Bob Eisenberg <bob.eisenberg@gmail.com>

Re: Definition of a Wall, Correlations, and dielectric coefficients

Bob Eisenberg <beisenbe@rush.edu> Mon, Nov 12, 2012 at 11:15 AM
Reply-To: beisenbe@rush.edu
To: Jinn Liu 劉晉良 <jinnliu@mail.nhcue.edu.tw>, Dezső Boda ++ Gmail <dezsoboda@gmail.com>, Bob Eisenberg <beisenbe@rush.edu>, Chun Liu <liu@math.psu.edu>

and I should add that in the attached papers
we ACTUALLY did include DFT into pnp

We did not present all the details but ALL the calculations
were done that way as well as with the LJ model.

As ever
Bob

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On Mon, Nov 12, 2012 at 8:55 AM, Bob Eisenberg <beisenbe@rush.edu> wrote:

Dear Dezso and Jinn

About the definition of a wall.

Chun Liu suggested the following treatment which we adopted in our paper

Hyon, Y., J. E. Fonseca, B. Eisenberg and C. Liu (2012). "Energy variational approach to study charge inversion (layering) near charged walls." Discrete and Continuous Dynamical Systems Series B (DCDS-B) 17(8): 2725 - 2743.

He suggested that we give the wall repulsion properties using the van der Waals formulation. This will automatically keep the centers of the spheres away analogously to the way they are kept away in MC of hard spheres. This is a brilliant suggestion of greatest importanceand I hope none of us forget that it was Chun's idea. These effects are large and maybe dominant and without this only confusion would result. In fact, the differences between DFTPNP and MC that Dirk and Dezso found might arise in this way.

about dielectric coefficients

There are MANY people who believe that the variation of dielectric coefficient with location (or with ionic concentration and composition) is very important and is the first thing that should be corrected (i.e., extended) in the classical primitive model. I do NOT NOT NOT think that Jinn should be discouraged from doing this. And thus I disagree with Dezso's advice. What I think should be kept very clearly is that this is a different approach in some ways orthogonal to the approach that says everything comes from the correlations of the ions in a uniform dielectric. There is nothing wrong with pursuing multiple avenues to unknowns at once as long as we resist the human tendency to become emotionally attached to one or two of them. The role of a scientist is to guess and check. These are different guesses. What is crucial is that we check them objectively by computing their consequences in a range of conditions and solutions.

About correlations:

Let's state the obvious here:
the correlations present in an MC simulation or an MD simulation without alias provoking idiotic spatial periodic boundary conditions are much richer than in PNP or than those in any low order truncation of the closure series that arises whenEVER PNP is derived (see

Schuss, Z., B. Nadler and R. S. Eisenberg (2001). "Derivation of PNP Equations in Bath and Channel from a Molecular Model." Physical Review E 64: 036116 1-14.
Schuss, Z., B. Nadler and R. S. Eisenberg (2001). "Derivation of Poisson and Nernst-Planck equations in a bath and channel from a molecular model." Phys Rev E Stat Nonlin Soft Matter Phys 64(3 Pt 2): 036116.
Schuss, Z., B. Nadler, A. Singer and R. Eisenberg (2002). A PDE formulation of non-equilibrium statistical mechanics for ionic permeation,. AIP Conference Proceedings , 3-6 September 2002: Unsolved Problems Of Noise And Fluctuations, UPoN 2002, 3rd International Conference on Unsolved Problems of Noise and Fluctuations in Physics, Biology, and High Technology Washington, DC,, AIP.

The same issue is found in innumerable closure attempts for equilibrium systems (the above are nonequilibrium).

in my view (and this is not shared by Dezso or any of the other physical chemists I know) we do not know how well the pde system deals with the correlations EVIDENT IN EXPERIMENTS (i.e., layering) until we compute those systems. the PDE's handle the correlations so differently from classical MC that we simply cannot compare them, in my view without doing them.

BUT the intuition of these superb scientists is NOT NOT to be ignored. So we need to say how

can we include further correlations corresponding to higher order terms in the closure expansion (i.e., BBGKY or whatever)

I do NOT know how to do that but I do know some things we must not do.

a) we must not assume that the closure series converges at all, let alone in a few terms. It may be a fool's errand to add terms. There are innumerable counterexamples of infinite series in which the first terms are not an approximation to the sum.

b) we must never confuse inputs and outputs. Correlations are OUTPUTs of calculations. The forces that produce the correlations are inputs. What we must do is to find a model that produces more realistic correlations and that model should be of forces, What we must NOT do is simply introduce the correlations into the system. The reason for this is simple. The correlations are SENSITIVE functions of everything in the system. So if we change anything we can not and MUST NOT use the same correlations. We must use the right ones for each condition. But we do not know what those are.

c) There are very very many models in the pchem literature seeking to compute higher order correlations. DFT is one of those with its mysterioius non local integrals (maybe not mysterious to Chun, who has done a great deal of thinking about this). I also like John Weeks models. Perhaps we should try to introduce them into PNP. John is eager to look over what we do but no more.

I hope this is helpful

As ever
Bob

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2 attachments

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