A Computational Method for Finding the Path of Approach of an Ion to a Reaction Site

Richard Miller and Matthew Semak

Department of Physics and Astronomy

University of Northern Colorado, Greeley, CO 80639

Abstract:

A mathematical scheme was employed to treat an ion as a classical point mass, which carries a charge and possesses potential energy as a result of being near an arrangement of charges. This type of behavior occurs during the saponification reaction that is considered for this project. This is similar to an object near Earth that experiences potential energy due to gravity. As expected, the equations that give velocity and position for the ion were similar to the kinematic equations that are solutions to Newton's Second Law. This model was not expected to be satisfactory because it could not account for the damped, erratic motion of a real ion in solution. A second model taking these effects into account is currently being developed.

Objectives

The model of a molecule is classically given as nuclei point masses connected by springs. But this model does not account for bonding behavior. So, the classical picture was modified to include charges and their coulombic interactions in an effort to examine whether the approach of two reagents can be viewed as a classical system.

With this, there are four goals for this work.

1. The first goal was to find a set of equations and write a computer script that could calculate and plot the ion's position and velocity at a given time as it approached a reaction site. This initial guess at a set of equations is not expected to be correct, but sets the foundation for a model that will be developed further.

2. Corrections to the initial model must be found that will describe the more erratic motion of an ion in solution as it moves through the solvent with no other ions present.

3. Additional corrections to the mathematical model are needed to account for the presence of other ions and to add potential energy surfaces that will keep the ion from occupying certain positions and account for the interaction between the ion and the chemical bonds.

4. The final goal is to generalize the computer script to accept additional molecules.

Methods

The saponification reaction was chosen because it involves two charged particles that may or may not interact as a coulombic force pair. Methyl formate was used as a test molecule because it is the simplest ester. It can undergo the saponification reaction and isn't too difficult to model. The ion chosen to drive the reaction was the hydroxide (OH-) ion because of its simplicity. To define the location of the charges, the methyl formate molecule was drawn using Avogadro Molecular Modeling software. The positions of the nuclei were then exported to a data file. Each atom was assigned an effective charge (z-value) based on the electron affinity of the two bonded nuclei. A carbon bonded to an oxygen atom would have an effective charge of +1 due to the strong electron affinity of the oxygen, a carbon double bonded to an oxygen would have a +2 charge, and a hydrogen bonded to a carbon would have a 0 charge because the hydrogen and carbon are approximately equal in their electron affinities.

Next, the coulombic force, F, of the effective charges of these atoms is considered to be the only force driving the approach of the ion:

$$F = ke_0^2 z_{oh} \sum_{n=1}^{8} \frac{z_n}{|\rho_n|^3} \overline{\rho_n},$$

where k is the Coulomb constant, e_0 the fundamental charge, z the effective charge of the nucleus, $\overline{\rho_n}$, the nth vector, between each point charge and the hydroxide ion and $|\rho_n|$ is the magnitude of the vector. The sum is over eight terms because each term represents an interaction between the ion and one of the eight nuclei in the molecule.

With Newton's Second Law, $F = ma = m \frac{d^2}{dt^2} r(t)$, a computer script was written in Matlab to numerically solve for the position and velocity as functions of time. The results of the computation appear to be linear, which is not the type of motion observed in the real world. Also, the results were nearly 10 orders of magnitude greater than expected. So, a new model was devised that would consider previously neglected influences that effect the hydroxide ion's behavior in the real world and that would, also, correct the order of magnitude issues with the previous equations.

The new model still makes use of Coulombic force, but it also adds a 'resistance' term due to the friction-like effect of the solvent on the hydroxide ion and accounts for the random collisions with the solvent molecules and changes in the density of the solvent. The new force equation is:

$$F = ke_0^2 z_{oh} \sum_{n=1}^{8} \frac{z_n}{|\rho_n(t)|^3} \overline{\rho_{n(t)}} - \gamma v(t) + \xi(t) = ma,$$

where γ is a drag coefficient that involves the geometry of the hydroxide ion and the viscosity of the medium and $\xi(t)$ accounts for other forces and interactions that occur randomly.

Results

Before implementing the changes referred to in the methods section, the Matlab script worked well and the path traveled by the ion was in the correct direction towards the expected reaction site. However, there were some issues with the speed and acceleration — also mentioned in the methods section. The first few trials gave an acceleration on the order of $10^{50} \frac{m}{s^2}$. Upon further inspection, the units in the calculations were incorrect. By going through the code and finding the mismatching units the acceleration was reduced to around $10^{10} \frac{m}{s^2}$.

The acceleration $\left(\sim 10^{10} \frac{m}{s^2} \right)$, which is still unreasonable, is due to the small mass of the hydroxide ion. Therefore, very little can be done to correct for this problem using the simplified model. In addition, the path of approach was a straight line, which does not agree with experimental evidence. So, the equations were not a good approximation for the physical situation. However, the computer script can easily be rewritten to accept a corrected set of equations.

A reworked set of equations were formulated as explained in the methods section. This gave the following Langevin equation:

$$F = kz_{OH} e_0^2 \sum_{n=1}^{8} \frac{z_n}{|\rho_n(t)|^3} \overline{\rho_n(t)} - \gamma v(t) + \xi(t) = ma.$$

Expressing the equation as a coupled set of stochastic differential equations for the velocity and position of the ion gives

$$\frac{dv}{dt} = C \sum_{n=1}^{8} \frac{z_n}{|\rho_n(t)|^3} \overline{\rho_n(t)} - \gamma' v(t) + \sigma' \xi(t)$$

and

$$\frac{dx}{dt} = v(t),$$

where $\gamma' = \frac{\gamma}{m_{OH}}$ is a mass weighted damping constant, $\sigma' = \frac{\sigma}{m_{OH}}$ is a mass weighted amplitude for the random force function, $\xi(t)$, and the constant $C = \frac{kz_{OH} e_0^2}{m_{OH}}$. As a side note, $\frac{1}{\gamma'}$ gives the damping time scale.

Future Work

1. Find better values for the constants in the model:
   - The model assumes spherical symmetry. However, there is elliptical symmetry in the hydroxide ion and other symmetries for the methyl formate and water that will need to be considered for more accurate results.
   - There is a viscosity term, η, that is part of the γ constant. The viscosity constant needs to be better understood or approximated. There are several different types of viscosity and, given the scale of the objects, it's difficult to find reliable values for the viscosity that apply to the system being studied.

2. Find a better expression for the Coulombic interactions:
   - The method of using an 'effective charge' needs to be refined. Replacing the point charges with a charge distribution that varies in space will most likely yield better results.
   - There are many positions that the hydroxide ion cannot occupy in the real world. These restricted regions need to be accounted for in the model.
   - Replacing the discrete charges with a charge distribution will make the restriction of certain regions of space possible, such that the ion won't be able to enter these restricted regions.

3. Find experimental evidence that confirms that the scaling constants are good approximations and that the equations correctly describe the motion.
   - This should include a literature review to find the data, or, if no data can be found, try to generate the results experimentally.

References

1. Gupta, N. (2011) Brownian Motion (Version 1.0) Source Code: https://www.mathworks.com/matlabcentral/fileexchange/32067-brownian-motion?focused=5191300&tab=function

2. Turq, P. and Lantelme, F. (1977) Brownian dynamics: Its application to ionic solutions. J. Chem. Phys. **66**(7). 3039.

3. Coffey, W.T. Kalmykov, Y.P., et. al. (2004) The Langevin Equation. World Scientific Publishing.

Acknowledgements