Monte Carlo Simulation of Interfaces

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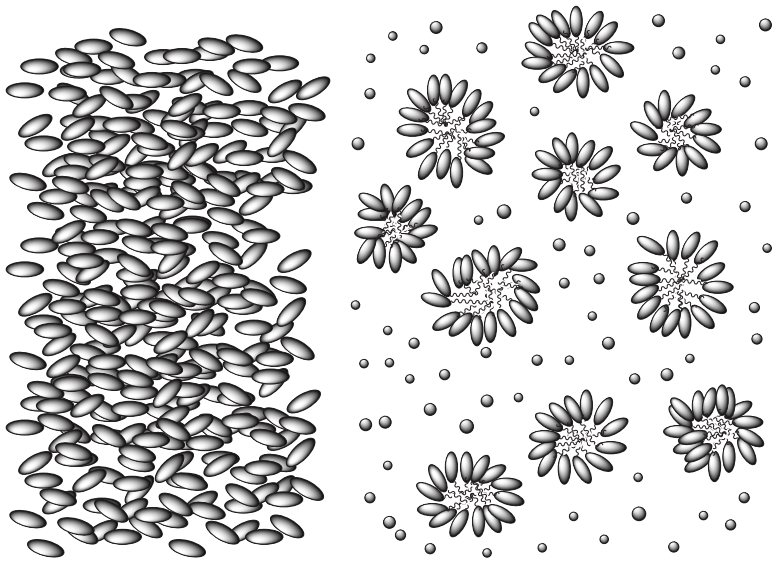
MIR@W day Monte Carlo: 07/03/2011

What is...?

Soft matter

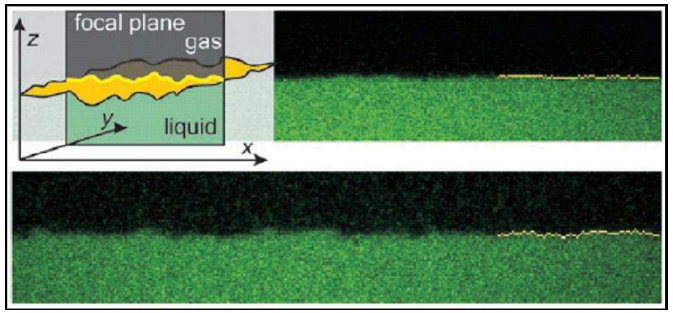
- liquids, liquid crystals, polymers, colloids, surfactants



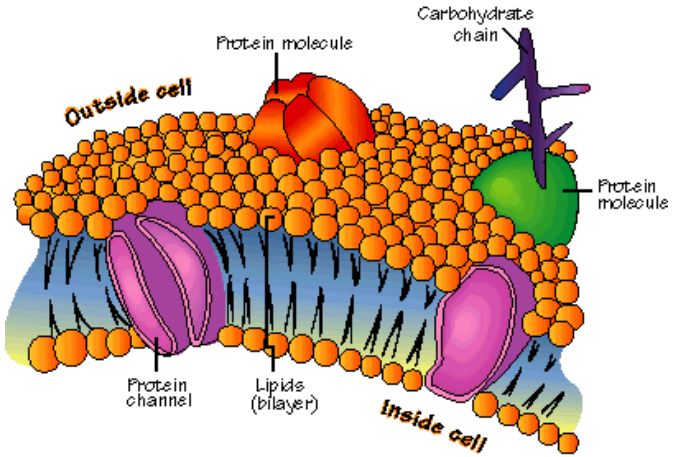
- soft (energies$\approx k_B T$)
- fluidity
- order
- self-organization

Interfaces

- liquid-liquid, liquid-gas



- solid-liquid
- membranes

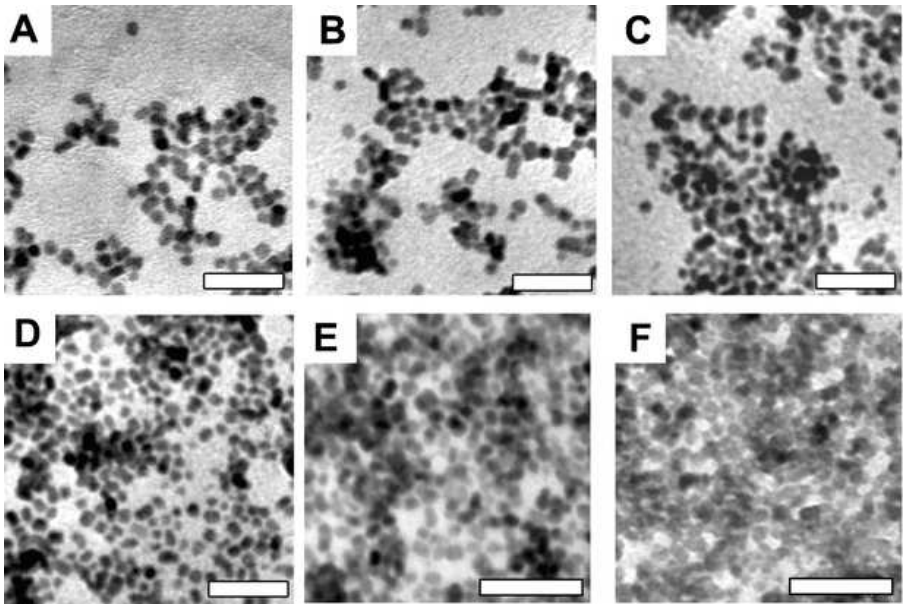


Outline

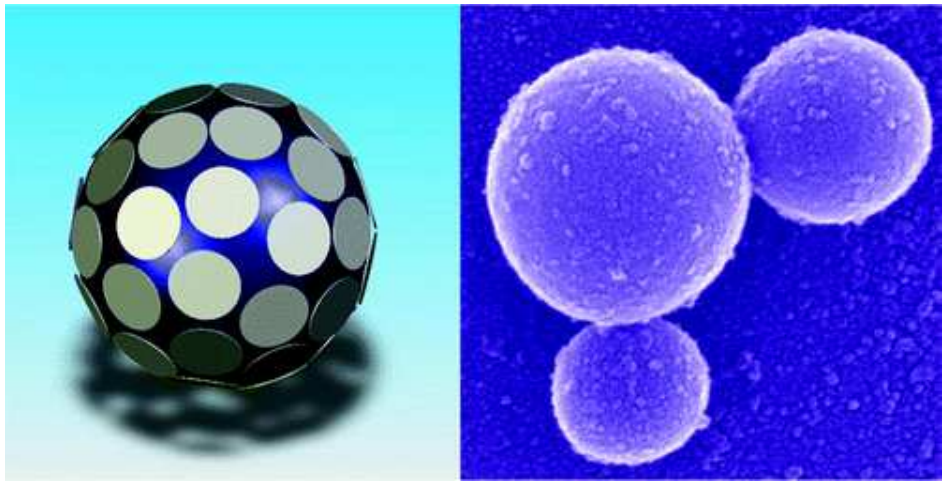
Nanoparticles at soft interfaces

- Nanoparticles
  - quantum dots, fullerenes, macromolecules, proteins...
- Soft interfaces
  - liquid-liquid (oil-water), polymer blends, membranes....

Nanoparticle monolayer



Nanoparticle stabilised droplet

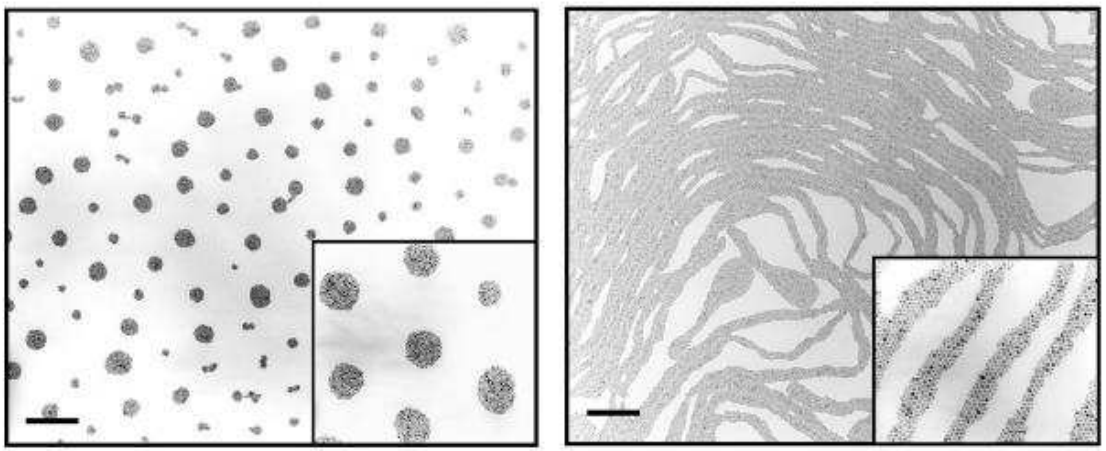


- Adhesion of nanoparticles onto soft interfaces
  - for ≈nm particles detachment energy 10 $k_B T$

