The Interaction of Propylene Carbonate with Graphite Surfaces via the Measurement of Contact Angles

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Abstract

Electrochemical double-layered capacitors that utilize carbon nanotube forests, with propylene carbonate (PC) as a solvent, have been simulated by Yang et al.[1] The aim of this study was to analyze the PC model used for the simulation and to verify if it matches experimental attributes of liquid propylene carbonate. This study specifically aimed to measure the contact angle made by propylene carbonate droplets on a graphite surface. Potentials for the propylene carbonate molecule models were taken from the Pratt group of Tulane University, while the graphite surfaces were made from scratch. Six hundred propylene carbonate molecules were allowed to equilibrate on three layers of graphite, each contacting 8856 atoms, for a time of 300 ps. The PC molecules formed a film over the surface, instead of the expected drop, giving a contact angle close to 0 degrees. These results were different from experimental contact angle of 37 degrees. However; the small contact angle still shows that wetting of the graphite surface is energetically favorable. Simulations with reduced PC-graphite interactions are currently being carried out, in an attempt to reproduce the experimental contact angle.

Simulation Details

- 600 Propylene Carbonate Molecules
  - Charge potentials are seen in Figure 1.
- 3 Graphite Layers
  - Each layer contains 8856 atoms
  - Roughly square, with side length ~140 Angstrom

- used AMBER simulation package [2]
- Molecular Dynamics simulation:
  - Step size = 0.001 ps
  - Total number of steps = 300,000 steps
  - Effective simulation time: 300 ps or 0.3 ns

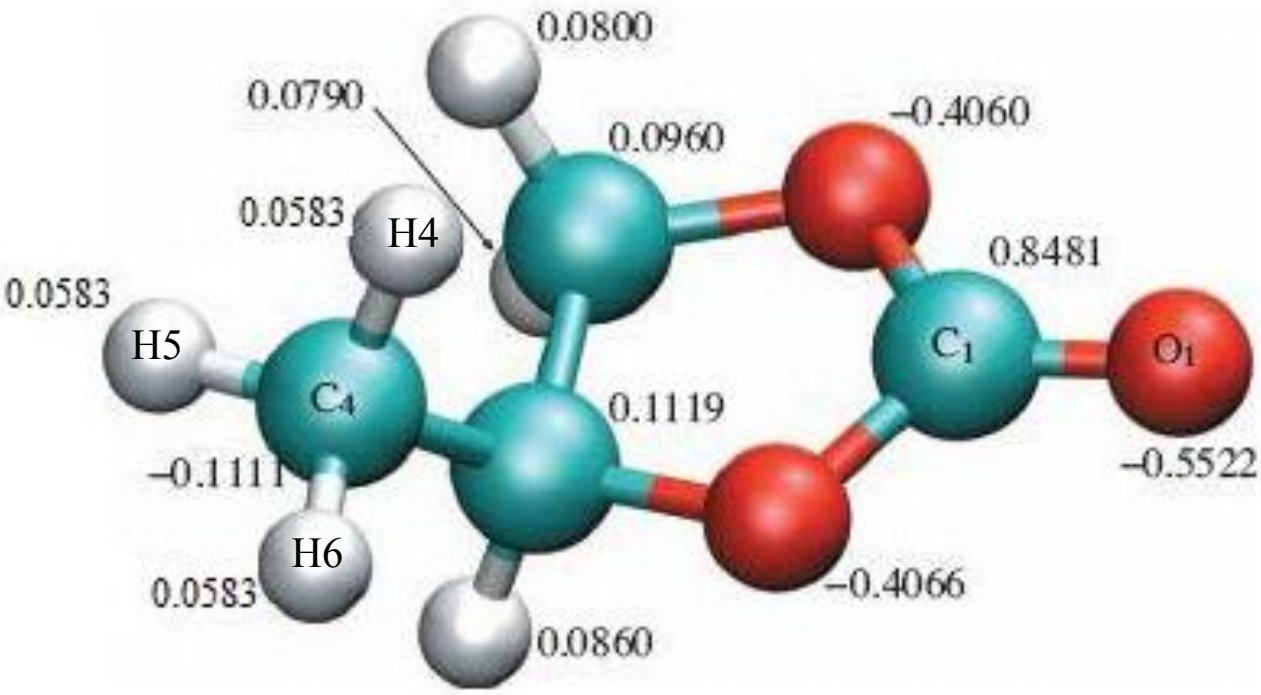


FIG. 1. Molecular model of PC showing the assigned partial charges relative to the magnitude of the charge of an electron.

