Charge Transfer from a Carbon Nanotube Electrode to Tetramethyl Ammonium Ions Investigated by *Ab Initio* Molecular Dynamics Simulation

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Abstract: *Ab initio* molecular dynamics (AIMD) are carried-out on systems of a molecular ion, either tetramethylammonium cation (TMA^+) or tetrafluoroborate anion ($BF4^-$), and a carbon nanotube (CNT) electrode in armchair configuration at several distinct charge states. ESP charges of the molecular ion are evaluated at the sampled configurations, and they are typically significantly reduced, reflecting electron donation from the CNT to the ion. The CNT electrode is thus an electron rich structure which typically donates electrons to nearby ions.

Keywords: supercapacitors, carbon nanotubes, tetramethylammonium (TMA^+), *ab initio* molecular dynamics (AIMD), charge transfer

1. Introduction

In recent years, carbon electrode materials of exotic type have become the basis of electrochemical double-layer capacitors (EDLCs) with impressive performance [1]. That performance will depend on the characteristics of the electrodes, the electrolyte solution, and the contacts between those subsystems, the so-called *double-layer*. Focusing for the moment on the liquid electrolyte solution, the molecular theory of electrolyte solutions is horrendously complicated and has degenerated into the disjoint activities [2]: (a) theory of primitive models in which the connection to experiments or simulation at a molecular level is not attempted, and (b) molecular simulation that does not address the physical issues that are basic to the theory which have been established albeit painfully. The challenge essential to re-animating the molecular understanding of these complex systems is achieving molecular realism on the basis of simulation while at the same time addressing the basic theoretical issues. For particular physical problems, a step in that re-animation is to secure the molecular-scale information that would be required for grounded theory. The present work attempts to follow that strategy for EDLCs based upon carbon nanotube (CNT) forests, and in particular evaluates charge transfer between CNT electrodes and the ions that might be present in realistic cases. The charges of the ions are possibly the most basic information required for serious statistical mechanical theory. Those theories will be sensitive to the ionic charges, and do not alternative sources of that information.

Here, specifically, we utilize *ab initio* molecular dynamics (AIMD) to treat ions involved in EDCLs, either the tetramethylammonium cation (TMA^+) or tetrafluoroborate anion ($BF4^-$), and together with a CNT in armchair configuration at several electrode charges. We then evaluate the charges on the ions that would be relevant to statistical mechanical theories of these solutions and interfaces.