A Böker *et al Soft Matter* 2007; S Bon *et al Langmuir* 2007

Nanoparticle-interface interaction

- Nanoparticle self-assembly
  - dynamics/kinetics
  - capillary forces between nanoparticles: structure formation



- Adhesion strength not measured experimentally
  - often estimated from continuum models
- Many contributions to interaction
  - difficult to isolate different effects experimentally

RP Sear *et al PRE* 1999

Model

- Solvent
  - non-additive hard sphere (Widom-Rowlinson) mixture
    2 components A and B

$$V_{\alpha\beta}(r) = (1 - \delta_{\alpha\beta})V_{hs}(r, \sigma)$$

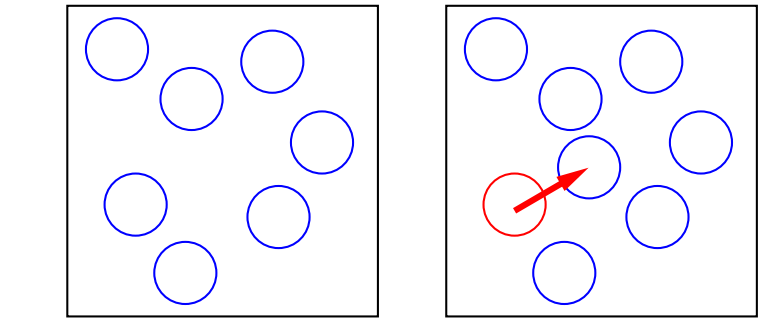
    (diameter $\sigma \approx 0.3$ nm)
  - demixes above critical density
- Nanoparticle
  - hard-sphere (diameter 3-6 σ)
- Grand-canonical Monte Carlo simulations
  - Free-energy profile (effective NP-interface interaction)

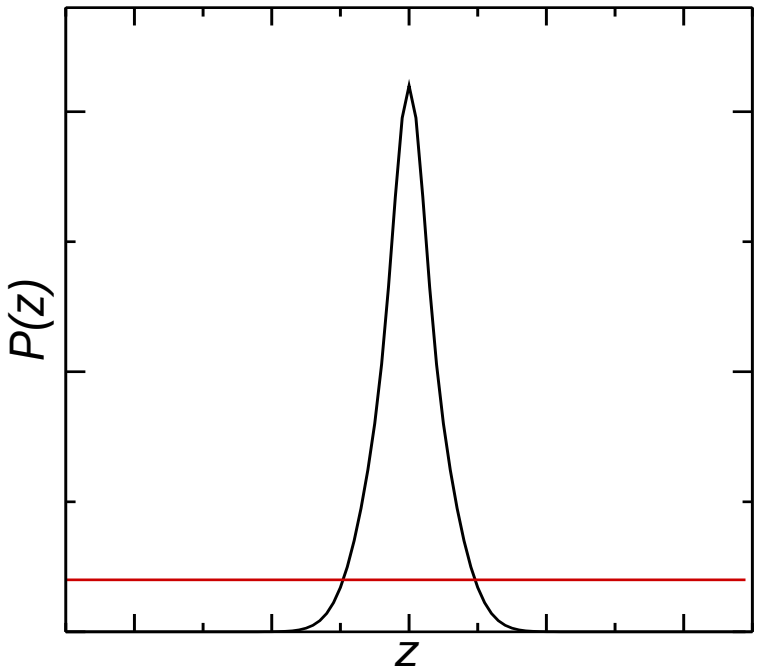
$$\beta F(z) = -\log \mathcal{P}(z)$$

  - Wang-Landau sampling

B Widom & JS Rowlinson *JCP* 1970; FG Wang & DP Landau *PRL* 2001

Why do we need Wang-Landau?

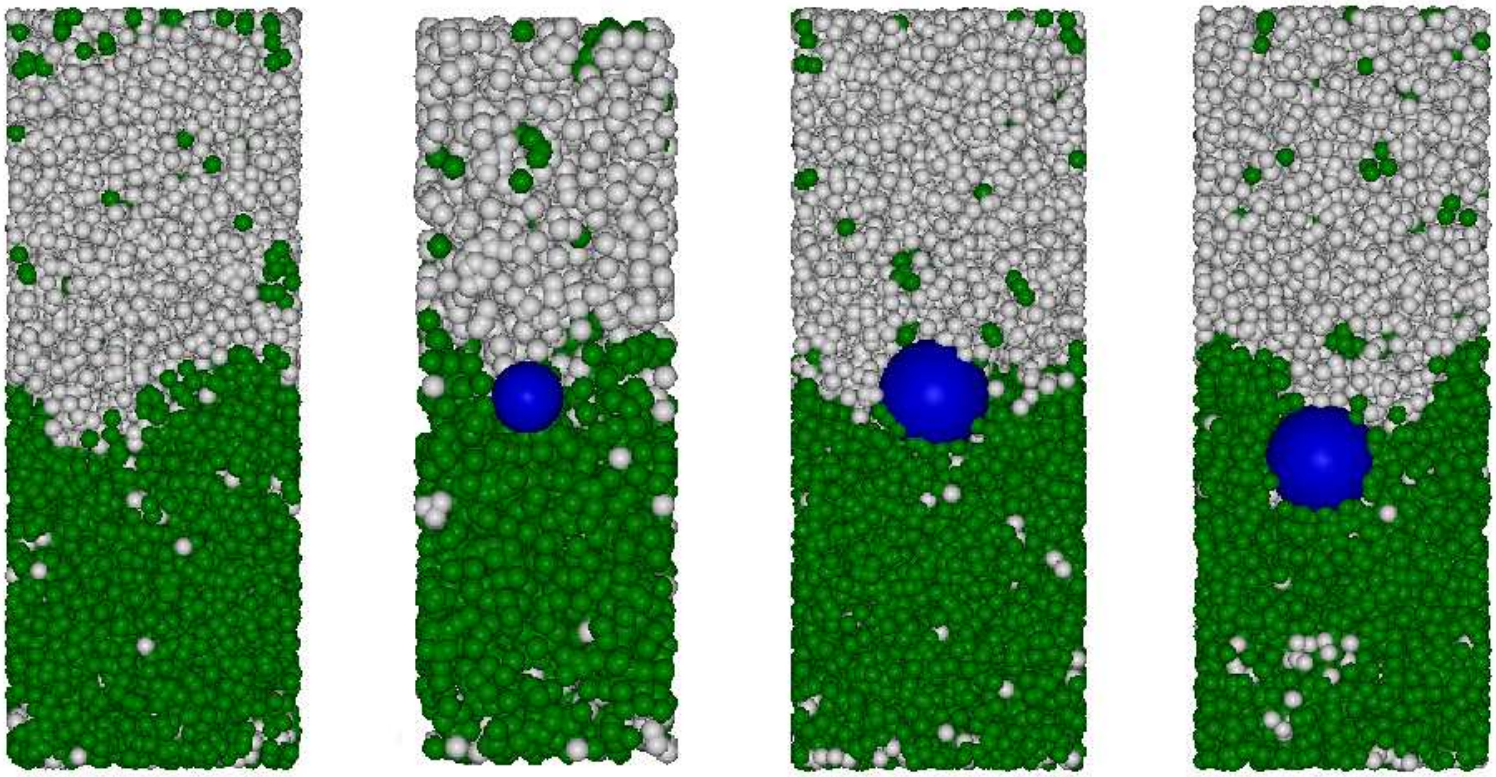




- Detachment energy$\approx 10\, k_B T$
- To accurately determine free energy profile need to sample uniformly across interface

