Molecular Simulation studies of Organic salts inside carbon nanopores

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What are Ionic liquids?

• An ionic liquid is a salt in liquid phase at room temperature.

• Made up of ions and have ionic bonds.

• Posses low vapor pressure and are moderate or low electric conductors.

• Highly tunable properties; $10^9 - 10^{18}$ ILs could be formed by varying cations, anions.

• Vast number of applications due to distinct properties in many fields such as Organic chemistry, Engineering, Electro chemistry, Catalysis and Physical chemistry. (Solvents, electrolytes, etc)

[Image of 1,3-dimethylimidazolium chloride $[\text{DMIM}^+][\text{Cl}^-]$]
Importance of Ionic Liquids (IL’s)

IL’s can be synthesized to possess fluorescent, magnetic and many other qualities according to necessity.

Ionic liquids can be synthesized from safe, FDA‐approved compounds; therefore could be used in Bio‐medical applications.

- Nanomaterials with **fluorescent properties** can be used to label tissues and cells for biomedical imaging

- Nanomaterials with **magnetic properties** can be used in cancer treatment (magnetic hyperthermia). After attaching them to cancer cells, the patient can be exposed to a safe **magnetic field** and the **heat** generated by the magnetic nanoparticles will destroy the respective cancer cells that they are attached to.
Why molecular simulation?

• The properties of ionic liquids confined inside nanopores can be very different from what we see in day to day usage (bulk systems).

• It is extremely difficult to extract experimental data regarding such systems.

• Molecular dynamics (MD) simulation is a very useful technique in such cases to give insights to experimental scientists and to complement their observations regarding properties and characteristics of molecules at nanolevel.
Overview of simulation methods

Atomistic simulation methods
- Semi-empirical methods
- Ab initio methods

Mesoscale methods
- Lattice Monte Carlo
- Brownian dynamics
- Dissipative particle dynamics

Continuum Methods
- Monte Carlo
- Molecular dynamics
  - tight-binding
  - MNDO, INDO/S

TIME /s
\(10^0\)
\(10^{-3}\)
\(10^{-6}\)
\(10^{-9}\)
\(10^{-12}\)

LENGTH/meters
\(10^{-10}\)
\(10^{-9}\)
\(10^{-8}\)
\(10^{-7}\)
\(10^{-6}\)
\(10^{-5}\)
\(10^{-4}\)

(ns) \(10^{-9}\)
(µs) \(10^{-6}\)
(ms) \(10^{-3}\)
(fs) \(10^{-15}\)
Molecular dynamics: a quick introduction

• In molecular dynamics (MD), we follow the positions and velocities of each molecule in time by solving Newton’s equations of motion:

\[ F_i = m_i a_i = m_i \frac{d^2 r_i}{dt^2} = -\frac{\partial U}{\partial r_i} \quad i=1,2,3,...N \]

\[ U = \text{inter/intra-molecular potential (i.e., interactions between atoms)} \]

\[ r_i = \text{position vector of atom } i \]

\[ F_i = \text{force acting over atom } i \]

\[ m_i = \text{mass of atom } i \]

• In MD these equations are integrated numerically to obtain the time evolution of the system
Pair Potentials: Large, Flexible Mols.

- Total pair energy breaks into a sum of terms:

\[ U(r) = U_{str} + U_{bend} + U_{tors} + U_{disp} + U_{elec} + U_{pol} \]

  - \( U_{str} \) - stretch
  - \( U_{bend} \) - bend
  - \( U_{tors} \) - torsion
  - \( U_{disp} \) - dispersion (van der Waals)
  - \( U_{elec} \) - electrostatic
  - \( U_{pol} \) - polarization

\[ U({r_i}) = \sum_{j}^{N} \frac{k_{ij}}{2} (l_j - l_{ij}^0)^2 + \sum_{j}^{N} \frac{k_{ij}}{2} (\theta_j - \theta_{ij}^0)^2 \]

\[ + \sum_{t}^{torsions} \frac{V_{n}}{2} (1 + \cos(n\varphi - \gamma)) \]

\[ + \sum_{i,j}^{N} \frac{q_i q_j}{r_{ij}} + \sum_{i,j}^{N} 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \]
In my summer project I will be investigating various properties of the ionic liquid [DMIM+][Cl-] when it is confined in a multi-walled carbon nanotube. I will be using Gromacs MD software to perform MD simulations of [DMIM+][Cl-].
[DMIM+][Cl-] molecules inserted into carbon nanotube

System without [Cl-] atoms
The [Cl-] ion has not been depicted for visualization purposes.
After running the system under bath conditions for approximately 10ns we can extract the data and analyze it to understand the molecular-level properties and characteristics of the system. This information can be useful to experimentalists.
End
Molecular dynamics: Introduction

- **MD simulations are similar to real experiments**
- In a basic MD simulation program:
  - ‘Prepare the sample’:
    - Initial energy (or temperature)
    - Number of particles $N$
    - Box size ($N/L^3 = \text{density}$)
    - Force field equations, parameters
    - Time step $dt$ for integrating equations of motion
    - Initialize positions and velocities of all particles
  - ‘Do the experimental measurement’:
    - Compute forces on all particles
    - Integrate Newton’s equations ($F = ma$)
    - Update particle positions and velocities
    - Calculate instantaneous properties
    - Stop after iterating $t_{\text{max}}$ steps

Repeat until we reach an appropriate ‘simulated time’

$$F_i = m_i a_i = m_i \frac{d^2 r_i}{dt^2} = -\frac{\partial U}{\partial r_i}$$