*Edited from Yang, et al. [3]

Charges of H4, H5 and H6 were normalized from 0.0568, 0.0522, and 0.0659 respectively.

Results

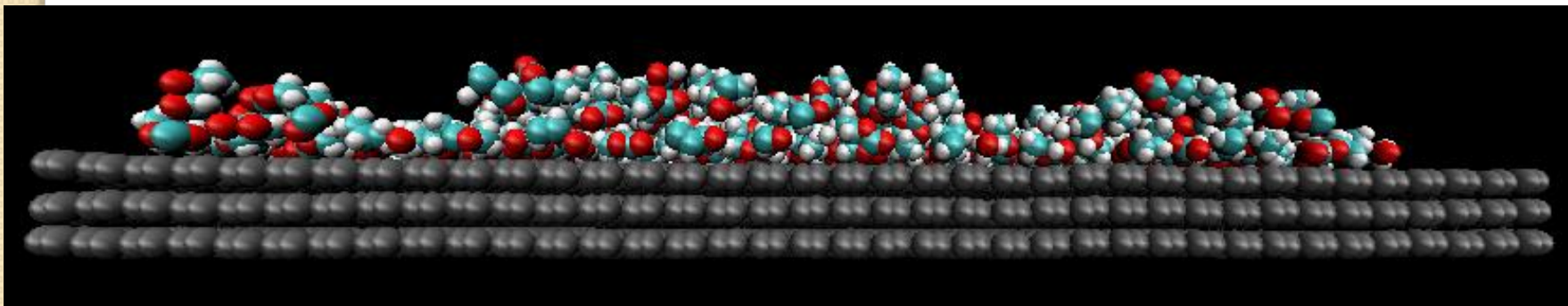
- PC molecules formed a layer instead of a drop. (FIG. 2)
- Layer was irregularly shaped and not circular/spherical. (FIG. 4 and 5)

Contact angle of simulation = ~0 degrees

vs

Experimentally measured contact angle [4] = 37 degrees

FIG. 2. PC molecules making a film on top of a graphite surface.