Interface structure

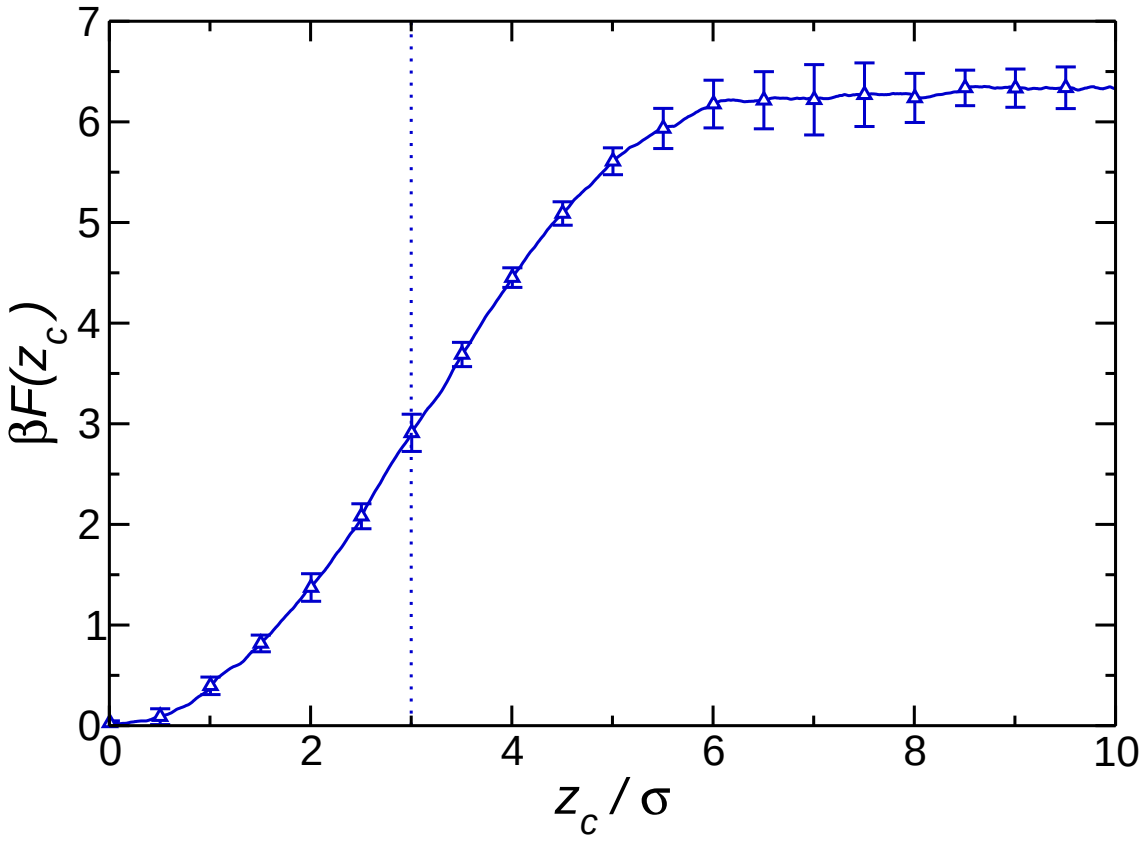
- Interface broadened by capillary waves
  - interface width comparable to nanoparticle size (1-2 nm)
  - bridging between nanoparticle and interface



DLC & SAF Bon *PRL* 2009

Nanoparticle-interface interaction

- Free energy profile

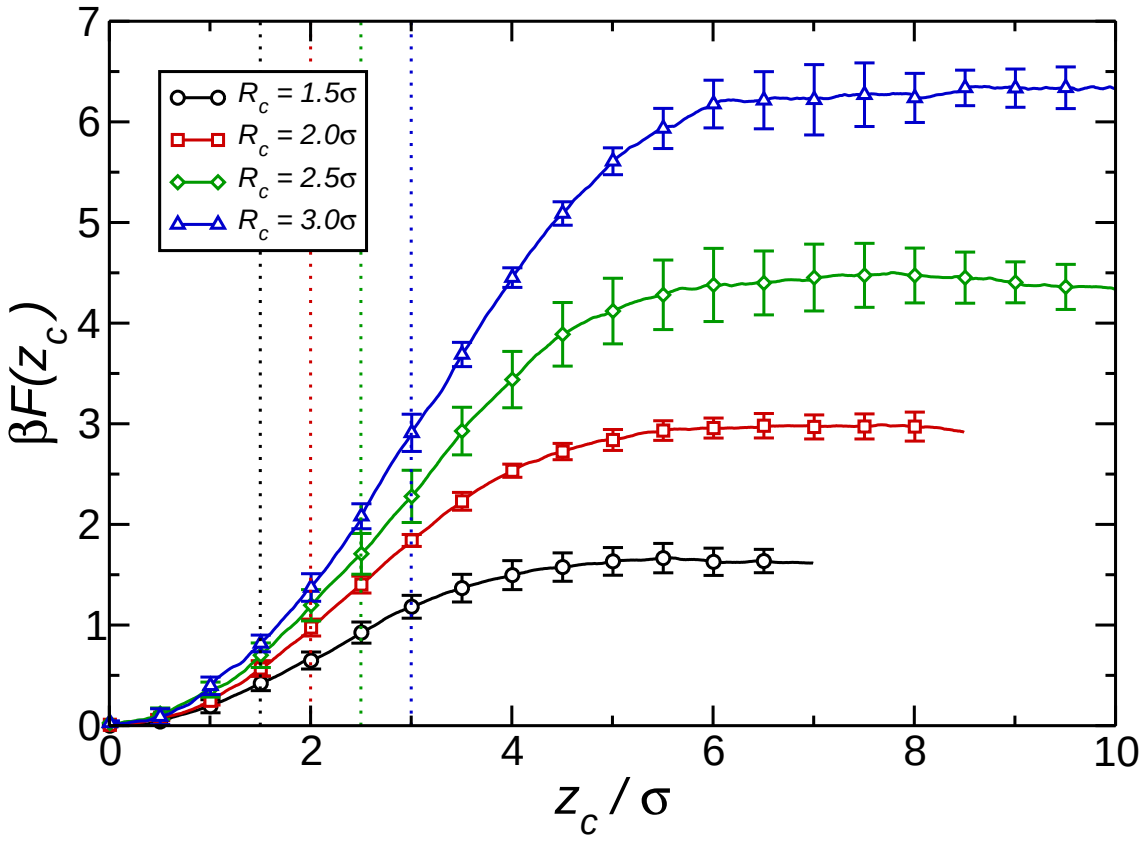


  - long-range interaction ($> R_c$)
  - detachment energy: 1-10 $k_B T$

DLC & SAF Bon *PRL* 2009

Nanoparticle-interface interaction

- Free energy profile

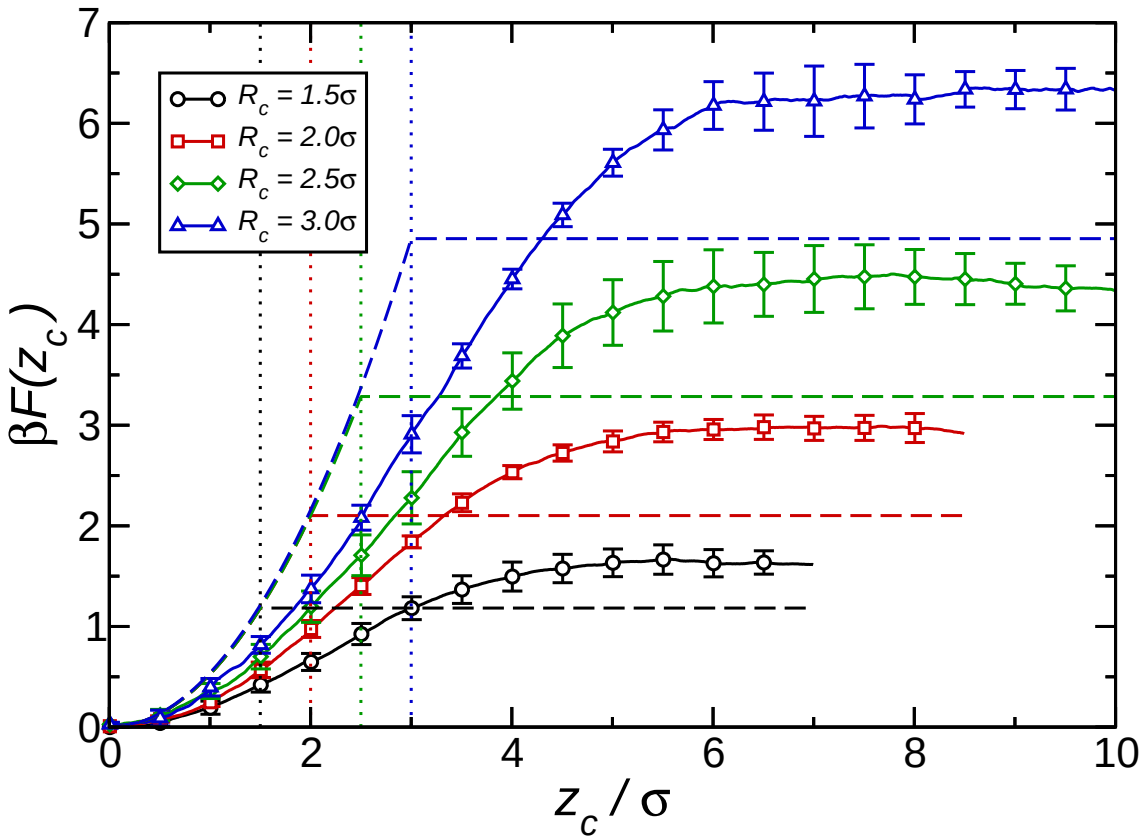


  - long-range interaction ($> R_c$)
  - detachment energy: 1-10 $k_B T$
  - detachment energy: $\propto R_c^2$

DLC & SAF Bon *PRL* 2009

Can we use continuum theory?

