Gmail by Google

Bob Eisenberg <bob.eisenberg@gmail.com>

Well posed electrochemistry ..... finally

Bob Eisenberg <beisenbe@rush.edu> **Thu, Feb 2, 2012 at 9:40 AM**
Reply-To: beisenbe@rush.edu
To: Tzyy-Leng Horng <tlhorng123@gmail.com>, Chun Liu <liu@math.psu.edu>, Tai-Chia Lin 林太家 <tclin@math.ntu.edu.tw>, Bob Eisenberg <beisenbe@rush.edu>

Dear Allen, Chun, and Tai Chia,

I finally understand how to make the electrochemical cell problem perfectly posed.

This takes care of both charge build up on electrodes and flux build up in the baths. The idea is to prevent both JUST THE WAY WE DO IN EXPERIMENTS. In experiments, we ALWAYS WITHOUT EXCEPTION have parallel paths (in parallel with the flux described by PNP) to take care of this. One parallel path is a capacitor ($I = C dV/dt$, i is electrical current. It is NOT carried by any ion of any type.) The other is a leak path specific for one ion (see below for details).

I suggest you just put a capacitor in parallel with your entire system (i.e., sum the fluxes, convert to current, add $C\ dV/dt$ to the flux current. That is the total current and includes charge build up.

To make the entire system well posed out to time infinity is slightly more tricky.

I suggest the following approach.

ALWAYS without exception view electrical current (including the capacitive current mentioned above) and electrical potential as fundamental variables to be measured or controlled by boundary conditions.

This causes problems because the system is overspecified. The current plus the all the individual fluxes of ions is one specification too many.

Here is how to fix that.

Put in parallel with the entire system (i.e., ionic fluxes, in parallel with capacitor) a leak resistor with properties I specify below. The total system then consists of N +2 additive components. N are the number of individual ionic fluxes . 1 is the capacitive current. 1 is the leak.

Choose the leak by the following criteria

a) find the flux which is smallest at long times (this does not have to be rigorous, just make a reasonable choice)

b) make the leak a Darcy/Ohm's law device (i.e, it has flux of one ion ONLY proportional to the gradient of ELECTROchemical potential across the device). Choose the numerical value of the leak "conductance" so it has no effect on the system in the times we are interested in. (This will depend on the size of the baths etc). A looser way to choose it is to make the leak conductance 0.001 times the conductance of the rest of the system.

This procedure corresponds to what is done experimentally. The capacitor guarantees that charge build up is handled correctly.

The leak conductor guarantees that flux build up is handled correctly.

NOTE THAT WITHOUT THESE PROCEDURES EXPERIMENTS CANNOT BE DONE. So it is not surprising that they are needed in theory. NOTE that the amazing thing is that idiots like me have taken so long to realize we need to specify all this to theoreticians.

Finally, you may need to extend your channel so it includes atria (i.e., entry spaces). This can easily be done. Just follow what is in Fig. of the attached paper, i.e., just make the channel get very wide very rapidly as it extends beyond the lipid bilayer. In that antechamber/entry space/atria region use BULK dielectric constant, diffusion coefficients etc.

Put boundary conditions at the end of the atria, not at the junction of the atria and the pore in the lipid bilayer.

We can also implement four electrode boundary conditions trivially if need be. This simply means that potential is measured away from the boundaries of the atria in places where boundary layers of the electrode (at the far end of the atria) or at the junciton between atria and the pore in the lipid bilayer.

If any of this confuses you, just let me know.

As ever
Bob

==========

Return Address for email: beisenbe@rush.edu

Bob aka RS Eisenberg

Bard Endowed Professor and Chairman
Dept of Molecular Biophysics & Physiology
Rush University
1653 West Congress Parkway
Chicago IL 60612 USA
Office Location: Room 1291 of

Jelke Building at 1750 West Harrison

Email: beisenbe@rush.edu
Voice: +312-942-6467
FAX: +312-942-8711
FAX to Email: +708-455-8542
Department WebSite: http://www.phys.rush.edu/Personal
WebSite: http://www.phys.rush.edu/RSEisenberg/

==========

On Thu, Feb 2, 2012 at 9:21 AM, Tzyy-Leng Horng <tlhorng123@gmail.com> wrote:

> Dear Bob,
>
> While I am applying Kong's rule, I digressed to do a little numerical experiment on 1D nanotube with constant cross-section area with both Fickian and single-file diffusion and LJ (finite-size effect), but no electrostatics. Just two-type diffusions and LJ potential. Number of species is just 2. Very fundamental system, and the equations are:
>
> u_t=a*u_{xx}-b*u_{xxxx}+LJ's;
> v_t=c*u_{xx}-d*u_{xxxx}+LJ's.
> Usually b<<a, and d<<c.
> LJ's for u is eps_{11}*integral_{11}+eps_{12}*integral_{12}; LJ's for v is eps{22}*integral_{22}+eps_{12}*integral_{21}. This system has totally 7 parameters: a,b,c,d,eps11,eps22,eps12. Here I simplify it by letting a=c, b=d, eps11=eps22. So reduces to 4 parameters. By scaling (letting a=c=1), it is actually 3 parameters.
> For example, I chose eps11=eps22=4, b=d=1e-4, and vary eps12 from 0 to 6. u(x,t) and v(x,t) will vary from stable steady state to periodic in x and t to stable steady state again to finally unstable with high-freq space mode amplifying in time. The interesting part is periodic-in-time state, that might point to gating. The key point is b=d can not be too large or too small for this to happen. If I add electrostatics, it will be ion channel again, and I

expect this will happen in ion channel too.

Allen

Allen

———————————————————
Professor Horng, Tzyy-Leng Allen
100 Wen-Hwa Rd., Seatwen
Department of Applied Mathematics
Feng Chia University
Taichung, Taiwan 40724
Office phone: 886-424517250 ext. 5126
Cell phone: 886-922263146
FAX: 886-424510801
E-mail: tlhorng@math.fcu.edu.tw
E-mail: allen.horng@msa.hinet.net
E-mail: tlhorng123@gmail.com
Homepage: http://newton.math.fcu.edu.tw/~tlhorng/
Homepage: http://newton.math.fcu.edu.tw/~tlhorng/index_eng.html
MSN: tlhorng@math.fcu.edu.tw
Skype: allen3344