Monte Carlo Simulation of Interfaces

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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

![Diagram of soft matter and interfaces](image)
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 \( \approx \) nm particles detachment energy \( 10 k_B T \)

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 $\sigma$)

Grand-canonical Monte Carlo simulations

- Free-energy profile (effective NP-interface interaction)

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

- Wang-Landau sampling

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
Nanoparticle-interface interaction

- Free energy profile

![Graph showing the free energy profile](image)

- long-range interaction ($> R_c$)
- detachment energy: $1-10 \ k_B T$
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 \( \rightarrow \) 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
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More complex particles: Janus spheres

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

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

Nanoparticles rotate

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

![Diagram of nanoparticles in two orientations with a graph showing the cosine of the angle and normalized distance $z/\sigma$]
Fixing the orientation

- Stability increased $\approx 50\%$ 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

1. Introduction

2. Nanoparticles at soft interfaces
   - Nanoparticle-interface interactions
   - Janus particles

3. Adsorption on polymer vesicles

4. Conclusions
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

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

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

Can this be mimicked in synthetic, polymeric systems?

Y. Shiraiwa, University of Tsukuba
Experimental system (Bon group, UoW)

Vesicle: poly\((n\text{-butyl methacrylate})-b-(N,N\text{-dimethylaminoethyl methacrylate})\) block co-polymer (1 \(\mu\)m radius)
Nanoparticles: 120 nm and 200 nm diameter anionic polystyrene 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 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
Armoured vesicles
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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
- $\beta F(z_c) = -\log P(z_c)$
- find probability distribution using Wang-Landau sampling
- divide separation into overlapping windows

Calculate interfacial tension

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MC simulation of Interfaces

System-size dependence

- System-size dependence (lateral box length $L_x$)

- Consistent with decrease in $\gamma$
  - interaction range increases
  - barrier decreases
Varying wettabilities

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

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

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

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

F Bresme & N Quirke, *PRL* 1998
Towards the continuum limit

- As particle size increases, continuum theory becomes more accurate.
Not just hard spheres

- Binary Lennard-Jones fluid

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