Armoured and swollen vesicles

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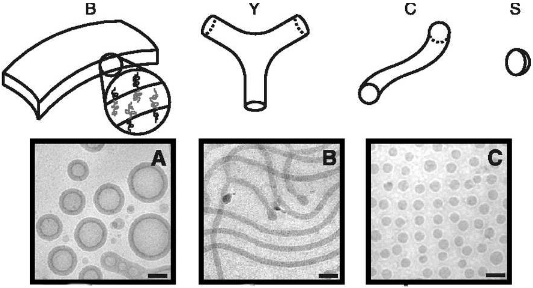
Polymers in solution

Macromolecular amphiphiles

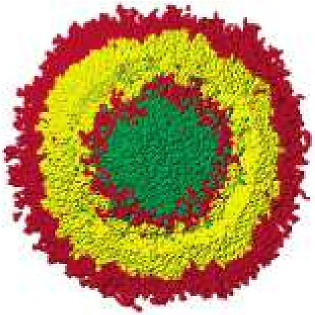
Self-assembly in solution



- similar to small molecule surfactants
- controlled by hydrophobic block length

S Jian & FS Bates *Science* 2003

Polymer vesicles



Polymer bilayers forming a fluid-filled sac

- polymersomes - analogous to liposomes
- synthetic minimal cells

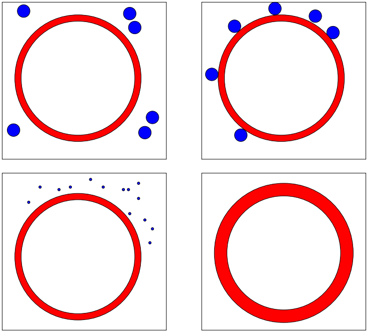
Use of polymers enhances the mechanical stability compared to liposomes

- reaction vessels
- drug delivery vehicles

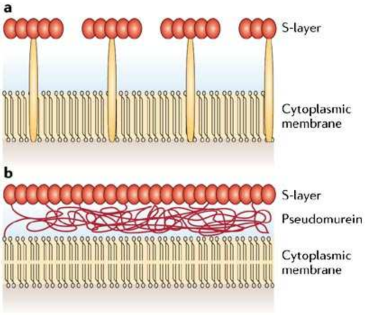
V Ortiz *et al*, *JPCB*, 2005

How to use vesicles

- In delivery applications vesicles undergo changes in
  - pressure
  - pH
  - concentration
- Need to stabilise vesicles
  - prevent collapse/rupture
- Explore two strategies
  - armouring
  - swelling/cross-linking



Armoured vesicles



The stability of polymer vesicles may be further enhanced by a coating of nanoparticles

This occurs in many naturally occuring systems

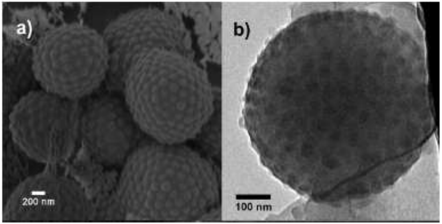
- bacterial S-layers
- nanopatterned calcium carbonate coating on coccolithophorids

Can this be mimicked in synthetic, polymeric systems?

SV Albers *et al Nature Rev Microbio* 2006

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?

R Chen *et al* *JACS* 2011

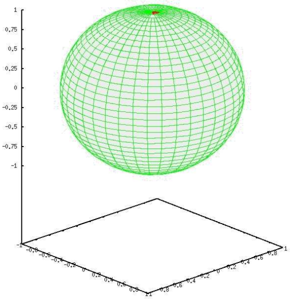
Simulations

Model

- model vesicle as large sphere
- 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



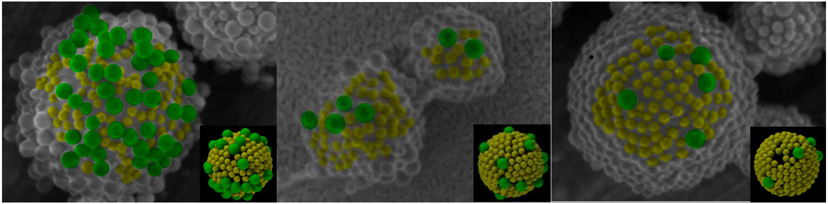
Simulations

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

R Chen *et al* *JACS* 2011

Comparison

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



- 56%, 79%, and 91% encounter probabilities (relative likelihood of smaller particle attaching to vesicle)

Good agreement between experimental and simulation packing patterns

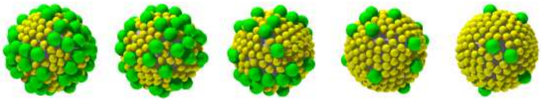
R Chen *et al* *JACS* 2011

Controlling the pattern

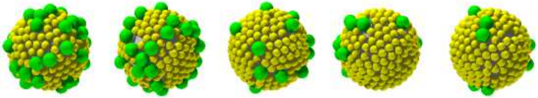
Study the effect of changing the the surface charge density

56 % small particles

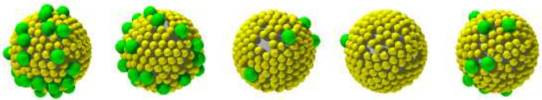
Increasing charge density→



79 % small particles



91 % small particles



R Chen *et al* *JACS* 2011

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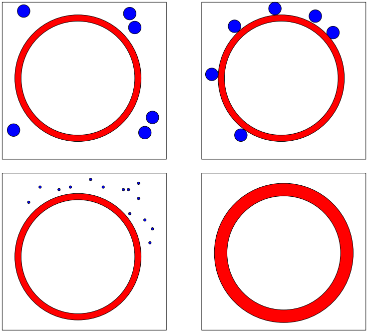
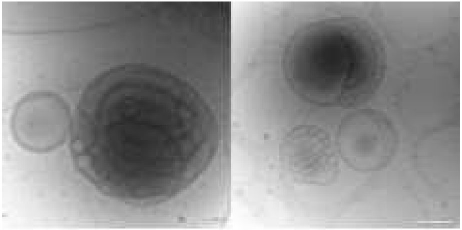