- Free energy profile: $F(z) = \pi\gamma z^2$ $(z \leq R_c)$

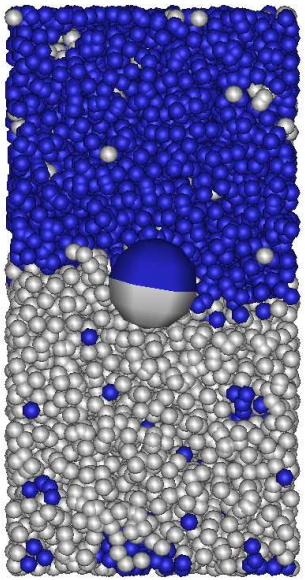


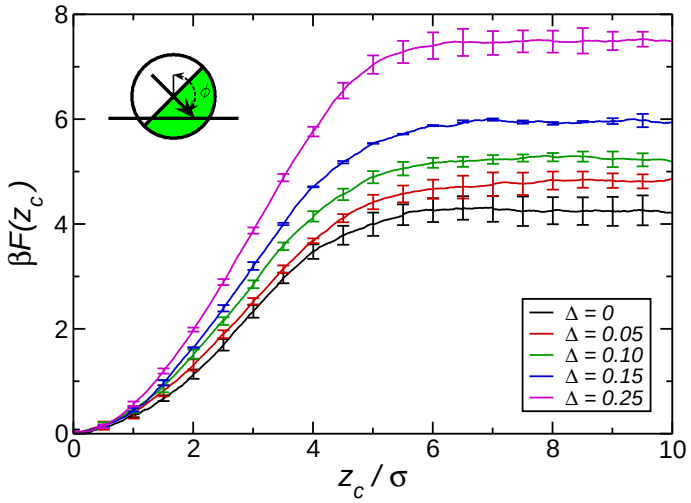
- Continuum theory in poor agreement with simulation
  - underestimates interaction range → flat interface approximation

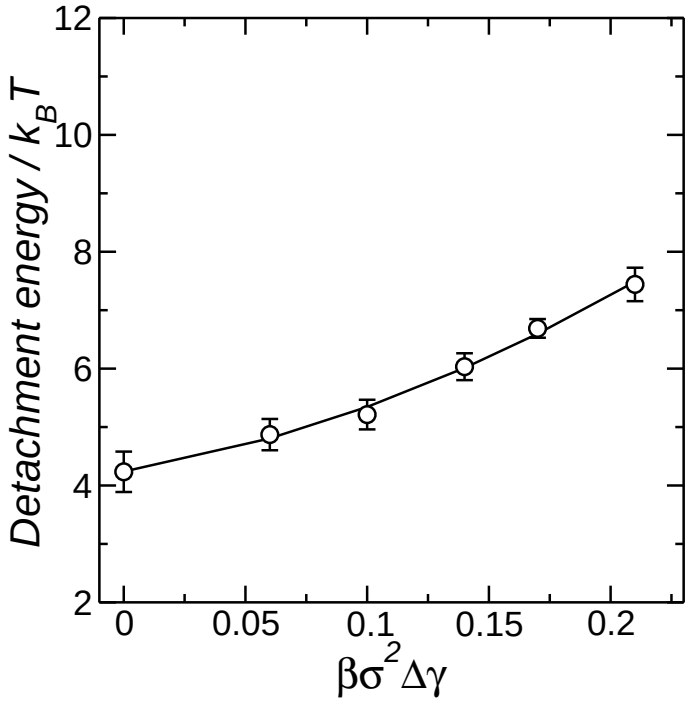
DLC & SAF Bon *PRL* 2009

More complex particles: Janus spheres

- Hemispheres of different (A-philic/B-philic) functionality





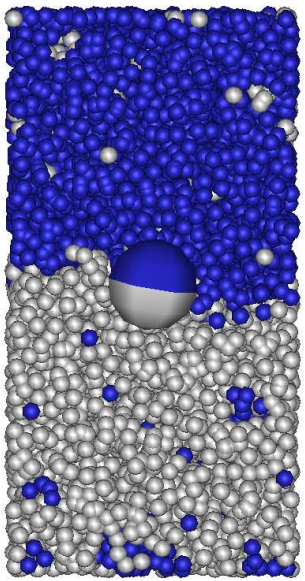


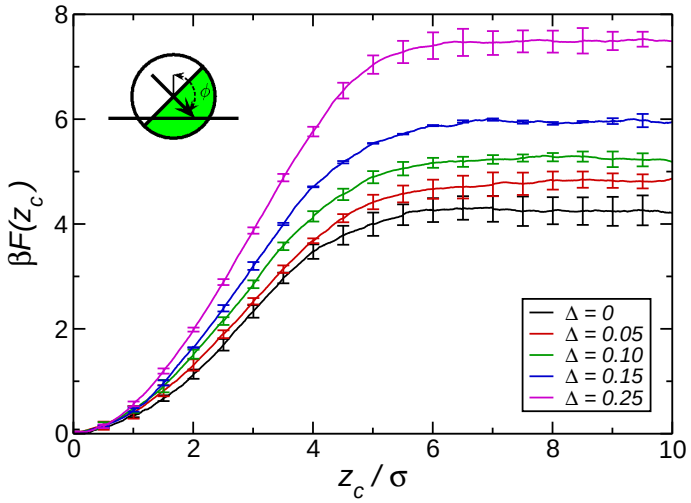
- Stability increases with $\Delta\gamma$

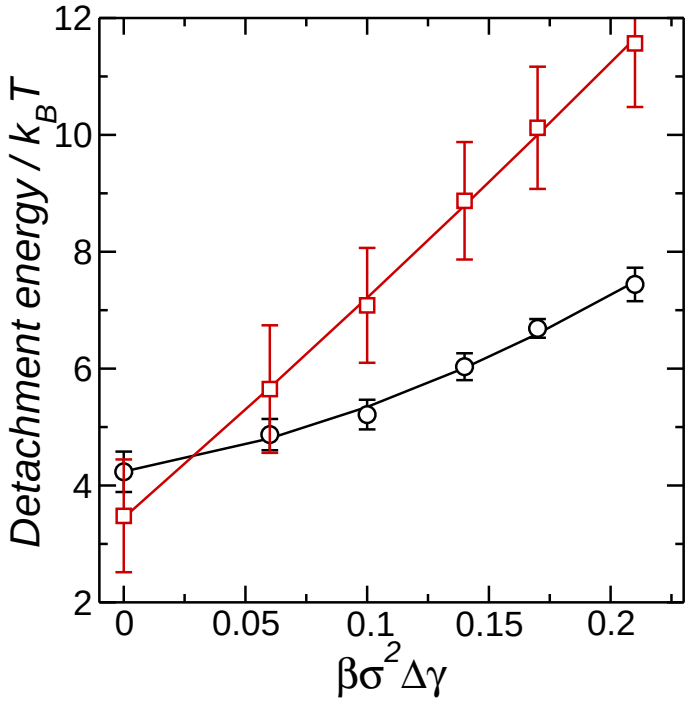
DLC & SAF Bon *Soft Matter* 2009

More complex particles: Janus spheres

- Hemispheres of different (A-philic/B-philic) functionality





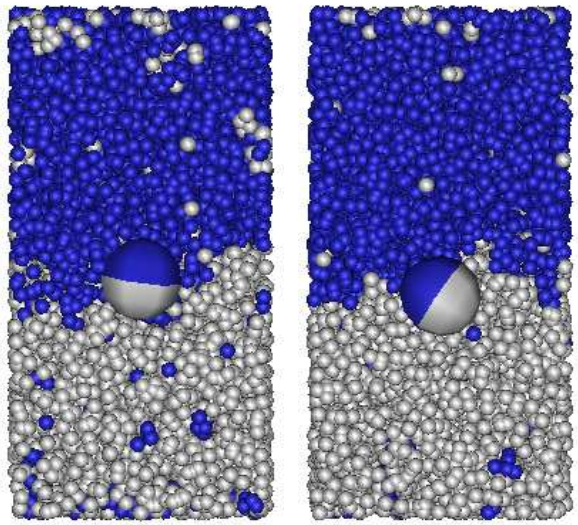


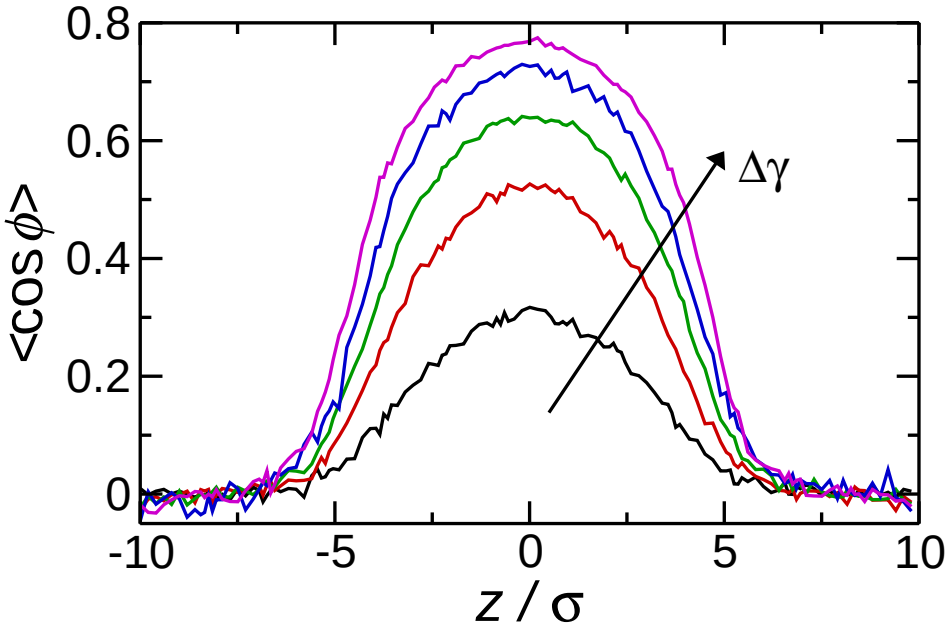
- Stability increases with $\Delta\gamma$
- Continuum theory: overestimates detachment energy

