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Subject: Re: Finite Size Effect paper from Benzhou Lu

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From: Bob Eisenberg (bob.eisenberg@gmail.com)

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To: jinnliu@mail.nhcue.edu.tw;

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Cc: beisenbe@rush.edu;

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Date: Sunday, June 1, 2014 2:25 AM

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Dear Jinn

Thank you for your deep and profound reply. I am sorry that I did not understand that all myself, despite your best efforts. Thank you for your patience with me.

I will try to persuade Benzhou (who is a very nice person but sometimes stubborn intellectually) to read our paper and to have HIM write you (or to have me introduce you to each other) AFTER he invests the effort to actually read our paper.

If he does not do that, we will need to quote him in our JCP paper (which me might be the referee for!) and elsewhere.

If he does read our paper, perhaps we can persuade him (with a combination of carrot and stick) to use YOUR expressions and apply them to real channel structures which he has in some of his papers.

With admiration  
Bob

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On Sat, May 31, 2014 at 11:54 AM, jinnliu <jinnliu@mail.nhcue.edu.tw> wrote:

Dear Bob,

Thank you for sending me Lu's paper.

Lu's steric term in eq. (27) seems to be phenomenological.

I have the following questions about this term:

1. It does not follow Boltzmann's law of entropy, i.e., does not have the form like  $C \ln C$  or  $(1-C) \ln(1-C)$ . What is the physical origin about the term  $\ln[(1-C)/(1-C_0)]$ ?
2. What is the physical meaning about the volume ( $a^3$ ) in the denominator in the energy functional?
3. What is the limiting value of the steric term  $\ln[(1-C)/(1-C_0)]/(a^3)$  as  $a$  goes to zero by using L'Hopital's rule in Calculus? The phrase just below eq. (27) states that the limit is PB (eq. (15)). It does not look very straightforward to me. Is there reference for the proof?

My major concern is question 1.

I knew his steric formula (extended from I. Borukhov, D. Andelman, and H. Orland, Phys. Rev. Lett. 79, 435 (1997) as stated in the abstract) before I derived our steric functional in our J Phys Chem paper. I even have my own extension in my J. Comp. Phys. to have nonuniform ion sizes (see the definition of  $v^{\text{bar}}$  in the attached paper). My extension still obeys the Boltzmann entropy law (see eq. (2.1)). However, the limit of my first Boltzmann term (same as Borukhov's) would blow up as the volume goes to zero (please note that the first denominator term in (2.1)).

That is why I said their steric term is phenomenological and hence why I derived the formula using the lattice model of configuration entropy in our J Phys Chem paper. I don't feel comfortable (from math point of view) of using Borukhov's formula although their Poisson Fermi equation works fine in their papers and in a lot of papers extended from their 1997 paper (including Lu's papers).

By the way in our next complete PNPf paper, we will show that our Poisson Fermi variational energy indeed converges to Poisson Boltzmann energy when all diameters of ions tend to zero.

Best,

Jinn

-----Original message-----

**From:** Bob Eisenberg Yahoo <beisenbe@rush.edu>

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**Date:** Sat, 31 May 2014 03:54:07

**Subject:** Finite Size Effect paper from Benzhou Lu

Dear Jinn

It seems I am surviving the heat in Beijing and meeting lots of bright students.

Of course, it is like America, colder inside in the summer than in the winter!

Benzhou Lu my host in Beijing just sent me the attached paper which

seems quite relevant to our work.

I will read it later today.  
Thought you would want to see it.

As ever  
Bob

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