Emerging Nano & Advanced Materials

Force-Field Parametrization of Polyaniline Emeraldine Base for Supercapacitor Simulations

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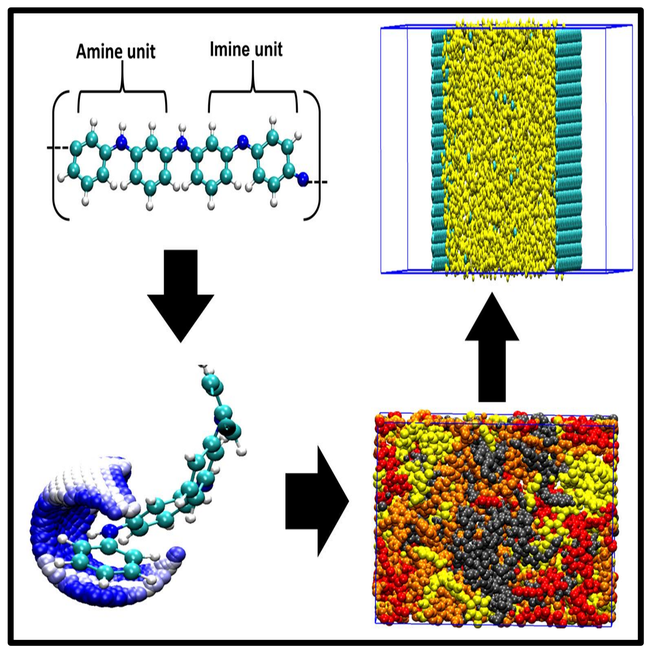
Abstract

- Force field parametrization methodology for molecular modelling of polyaniline (a conductive polymer) in OPLS
- The most useful form of polyaniline (PANI) is Emeraldine base (PANI-EB)
- Density functional Theory (DFT) method is used to derive the atomic point charges of PANI-EB
- Validated by molecular dynamic (MD) simulation.
- Analysis and comparison of the computed total radial distribution function and density of PANI-EB with experimental results



Charge Anisotropy

- The point charges are not able to account for the lone pair of atoms [3].
- RMSE and RRMSE measures the quality of fitting of charges by comparing the electrostatic potential (ESP) distribution obtained by the charges with quantum ESP.

CM5-PCM charges are better than 1.2 CM5

Result and Discussion

A comparison of the RMSE and RRMSE charges of the two set of charges obtained shows that the CM5-PCM charges are better than the 1.2 CM5 charges.

$$RMSE = \sqrt{\frac{\sum_i [V_q(r_i) - V(r_i)]^2}{N}}$$

$$RRMSE = \sqrt{\frac{\sum_i [Vq(r_i) - V(r_i)]^2}{\sum_i V(r_i)^2}}$$

Vq(r)= ESP from quantum
V(r)=ESP from charges
N=no. grid points (DFT)

