Deformation of Poly(amido amine) Dendrimers at Surfaces

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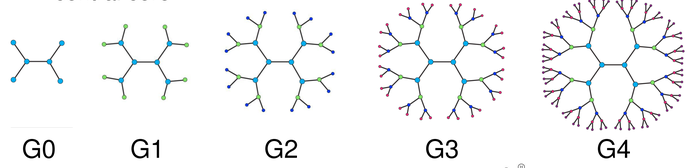
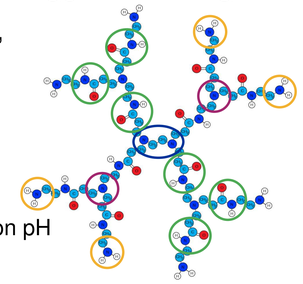
What are Dendrimers?

- Repetitively branched polymers
  - classified by generation, the number of layers surrounding a central core



- Poly(amido amine), or PAMAM, is a common dendrimer
  - ethylene diamine core
  - tertiary amines at branch points
  - second amine linkers
  - primary amine end groups
- PAMAM is a polyelectrolyte
  - degree of protonation depends on pH
    - high pH: no amines protonated
    - neutral pH: primary amines
    - low pH: primary & tertiary amines
- Size and shape are precisely controlled
  - determined by generation
- Attractive for supercapacitor applications!

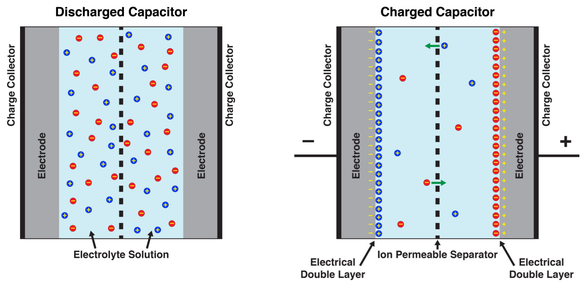


dendrimer charge

	pH 7	pH 2
G3	32	62
G4	64	126
G5	128	254

What are Supercapacitors?

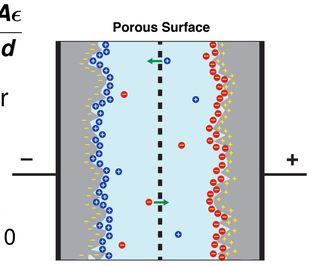
- Two electrodes in contact with a liquid electrolyte separated by an ion permeable membrane
  - common electrodes: activated carbon, graphene, and carbon nanotubes
- When charged, an electrical double layer forms at the electrode/electrolyte interface
  - does not require a chemical reaction
    - fast charge/discharge times and long device lifetimes



- The *capacitance* (ability to store electrical charge) depends on the surface area (A) and the double layer thickness (d)
  - increase surface area to increase energy density

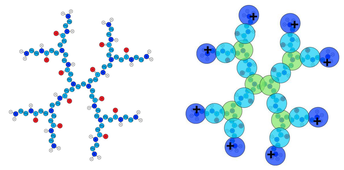
$$C \propto \frac{A\epsilon}{d}$$

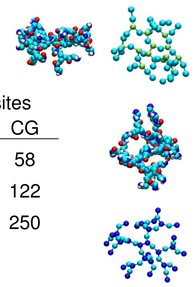
- Matching the pore size in the electrode to the electrolyte further increases capacitance
  - dendrimer sizes match activated carbon pores
    - 0.5 – 5 nm for carbon pore radii
    - 0.8 – 6 nm for PAMAM G0 – G10



Modeling PAMAM Dendrimers

- Classical MD at T = 353 K, p = 1 atm using GROMACS
- Test two different models for PAMAM
  - TraPPE (united-atom) and MARTINI (coarse-grain)

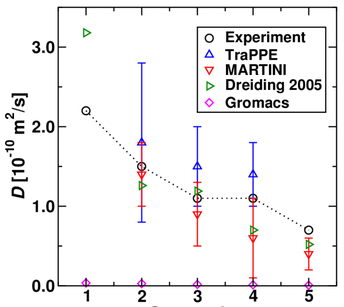


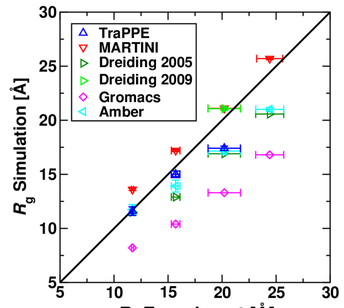


interaction sites

	AA	UA	CG
G2	586	288	58
G3	1092	608	122
G4	2244	1248	250

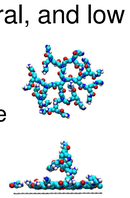
- Excellent agreement with the available experimental data for the radius of gyration and self-diffusion coefficient in aqueous solution