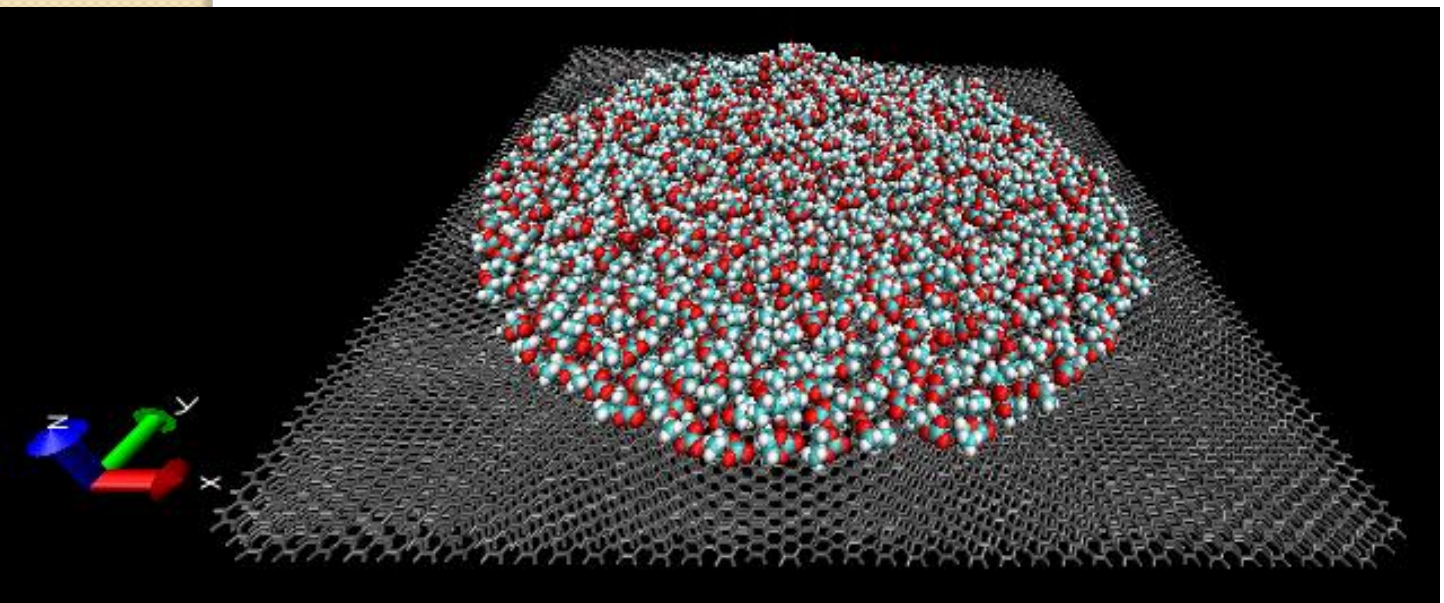
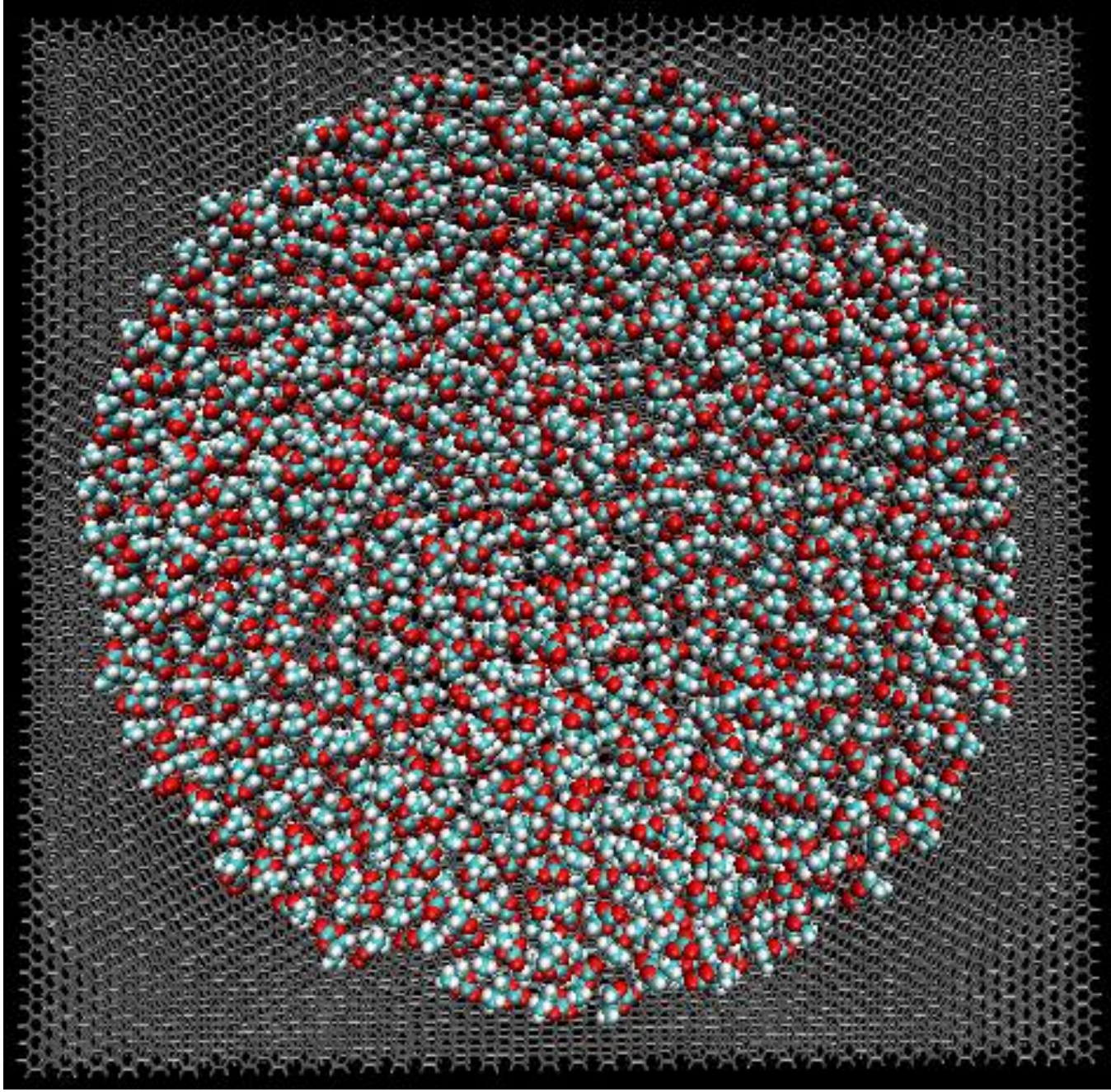