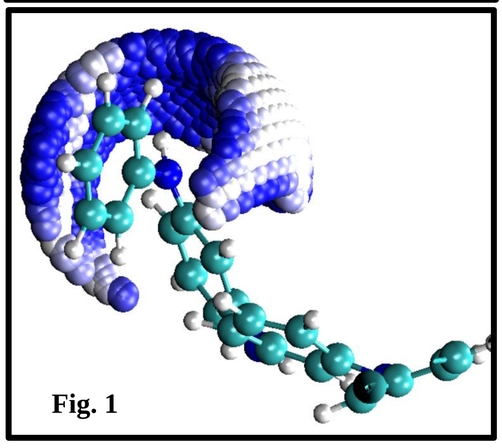


Fig. 1

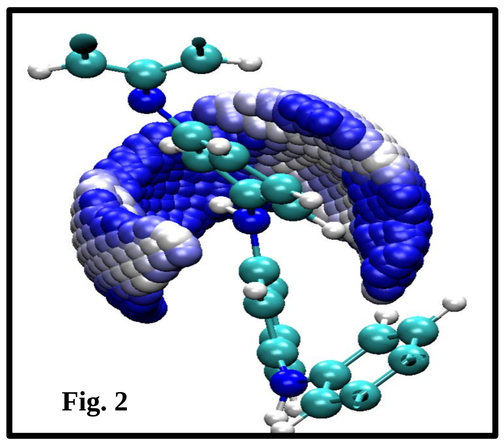
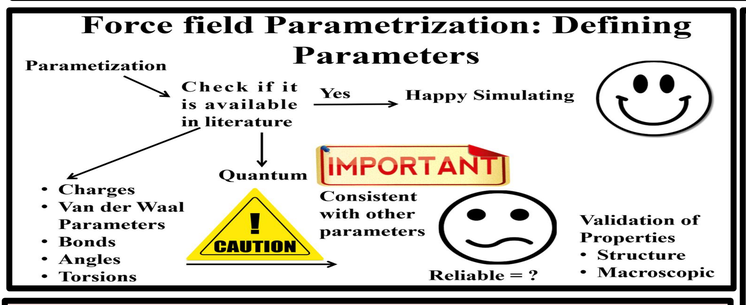


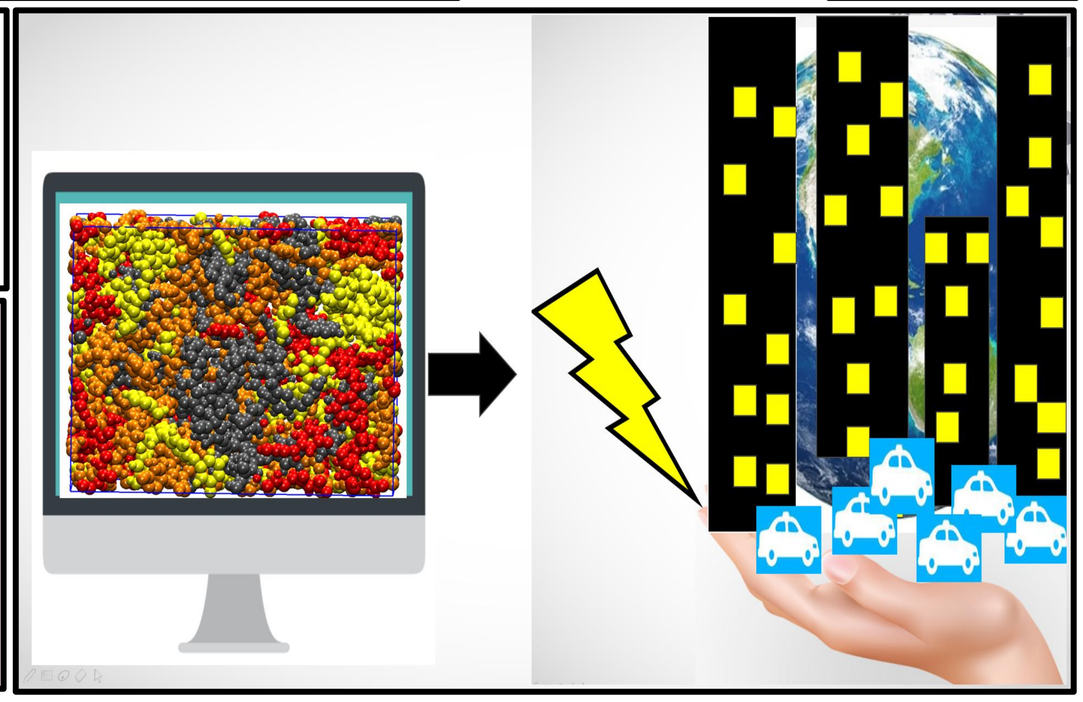
Fig. 2

Fig. 1 and Fig. 2 shows the ESP reproduction error of the amine and the imine units using CM5-PCM charges. Blue region shows more ESP reproduction error and white regions show that the ESP can be reproduce well with the charges. It can be seen that the charges are not able to reproduce the imine unit well because of the lone pair present over the nitrogen atom. This suggest that there may be the need of off-centered sites to account for the lone pair in imine nitrogen.

Introduction

PANI is used as a electrode material in Supercapacitors for enhanced capacitance. Computational tools aid in studying the properties of PANI-EB at the molecular level in both doped and undoped state. So, a suitable force field is required for the molecular modelling of PANI-EB. Many earlier works are based on OPLS for parametrizing force fields for conjugated polymers [5]. So, OPLS scheme would be used for PANI-EB parametrization in this work ,which has a much simpler force field form and can accurately account for the condense phase properties of many molecules.