DLC & SAF Bon *Soft Matter* 2009; BP Binks *et al Langmuir* 2000

Nanoparticles rotate

- Theory assumes fixed particle orientation
- nm-sized particles have significant orientation freedom
- Angle between particle orientation and *z*

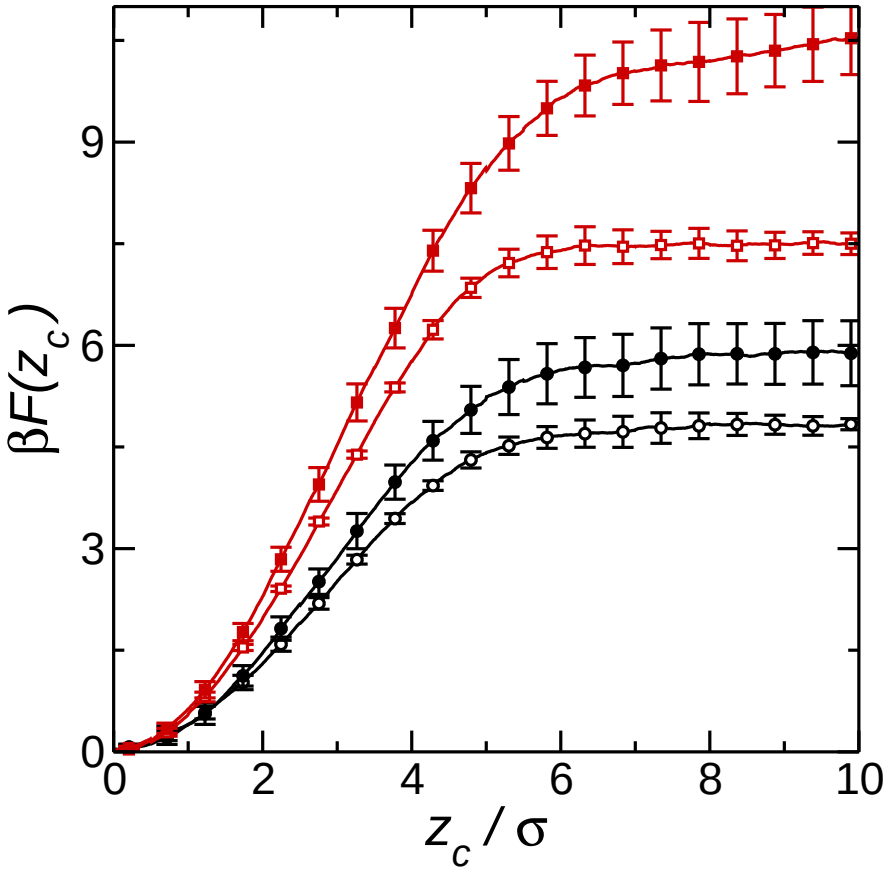


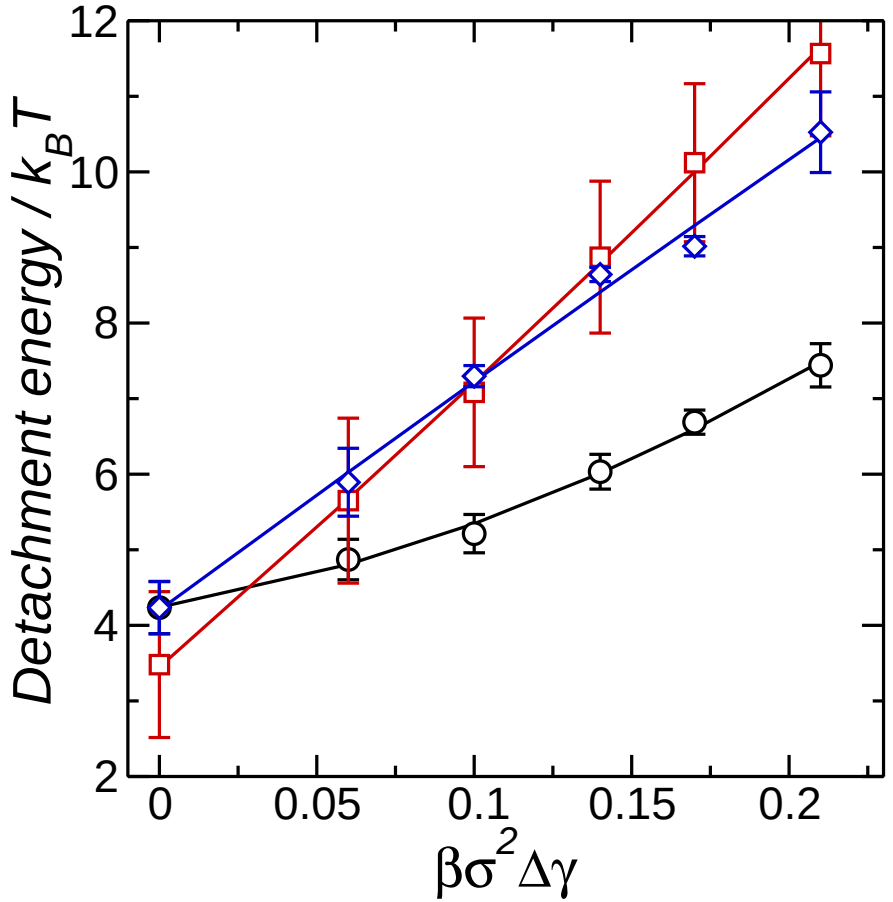


DLC & SAF Bon *Soft Matter* 2009

Fixing the orientation

- Stability increased ≈50% for fixed orientation





  - fix orientation experimentally (***E*** or ***B*** field?)

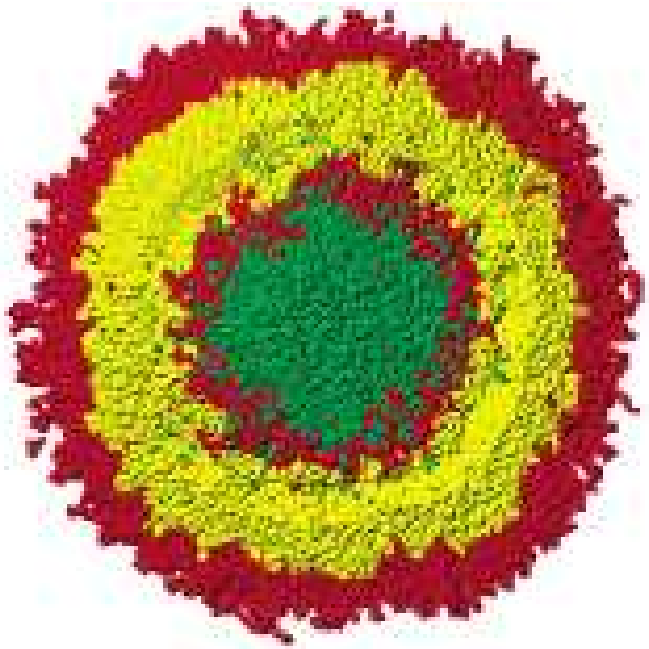
DLC & SAF Bon *Soft Matter* 2009

Nanoparticle-interface interactions

- Have used molecular simulation to study interaction of nanoparticle with liquid interfaces
  - interaction is longer ranged than expected - capillary waves
  - detachment energy is $1 - 10\ k_B T$
  - detachment energy $\propto R_c^2$
- Comparison with continuum theory (Pieranski approximation)
  - underestimates detachment energy
  - underestimates range of interaction - neglect of capillary waves
- Janus particles
  - more stable on interfaces, although orientational freedom important

