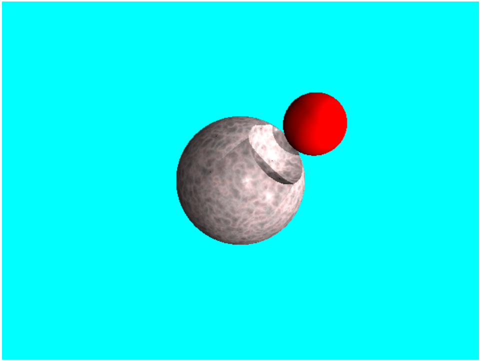
Key-Lock



inspiration: non covalent DNA / metallo-supramolecular cylinder binding

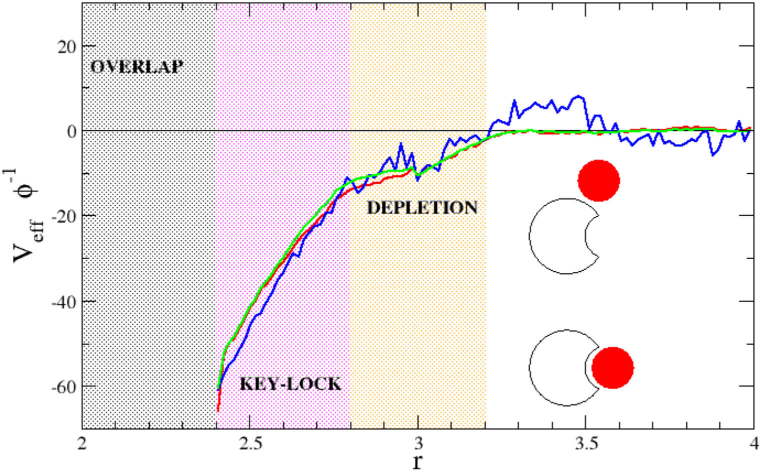
- caveat: real Key-Lock mechanism happen in crowded enviroment and ARE NOT due to depletion
- neverthless, we test depletion induced key-lock for engineering interactions via shape

Chunk Sphere



MC results

key-lock comes from negative curvature surface exposed to positive curvature surface (even better than flat face - flat face interaction)

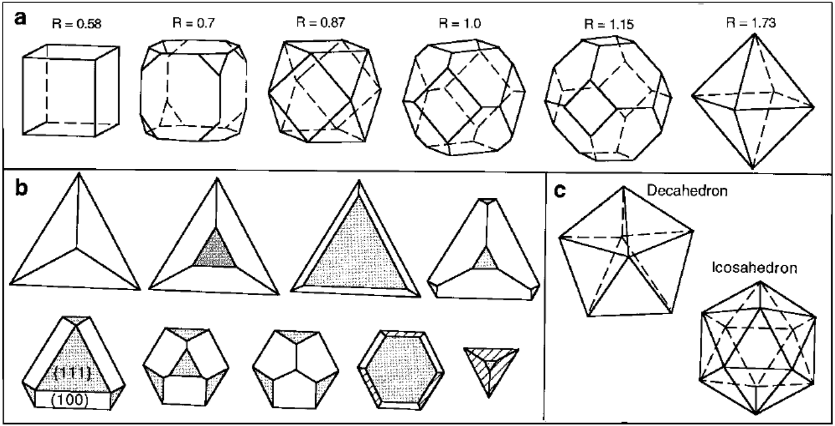


key-lock depletion interaction is $\sim$ 1 order of magnitude bigger

Quest for shaped particles

Nano Crystals

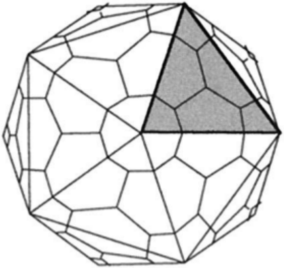
$$\lesssim 10\,nm$$



Zhong Lin Wang, Adv. Mater. 10, pp. 13-30, 1998

Viral Capsids

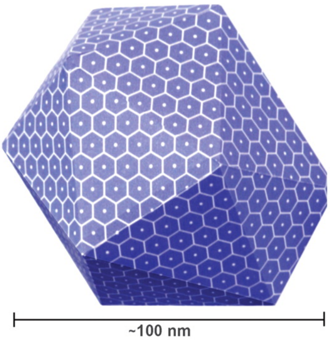
$\sim 20\, nm$ up to $\sim 120\, nm$



Viral capsids are often monodisperse and highly symmetric nanocontainers

Cellular Microcompartments

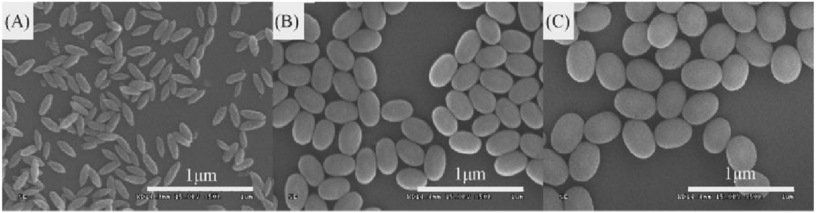
$\sim 100\ nm$



Shiho Tanaka et al, Science 327, pp. 81 - 84, 2010

Colloidal Ellipsoids

$\sim 0.1\ \mu m$ up to $\sim 1\ \mu m$



Tao Ding et al, Adv. Mater. 21, pp. 1936–1940, 2009

Conclusions

- Shape allows *directional interactions*
- Shape induces *Key-Lock mechanisms*
- Complex phase diagram (multiple phases)
- Self Assembly
- How to shape particles?
- How to combine the effects of the shape with other interaction?

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THANKS !!!

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