Mechanical Properties of Surfactant Aggregates at Water-Solid Interfaces Using Micelle-MD

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Surfactant Details

- Surface active agent has amphipathic structure
- In aqueous media, surfactants may aggregate into micelles
- At water-solid interfaces, micelles adsorption may occur

- Hydrophilic cationic head group
  - Trimethyl ammonium ($N^+(CH_3)_3$)
- Anionic counter ion
  - Bromide ion ($Br^-$)
- Hydrophobic tail
  - 12 hydrocarbon unit ($CH_3CH_2$)

Molecular Dynamics Procedure in Micelle-MD

- Initialize conditions such as coordinates of all atoms in the system, temperature, time step value, number of time steps, and periodic conditions.

- Intermolecular potential energy:
  \[
  \Delta \varepsilon_{ab} = \sum_i \sum_j \left( \frac{1}{4\pi \varepsilon_0} q_i q_j e^2 / r_{ij} + A_{ij} / r_{ij}^{12} - C_{ij} / r_{ij}^6 \right)
  \]
  Ionic Potential Lennard-Jones

- Force calculations:
  \[ F = ma \text{ where } F = -\frac{\delta (PE)}{\delta r} \text{ and } a = \frac{\delta^2 r}{\delta t^2} \]

- New position of atom after \( \delta t \):
  \[ r(t + \delta t) = r(t) + \delta t \, v(t) + 1/2 \, \delta t^2 \, a(t) \]

- Velocity of atom after \( \delta t \):
  \[ v(t + \delta t) = v(t) + 1/2 \, \delta t \, [a(t) + a(t + \delta t)] \]

Vertical Silica Indentation

- Experimental hypotheses:
  - no breakage: micelle structure slips out of area between tip and surface
  - breakage: micelle structure fails under applied load
- Computational results agree with breakage
  - Surfactants stay adsorbed on surface and stay close to each other

Comparison of Computational & Experimental Results

Simulations at different indentor velocities

Silica Indentation at an Angle

- Indentor tip approaches at 45° angle
- Breakage of micelle occurs
- Surfactants stay adsorbed on surface and stay close to each other

Graphite Indentation

• In graph, large peak is resistance from monolayer due to very strong hydrophobic interactions between the surfactant tails and surface
Conclusions

• Indentation results on silica:
  – The micelle breaks down during the indentation process
  – Force required to break the micelle agrees well with measured atomic force microscopy (AFM) force curves obtained during indentation of micelles on silica
  – Location of breakage (force and amount of indentation) agrees with AFM data
  – After the micelle breaks apart, the adsorbed surfactants provide resistance to the indenter

• Indentation results on graphite:
  – Structure breaks down during the indentation process
  – After the micelle breaks apart, the adsorbed surfactants provide more resistance to the indenter than was the case on silica
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