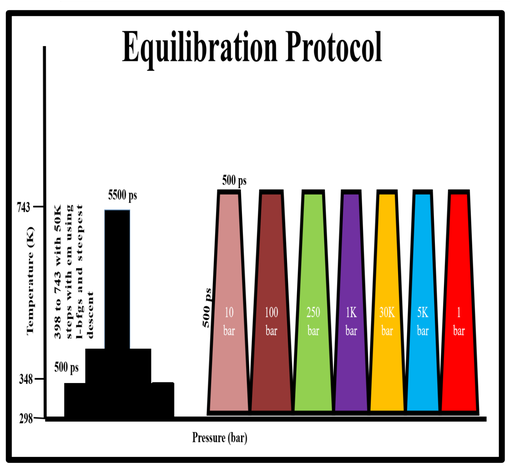


Problems encountered and Solutions

- The force field parameters(charges and torsions) of PANI-EB (both amine as well as imine) are not present in the OPLS-AA force field.
- Only parametrization of charges are reported here.Two sets of charges are used in the method, 1.2 CM5 and CM5-PCM.
- Rest of the topology parameters are taken from Ligpargen server.

Method for validation of parameters

MD simulations was performed using the GROMACS. A time integration step of 1 fs is being selected for the simulation of four chains of the PANI-EB. Atom pair distance cut-offs which are force field specific were applied at 12.0 Å to compute the van der Waals interactions. Electrostatic interactions were computed by using PME with cut offs being 12.0 Å.



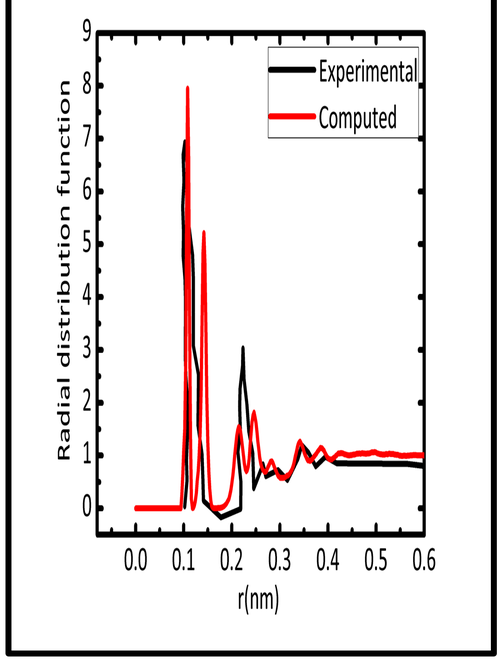
Result and Discussion of MD validation

RDF

Density

RDF is a measure of the probability of finding an atom (which is located in a sphere of infinitesimal thickness) at a certain distance from a reference atom. . The positions of the peaks of the total G(r) obtained through computational studies are in good agreement with the experimental studies [1].

Experimental Density: 1.230 g/cc
Computed Density= 1.125 g/cc



Conclusion

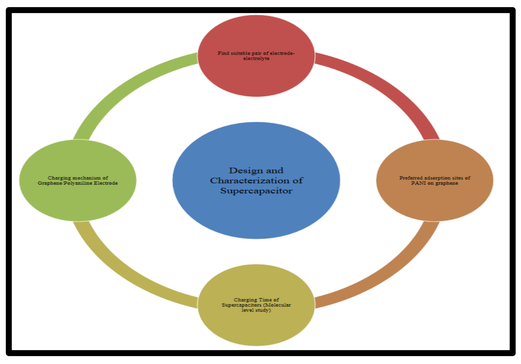
- PANI-EB is used in wide variety of applications.
- Need of accurate force -field
- Our methodology which is consistent with the known parameters of the force field validated with MD simulation would open ways to tune the properties of the polymer in scheming optimized performance.

Industrial Significance

The force field parametrization would aid in molecular level study of Supercapacitors. A Computational study would help to design and characterize the supercapacitor for optimized performance for various applications

Technology Readiness level

TRL 1: Basic Technology Research



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