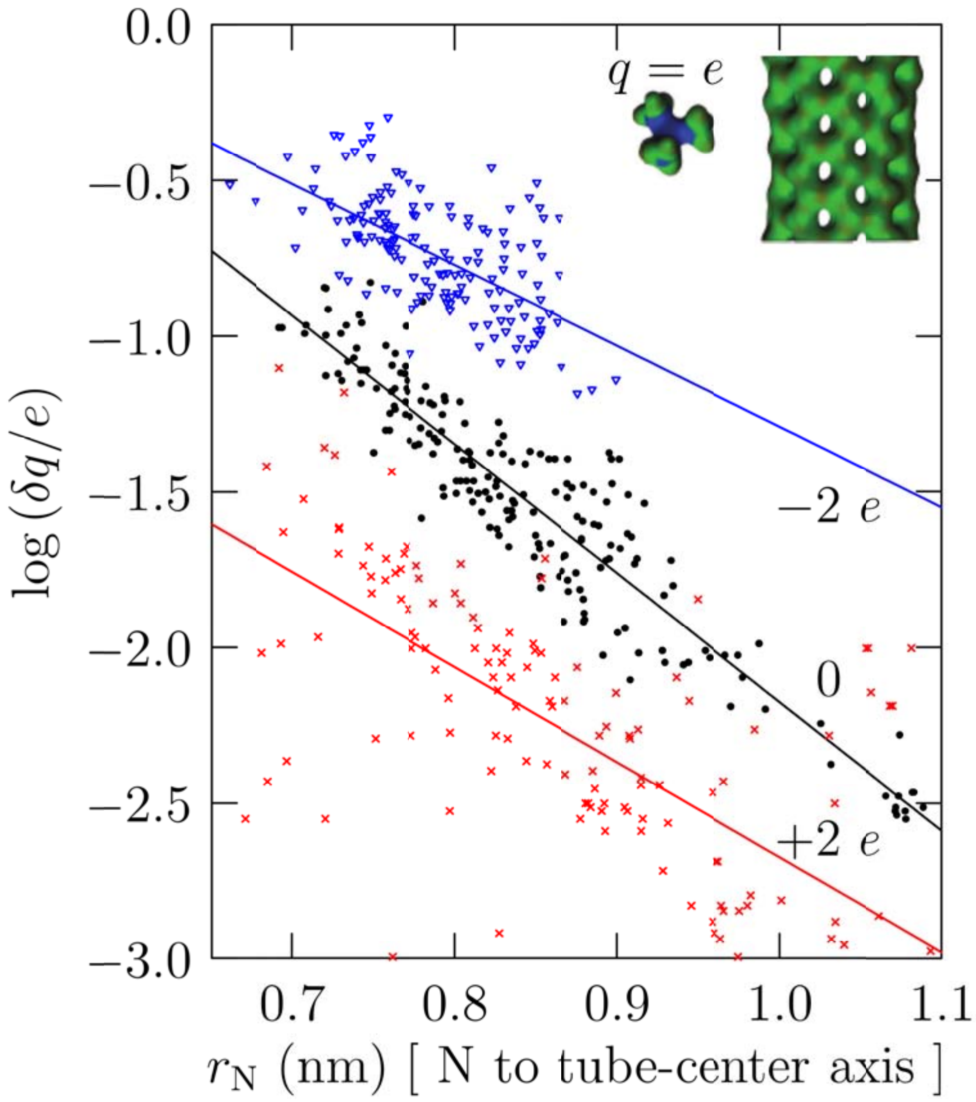

Figure 1: Electronic charge transferred to the TMA$^+$ ion from the CNT at configurations sampled by the AIMD simulations, *q=e-δq* with *q* the ESP charge on the ion. Blue: The CNT electrode is negatively charged, the system having an overall charge of –*e*. The TMA$^+$ cation stays close to the CNT, and exhibits an ESP charge in the neighborhood of 0.6*e*. Black: The CNT electrode is uncharged, but still donates substantial electron density to the TMA$^+$ cation, as much as 0.3*e* as judged by the ESP charge. Red: The CNT is positively charged, the system having an overall charge of +3*e*. Here at the largest distances from the electrode, the ESP charge of the TMA$^+$ cation approaches +*e*.

2. Methods

Our AIMD calculations and analysis used the CPMD package [3] with periodic boundary conditions in all three spatial dimensions. All the calculations utilized the PBE-D electron density functional model [4], a norm-conserving pseudo-potential (NCPP), and a plane-wave basis cut-off of 85 Ry. We carried out a standard AIMD trajectory for 10ps at the high temperature of T=1200K, thermalized using Nose-Hoover thermostat [3], to achieve broad configurational sampling. Deuterium (D) was used instead of protium (H) because propagation of the classical trajectories is slightly easier with smaller mass differences. We calculated the ESP charges [2,3] on the molecular ion at the configurations sampled by AIMD simulation.

All systems studied included an 80-carbon-atom nanotube (CNT) in armchair conformation and one molecular ion, either TMA^+ (97 atoms in all) or BF_4^- (85 atoms). We additionally studied cases with two more or two fewer electrons, corresponding prosaically to "CNT^{2-}" or "CNT^{2+}". The system size was L_x=L_y=1.8nm, L_z=1.05nm. These simulation calculations were performed on LONI [7], and utilized about 200K service units.

Further *ab initio* calculations were carried for TMA^+ and $BF_4^{\square}$ to determine the amount of charge transfer between the ion pair. The program NWChem, version 6.1, was used [8]. For this relatively small system, a variety of quantum theories and electron partitioning schemes can be used. Calculations at the Hartree-Fock level as well as DFT with different functionals were used. All calculations used an aug-cc-pvdz basis set. The amount of charge transfer was determined using two methods, ESP, as for the CNT .. TMA^+ system, and Bader partitioning.[9]

3. Results

For TMA^+ (Figure 1), the CNT donates electrons to the molecular ion at all electrode charges considered. When the CNT is negatively charged (CNT^{2-}) likely cation-CNT distances are more probable (Figure 2), and the probability density more strongly structured than for the cases where the CNT has less charge.

Even for the BF_4^- anion, our results are consistent with the picture the CNT is an effective electron donor. Except for a possibly more complicated behavior of the BF_4^- .. CNT^{2+} , the anion can still acquire some electron density from the nanotube. The more complicated behavior of that BF_4^- anion will be discussed elsewhere, in circumstances that permit a more detailed analysis.

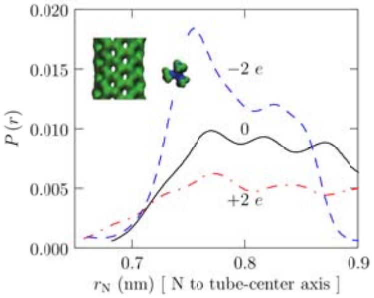

Figure 2: Probability density for the radial displacement of the N atom of the TMA^+ ion from the center axis of the CNT, for the AIMD sampling calculation at T=1200K. Labeling of the three curves is the same as in Figure 1. As expected, probable distances for the cation are most probable with CNT^{2-} tube, and least probable with

The results for the ion pair in its minimum energy structure, with a distance between ion centers equal to 0.437 nm, show (Table 1) more charge transfer predicted by DFT than by Hartree-Foch and more charge transfer when using ESP than Bader partitioning to determine charges. The results show less charge transfer between the ion pair than between TMA^+ and the carbon nanotube.

Theory	TMA^+ charge, ESP (*e*)	TMA^+ charge, Bader (*e*)
Hartree-Fock	0.892	1.000
DFT, B3LYP	0.892	0.975
DFT, PBE0	0.890	0.977
DFT, XPBE96/CPBE96	0.879	0.962

Table 1: Charge of the TMA^+ ion in contact with the BF_4^- ion.

4. Conclusions

The CNT is an electron-rich material that readily donates electrons to the TMA^+ cation. At distances of closest approach to the neutral CNT electrode, a TMA^+ cation has an ESP charge reduced to a value between 0.6-0.7*e*. For a negatively charged CNT electrode, a TMA^+ cation in the corresponding probable configuration has an ESP charge reduced to values as low as 0.3*e*. There is charge transfer between the TMA^+ and BF_4^- ions as well. These values will be of dominating concern for physical theories of the performance of electrochemical double-layer capacitance.

5. Acknowledgments

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6. References

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