Outline

Polymer vesicles



Polymer bilayers forming a fluid-filled sac

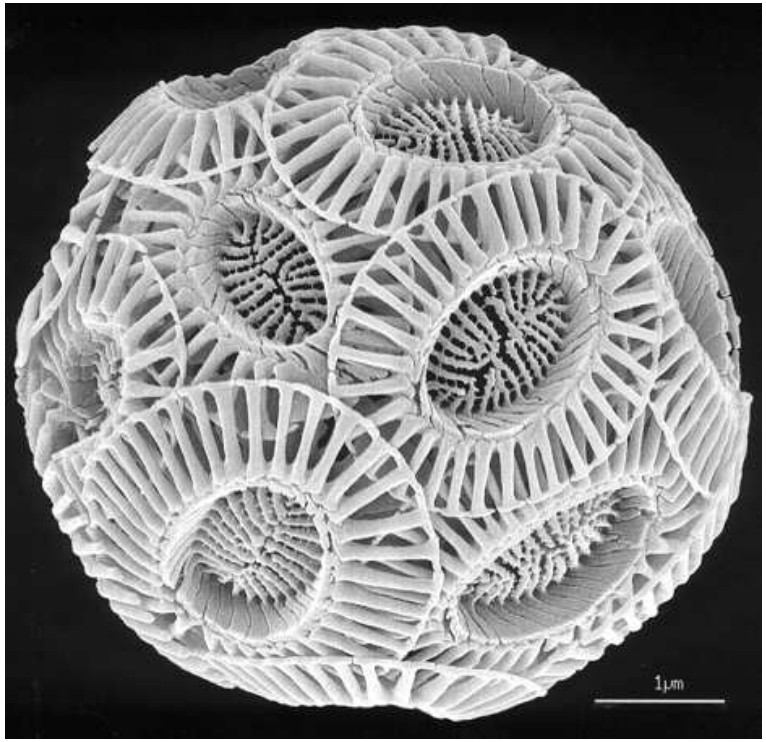
- polymersomes - analogous to liposomes
- synthetic minimal cells

Use of polymers enhances the mechanical stability compared to liposomes

- reaction vessels
- drug delivery vehicles

V Ortiz *et al*, *JPCB*, 2005

Armoured vesicles



Y. Shiraiwa, University of Tsukuba

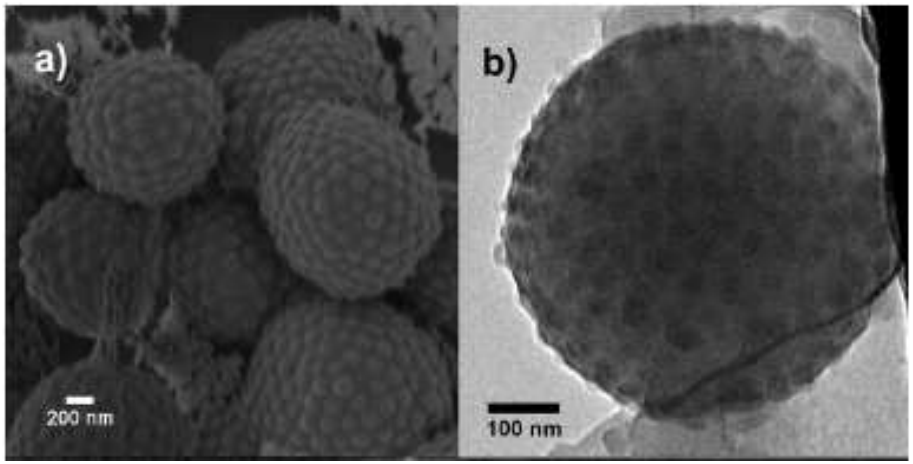
The stability of polymer vesicles may be further enhanced by a coating of nanoparticles
This occurs in many naturally occuring systems

- bacterial S-layers
- nanopatterned calcium carbonate coating on coccolithophorids

Can this be mimicked in synthetic, polymeric systems?

Experimental system (Bon group, UoW)

Vesicle: poly(*n*-butyl methacrylate)-*b*-(*N*,*N*-dimethylaminoethyl methacrylate) block co-polymer (1 μm radius)
Nanoparticles: 120 nm and 200 nm diameter anionic polystyene latex particles



Distinct packing patterns of nanoparticles on vesicle surface

- can we reproduce/predict these packings from simulations?

Simulations

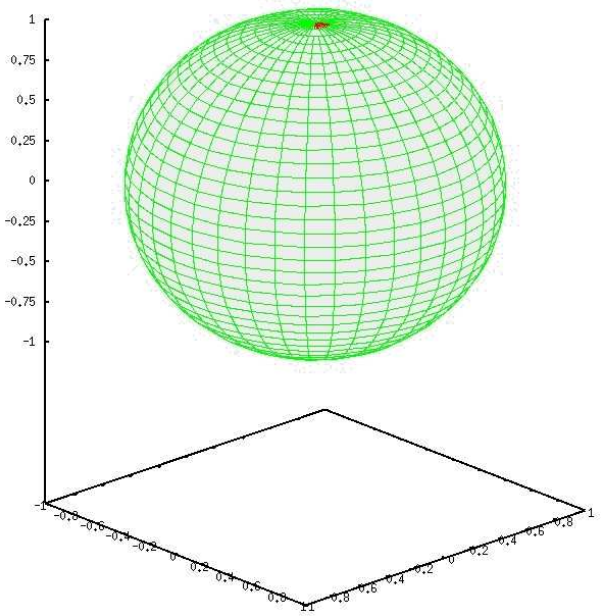
Monte Carlo simulations

- nanoparticles interact through modified LJ+Yukawa potential

$$V(r) = \epsilon \left[\left(\frac{r_{eq}}{r} \right)^{24} - 2 \left(\frac{r_{eq}}{r} \right)^{12} \right] + A \frac{\exp(-r/\xi)}{r/\xi}$$

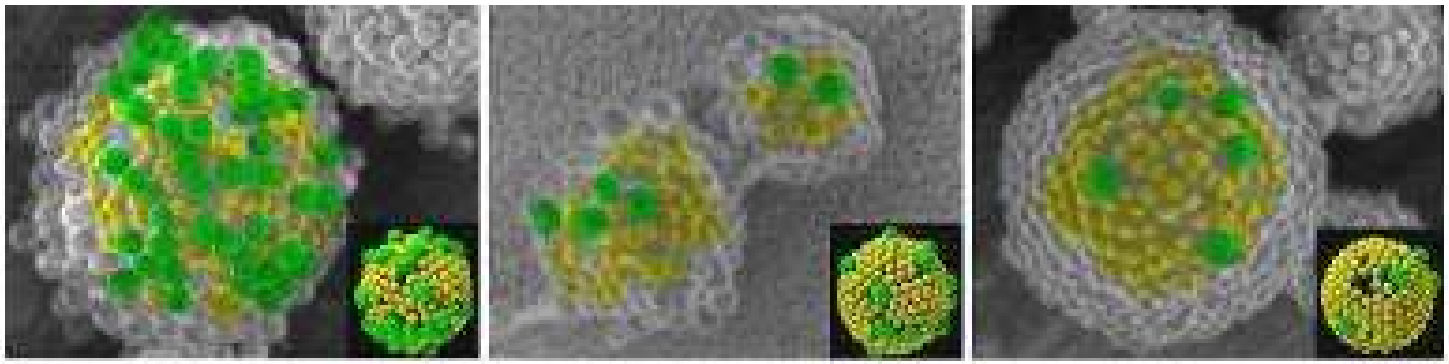
  A is related to the charge density on the particle surface

- model vesicle as large sphere
  - gradually add particles onto vesicle - NPs irreversibly adsorbed
  - NPs move on the surface (modify normal move acceptance to ensure uniform sampling on spherical surface)



Comparison

Packing patterns on polymer vesicles (after 14 hours annealing) and from simulations (insets)



- 56%, 78%, and 91% encounter probabilities (relative likelihood of smaller particle attaching to vesicle)

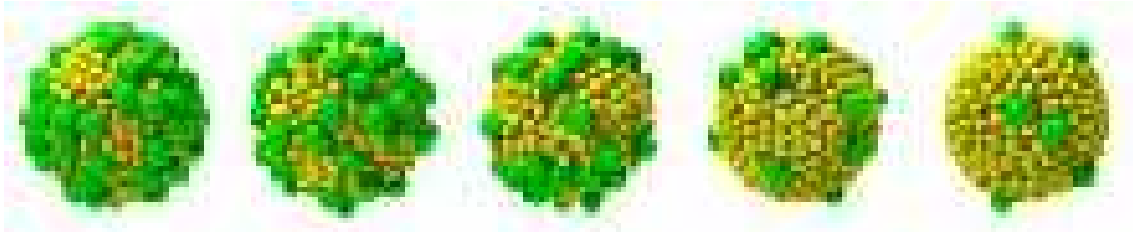
Good agreement between experimental and simulation packing patterns