FIG. 3.
<Top> Contact angle of a propylene carbonate droplet on a graphite surface. [4]

<Bottom> Ideal formation where PC droplet forms (not result of simulation)

FIG. 4.

Top view of ideal formation of PC droplet. (not result of simulation)



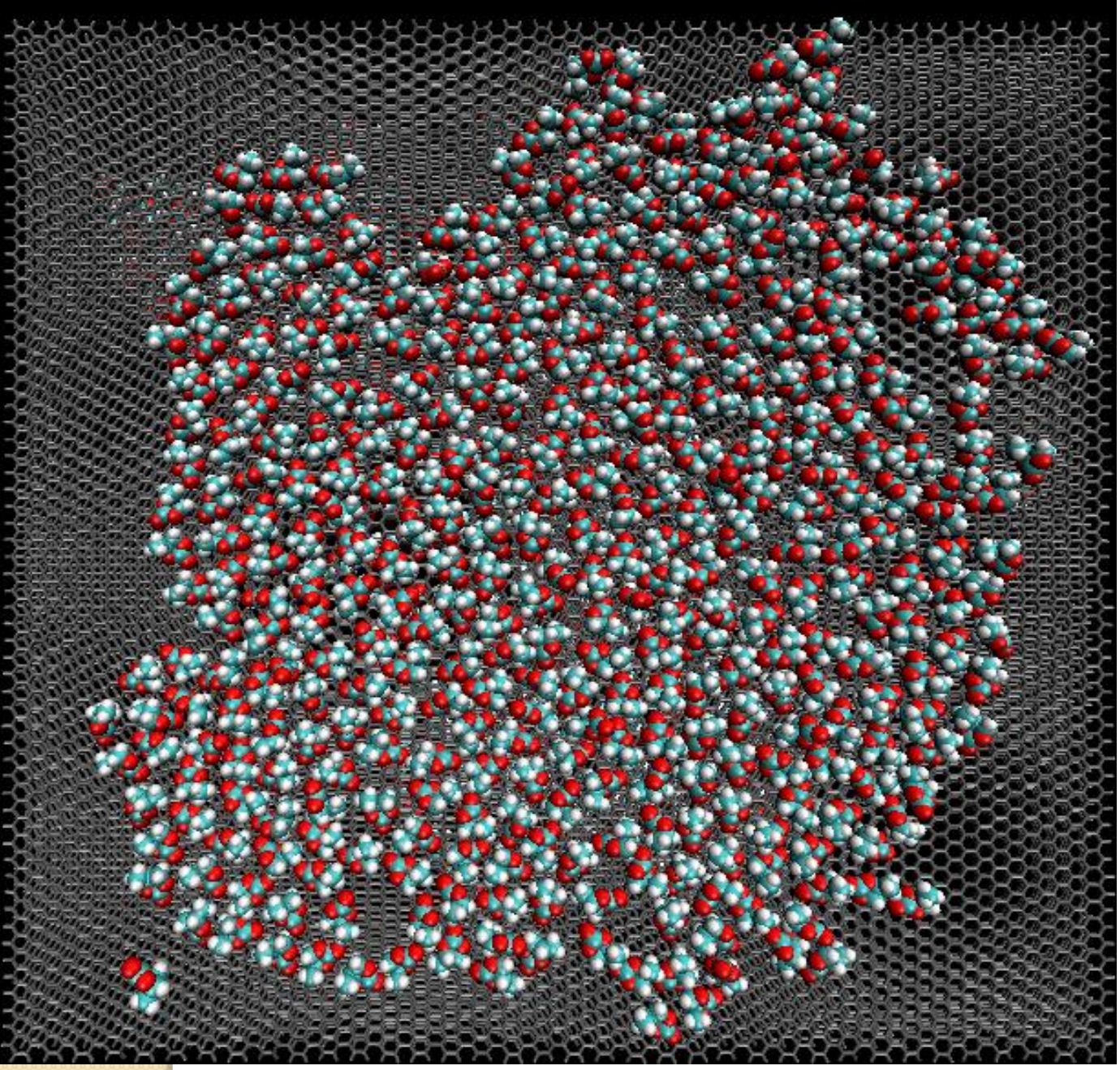
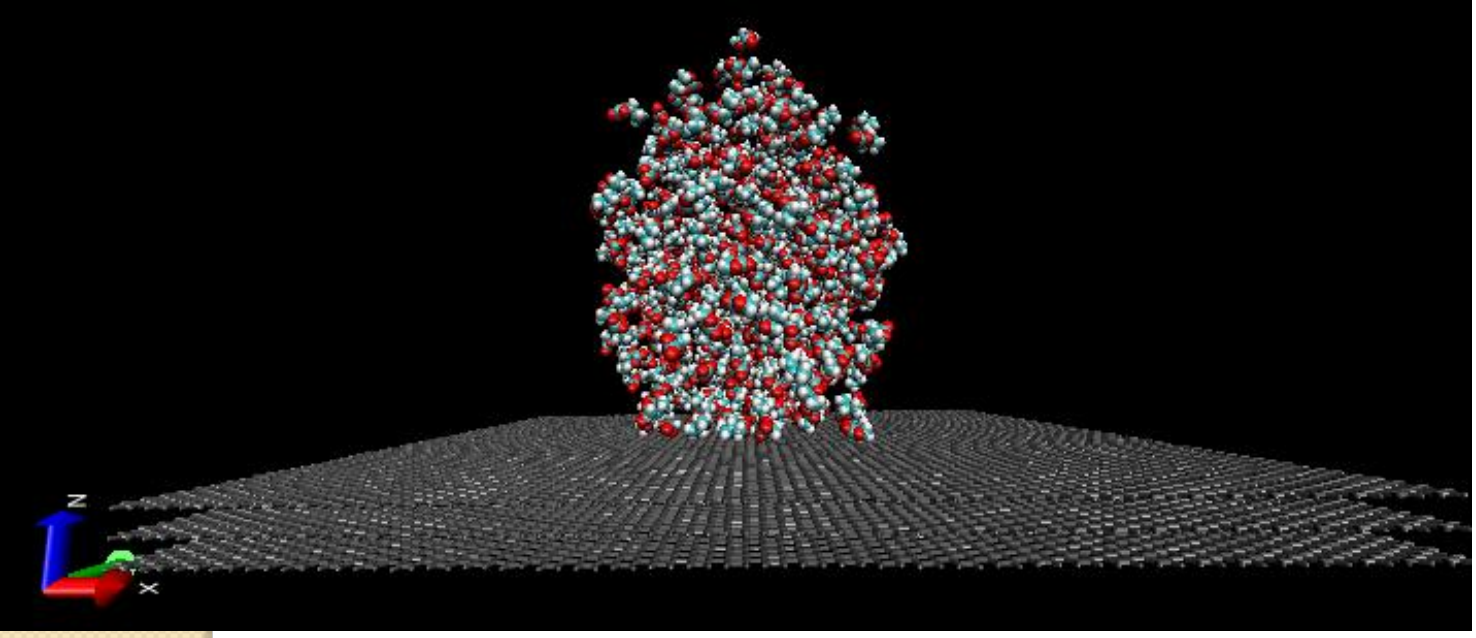


FIG. 5.

Top view of layer of PC molecules formed in simulation.



