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Dear Prof. Gillespie, or Dan, if first names are OK,

Please excuse this email 'out of the blue' but it addresses an issue in your wonderful J Chem Phys review that needs (in my not so humble opinion) further thought. I leave professional introductions and other matters to the P.S .in case you want to read that far in this letter.

I present this case in a stylized overdramatized example to make my point.

- 1) Consider a covalent chemical reaction in which the actual movement of electrons occurs on a time scale of $1E(-18)$ sec. (Of course, not all reactions occur this fast. I choose this time scale because many classical reactions of organic chemistry do occur this fast or faster and to illustrate my point).
- 2) Consider a covalent chemical reaction in which the flows in the reaction are a steep function of concentration.
- 3) I assert that in solutions these reactions will occur to large extent in spatial domains that are fluctuations. In these regions, the concentrations will be far from the spatial mean of the concentration of reactants (I assert).
- 4) Why? Fluctuations of many orders of magnitude of concentration occur in solutions (of the ordinary type and concentrations in water) on time scales of $1E-9$ usually and 'always' on time scales of $1E(-11)$. **Many fluctuations to concentrations far from the mean will persist a very long time compared to the time scale of chemical reactions $1E(-18)$. These fluctuations will be the environment in which most reactions occur.**
- 5) **The analysis of a system like this will require a coupled system of field equations (pde's or integro/pde's) that link the electrodiffusion of substrates and products with the electron transfer reaction itself. Or they will require simulations that contain the same physics and compute the physics in an accurate and calibrated way.**
- 6) I write **electrodiffusion** because almost all substrates and products in water have significant even large regions of electric charge, and many have net charge. Electric forces are strong and act on all scales. When involved on time

scales where they are not ‘perfectly’ screened, I believe they always require field equations either Poisson (as is customary) or Maxwell (as I suspect is needed when time scales are so short that displacement currents are large. In typical ionic solutions displacement currents are large, as an experimental fact, at times faster than say $1\text{E}-6$ sec.

Thank you for reading this far.

All questions, comments, suggestions, and criticisms are MOST welcome

As ever

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Professional Introduction

- a) CV can be found as a link on the webpage <http://www.phys.rush.edu/RSEisenberg/physioeis.html>
- b) I have a series of papers on “Diffusion as a Chemical Reaction” with Zeev Schuss that can be found in my CV by searching on ‘Schuss’ (without the quote): live links in the CV are supposed to give you easy access to the papers. If you wish, I am happy to send PDF’s
- c) The paper below summarizes some of that work in what I hope is an accessible even amusing form. **Eisenberg, B. 2011. Mass Action in Ionic Solutions. Chemical Physics Letters 511:1-6.**
- d) The role of the electric field and interactions in general are discussed at length elsewhere. Ask for specifics if you want to see more.