Controlling the pattern

Study the effect of changing the the surface charge density

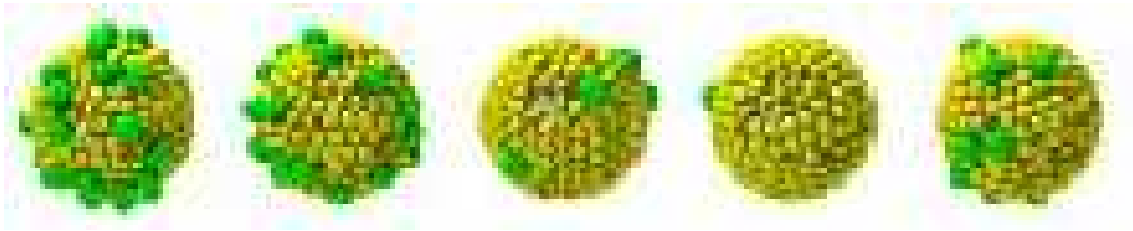
56 % small particles

Increasing charge density→



79 % small particles

91 % small particles



Adsorption on polymer vesicles

- Experimentally it has been shown that it is possible to coat polymer vesicles in 'nanoparticle-armour'
- Using simple MC simulations can reproduce experimentally observed packing patterns on polymer vesicles
- Find changes in packing patterns with increasing surface charge density
- Further work is to quantify the simulation and experimental packing patterns

Conclusions

- Molecular simulation provides a powerful tool for the investigation of interfacial systems
- Gives molecular insight that is complementary to experimental studies
  - test/refine theories
  - study molecular details difficult/impossible to resolve experimentally
  - gives precise control over the system parameters

References:

Nanoparticle-interface interactions

DLC & S. Bon, *Phys. Rev. Lett.*, **102**, 066103 (2009)
DLC & S. Bon, *Soft Matter*, **5**, 3969 (2009)

Armoured vesicles

R Chen *et al*, *J. Am. Chem. Soc.*, **133**, 2151 (2011)

Acknowledgements

Collaborators

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- Martin Oettel, Friederike Schmid (Mainz), Matthias Schmidt (Bayreuth/Bristol)

Computers

- Centre for Scientific Computing, UoW

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- EPSRC, ERC, Leverhulme Trust, University of Warwick

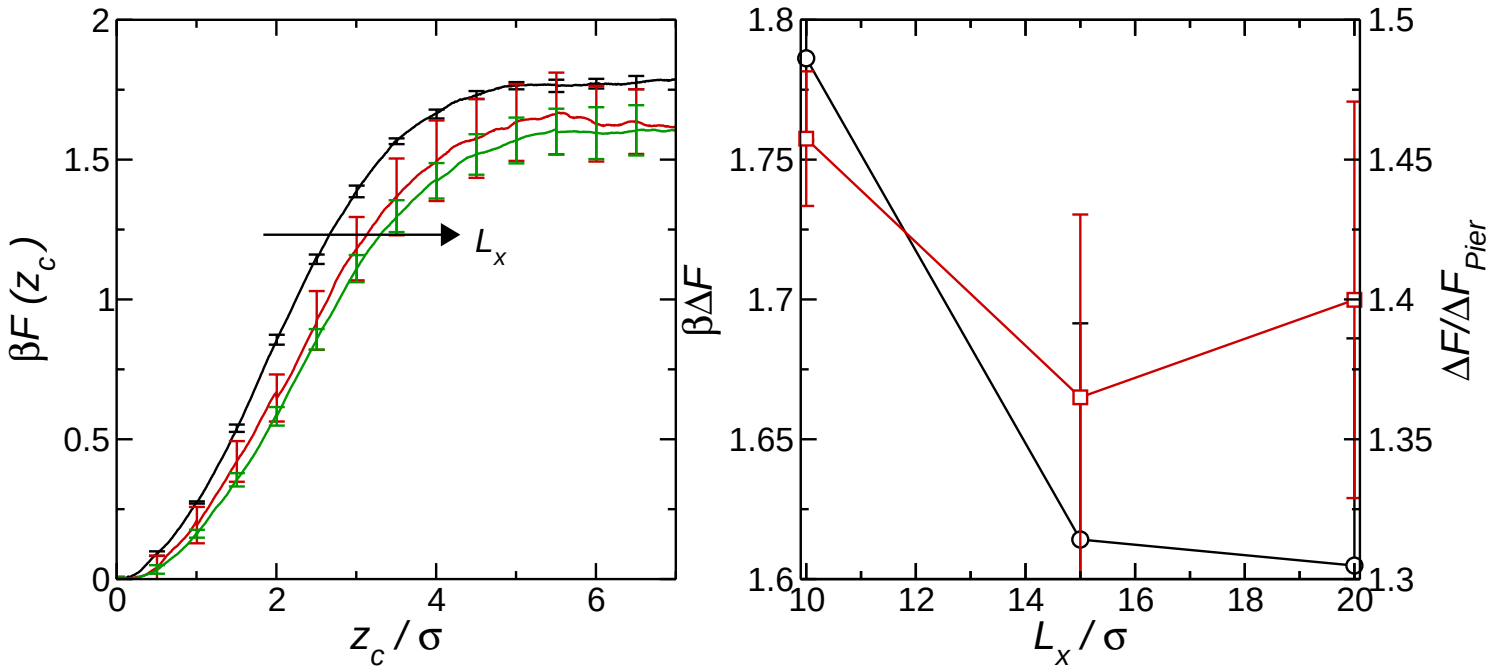
Model & method

- Study system using grand-canonical MC simulations
  - simulations at different (solvent) chemical potentials $\beta\mu = 0.15...0.35$ ($\beta\mu_c \approx 0.04$)
  - confine system in z-direction: localises the interface near cell centre
- Calculate free energy profile
  - $\beta F(z_c) = -\log \mathcal{P}(z_c)$
  - find probability distribution using Wang-Landau sampling
  - divide separation into overlapping windows
- Calculate interfacial tension

FG Wang & DP Landau, *PRL*, 2001

System-size dependence

- System-size dependence (lateral box length L_x)

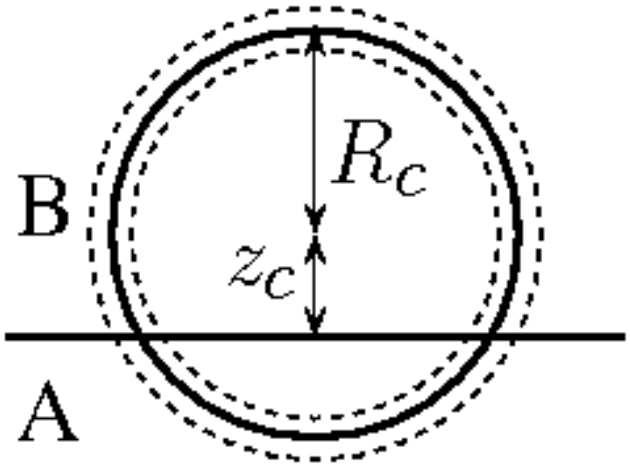


- Consistent with decrease in γ
  - interaction range increases
  - barrier decreases

DLC & SAF Bon *PRL* 2009

Varying wettabilities

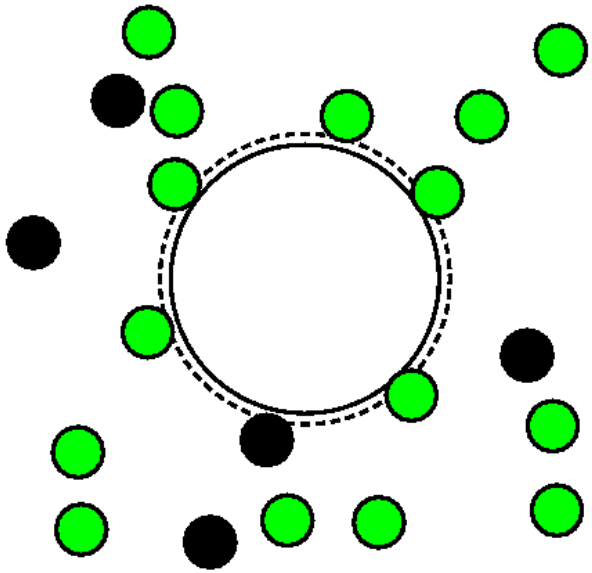
- Stability controlled by changing surface tensions
  - Experimental systems: different γ for two components
  - polystyrene-water: γ=32 mN m^{-1} polystyrene-hexadecane: γ=14.6 mN m^{-1}
- Simulate non-symmetric case
  - use different radii for the two components $R_{A/B} = R_c \mp \Delta$
  - $R_c = 2.5\sigma$ and $\Delta \leq 0.1 R_c$
  - $\beta\mu = 0.15$