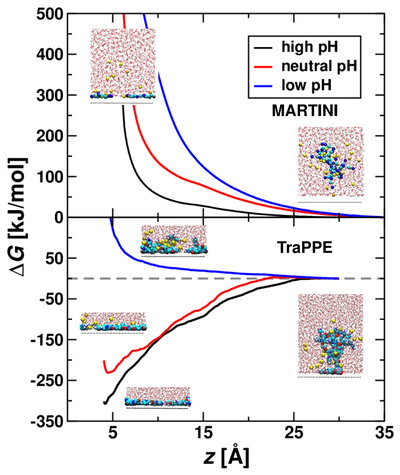




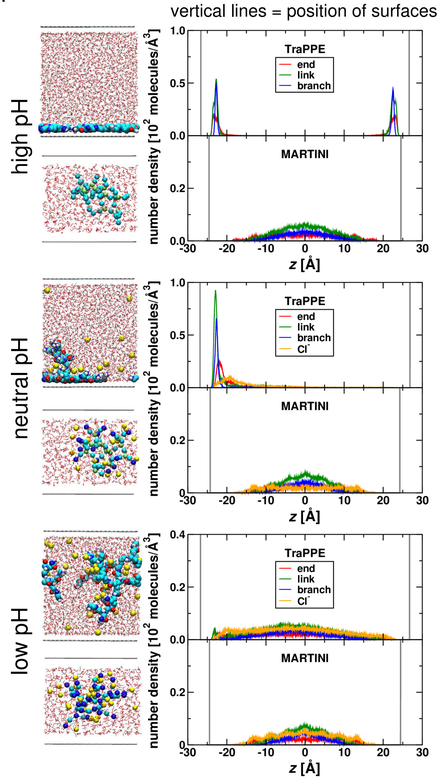
G2 PAMAM at a Graphene Surface

- Two graphene sheets in the *xy* plane surrounding an aqueous solution at high, neutral, and low pH
- High and neutral pH
  - TraPPE dendrimer adsorbs on one of the graphene surfaces
  - MARTINI does not
- Low pH
  - neither model dendrimer adsorbs on the surface
- Potentials of mean force are consistent with this behavior



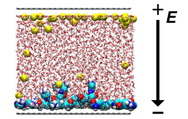


zero = center of the box
vertical lines = position of surfaces



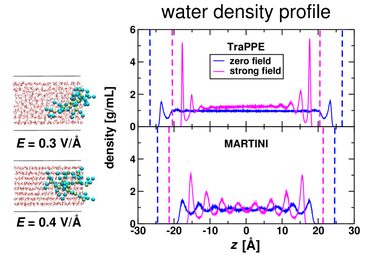
G2 PAMAM with Electric Fields

- Apply a strong electric field in the z direction to try to flatten dendrimers against the surface
  - form electrical double layers

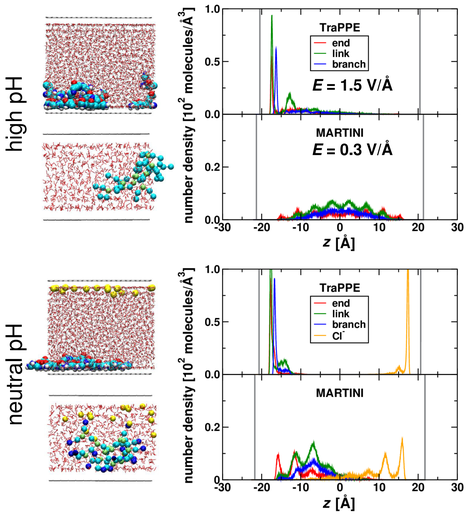


- High pH
  - TraPPE dendrimer was already adsorbed on the surface
    - the electric field drives water to the surface and disrupts the flat dendrimer structure
  - MARTINI water freezes before the dendrimer can adsorb

water density profile



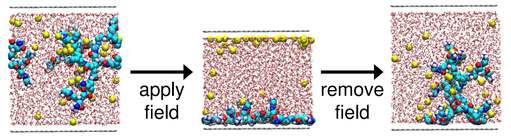
dendrimer density profile



- Neutral pH
  - TraPPE dendrimer further flattens, counterions move to the opposite surface
  - MARTINI dendrimer begins to flatten, then freezes
- Low pH
  - TraPPE dendrimer adsorbs and mostly flattens, counterions move to the opposite surface
  - MARTINI dendrimer begins to flatten, then freezes

Conclusions

- Which model is correct?
  - there is some experimental evidence that PAMAM ***will adsorb*** on graphite/graphene and that this behavior is ***pH-dependent***
    - high pH most likely to adsorb
  - TraPPE reproduces this behavior; MARTINI does not
    - surface-dendrimer interactions not properly parameterized for MARTINI
- What about supercapacitors?
  - low pH PAMAM behaves the a supercapacitor electrolyte should!



  - flattens at the surface as the field is applied to form electrical double layers
  - desorbs as the field is removed

Acknowledgements

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