Swelling vesicles

- Experimental
  - PEG-PMMA vesicles swollen with MMA monomers



Normal, patchy, and coiled vesicles

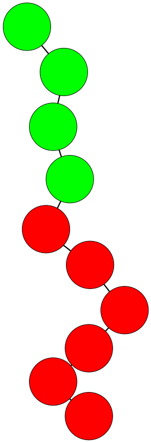
- What causes this change in morphology?
- When is it happening?

CDJ Parmenter *et al Soft Matter* in press

Simulations

Use simulations to study initial details stages of swelling

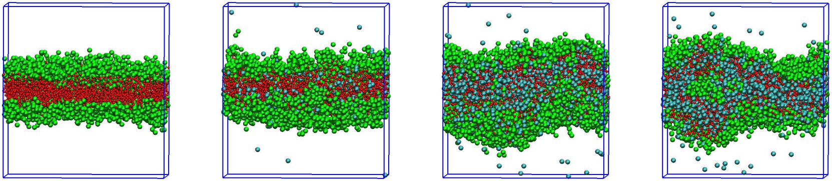
- Dissipative particle dynamics (DPD)
  - mesoscale MD simulation
- Study bilayer of A_4B_6 polymers (500 chains) in solution
  - sequentially change solvent particles into solventphobic monomer beads (prefer polymer tail)
  - change in bilayer morphology as ρ_{mono} increases (overall $\rho = 3$)



CDJ Parmenter *et al Soft Matter* in press

Simulations

Increasing concentration of hydrophobic monomer

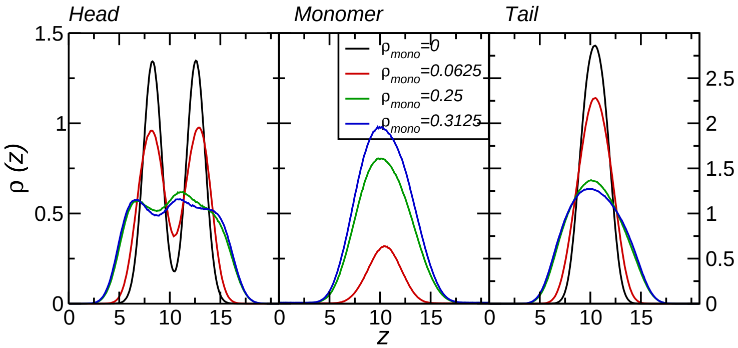


- Budding transition
  - phase separation within bilayer

CDJ Parmenter *et al Soft Matter* in press

How does the bilayer change?

Bilayer density profiles



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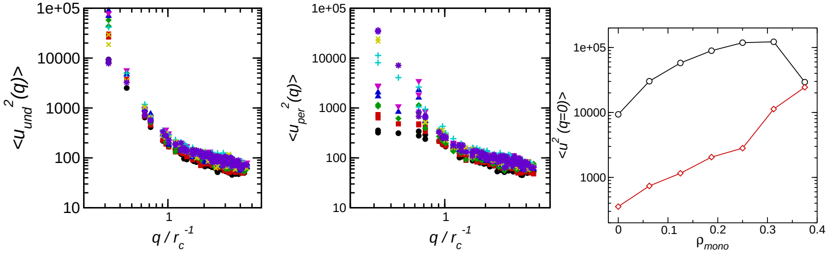
How does the bilayer change?

Biilayer fluctuation spectra

- undulatory - position
- peristaltic - thickness

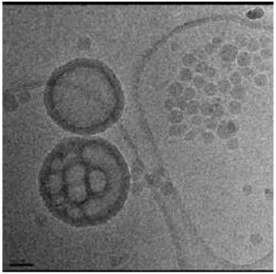


Magnitude of thickness fluctuations grows with ρ_{mono} - formation of bud
Magnitude of undulatory fluctuations decreases at high ρ_{mono} - stiffening of bilayer

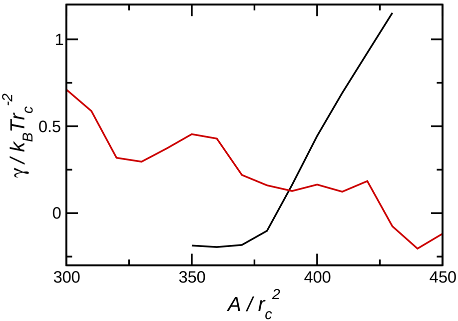
CDJ Parmenter *et al Soft Matter* in press

Coexistence of different structures

Cryo-TEM images



Surface tension against area



- $\rho_{mono} = 0$ (flat bilayer)
- $\rho_{mono} = 0.3125$ (budded bilayer) - multiple minima of $\gamma(A)$

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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
- Swelling polymer vesicles show range of complex morphologies
  - budding transition - phase separation in bilayer
  - bilayer surface tension has multiple minima in budded state
  - how do these buds lead to complex structures seen experimentally?

References

R Chen, DJG Pearce, S Fortuna, DL Cheung, & SAF Bon, *J. Am. Chem. Soc.*, **133**, 2151 (2011)
CDJ Parmenter, R Chen, DL Cheung, & SAF Bon, *Soft Matter*, in press

Acknowledgements

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Computers

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