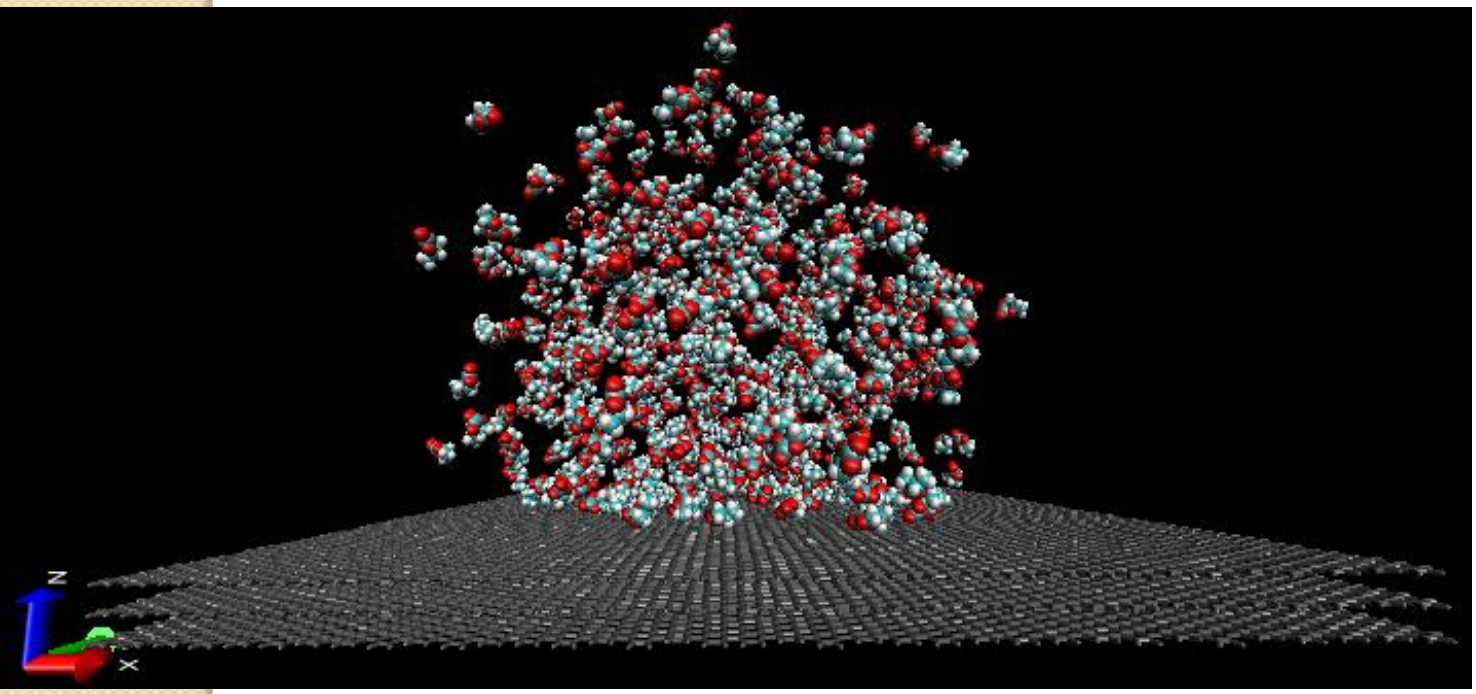


FIG. 6.
Sample view of Molecular Dynamics simulation steps

<Top>
PC droplet at
t = 0 ps

<Bottom>
PC droplet at
t = 1 ps

Conclusion

- The PC model is somewhat accurate, since:
  - it likes to wet the graphite surface; and
  - it forms a small contact angle with the surface.
  - The contact angle of the model does not agree with experimentally measured contact angles.

- Further investigation is necessary for improvement of the PC model.

Remark: Simulations with reduced PC-Graphite attractions are currently being carried out, in an attempt to reproduce experimental results.

References

[1] Yang, L., Fishbine, B. H., Migliori, A., & Pratt, L. R. (2009). Molecular Simulation of Electric Double-Layer Capacitors based on Carbon Nanotube Forests. Journal of the American Chemical Society, 131, 12373-12376

[2] http://ambermd.org

[3] Yang, L., Fishbine, B. H., Migliori, A., & Pratt, L. R. (2010). Dielectric Saturation of Liquid Propylene Carbonate in Electrical Energy Storage Applications. The Journal of Chemical Physics, 132. Retrieved January 29, 2010.

[4] Hoffman, G. G., Mariano, R., Pesika, N., Pratt, L. R., Rick, S. W., & You, X. (2011). Simulation of Propylene Carbonate as a Solvent for Electrochemical Double-Layer Capacitors. Proceedings of Louisiana EPSCoR RII LA-SiGMA 2011 Symposium. Unpublished Manuscript.

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