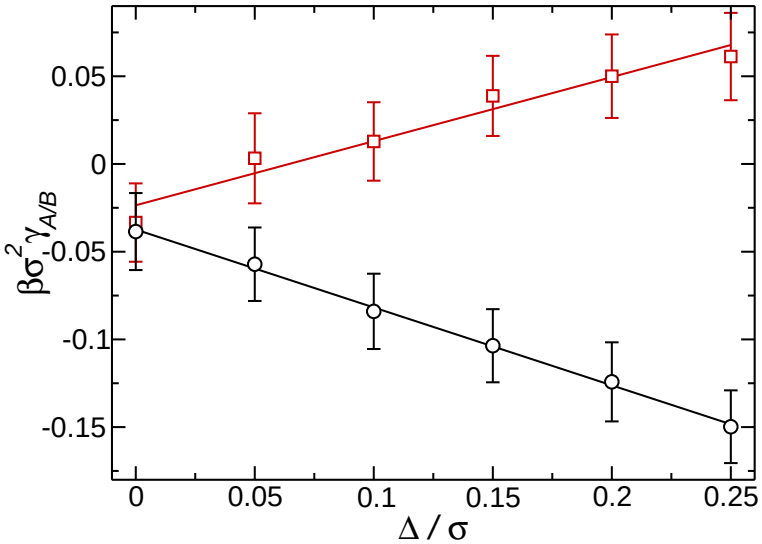


Diversion: calculating γ_{iP}

- To make contact with continuum theories need to calculate γ_{AP} and γ_{BP}
- Bresme & Quirke
  - free energy change from change in nanoparticle radius

$$\Delta F = (4\pi R_c^2 \Delta R)P + (8\pi R_c \Delta R)\gamma$$



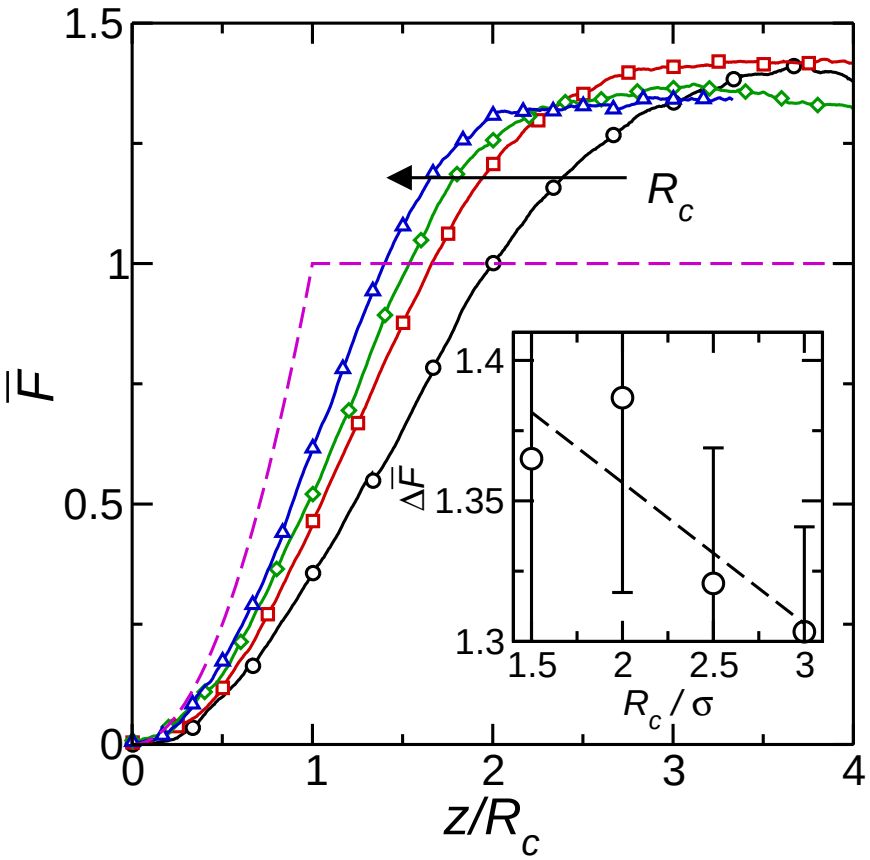


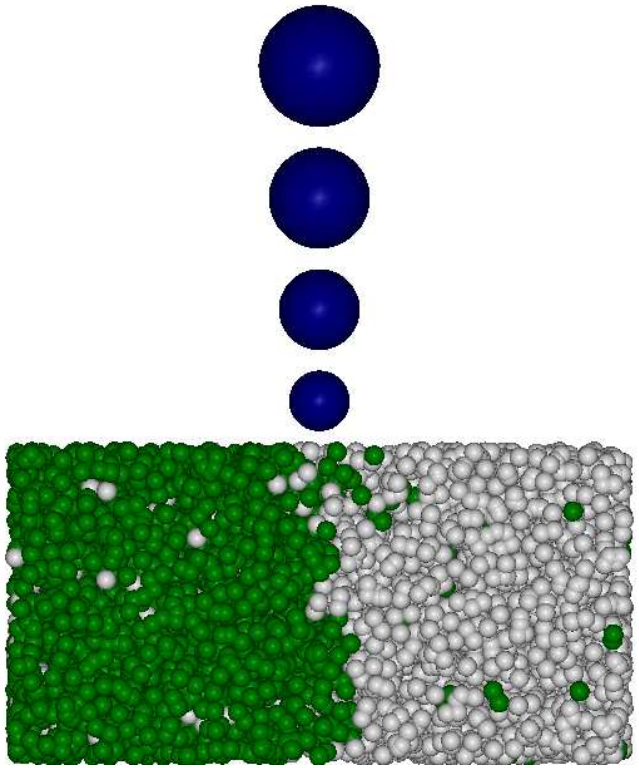
- $\Delta\gamma < 8$ mN m^{-1}

F Bresme & N Quirke, *PRL* 1998

Towards the continuum limit

- As particle size increases continuum theory becomes more accurate

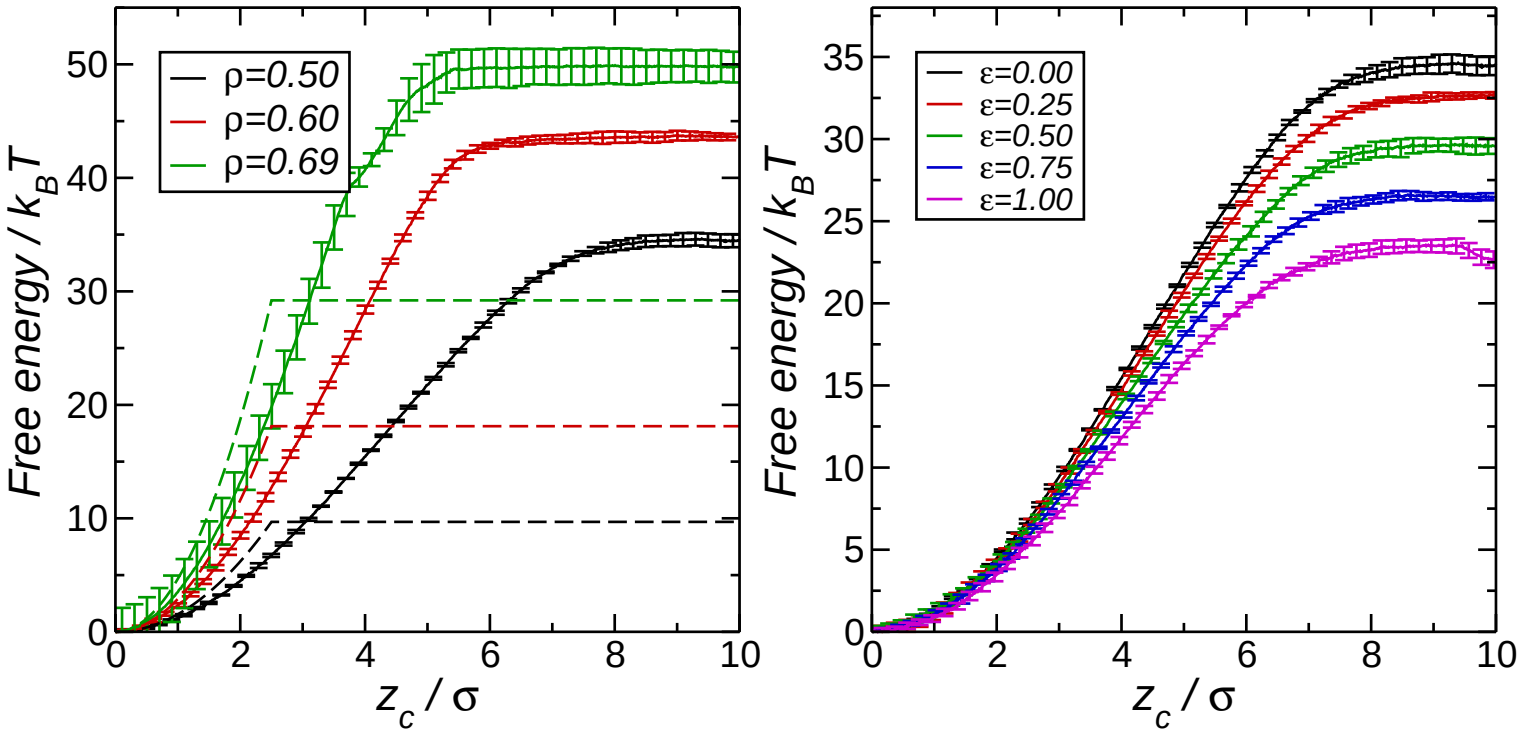




DLC & SAF Bon *PRL* 2009

Not just hard spheres

- Binary Lennard-Jones fluid



- Qualitative results same as for WR mixture
- Attractive NP-fluid interactions decrease NP stability