Modified Poisson-Nernst-Planck Equation for Charge Inversion near Charged Wall

Yunkyong Hyon, Jim Fonseca, Chun Liu, and Bob Eisenberg (in some order or another)

Introduction

Ionic solutions are in many ways the most important mixtures people encounter. All of life occurs in ionic solutions; much of chemistry is done in ionic solutions. Understanding ionic solutions has been entwined with understanding life since ions were discovered and their fluxes investigated by Fick, a biologist, actually a physiologist (*1, 2*). Ionic solutions have usually been treated as simple fluids (*3-5*) with complex properties (*6-20*). Here we take a different approach. We view ionic solutions as complex fluids with simple components.

We view ionic solutions as complex fluids because ions come 'in pairs'; that is to say, electrostatic interactions are so strong that ions come (always) in (strictly) neutral combinations. The interactions between positive ions (cations) and negative ions (anions) are so strong that deviations from electroneutrality are always tiny. Strong deviations would produce electric fields comparable to the electric field between valence electrons and nuclei inside an atom. Such strong electric fields would destroy these atoms, producing atomic plasmas incompatible with life.

The salts which dissolve in water to create ionic solutions are always strictly neutral (*21*). If the salts are made of ions with equal charge (i.e., valence) like $Na^+ Cl^-$, ions come in pairs; the neutral combination (which is in fact the definition of a 'molecule' in the periodic lattice of a salt crystal (*22*)) has two atoms. If the salts are made of elements with unequal charge (like $Ca^{2+} Cl_2^-$), the neutral molecule has three atoms. The macromolecules of life—proteins, nucleic acids, and lipids—always appear in electroneutral combinations with ions (and/or each other). The 'permanent' charges of DNA and proteins (that chemists call their acid and base groups) are balanced by an exactly equal number of ions. Molecular biology is the science of complex fluids with complex elements. The fluids of life are mixtures of ionic solutions, and the macromolecular minielements called organic molecules (like glucose or amino acids), proteins, nucleic acids, and lipids.

In biological and chemical solutions the amount of positive and negative charge in a volume are nearly the same. Macroscopic and mesoscopic amounts of ionic solutions (e.g., tissues and cells in the biological context) are equal within a tolerance of the order of 10^{-15}. The 'sum rules' of equilibrium statistical mechanics (*23, 24*) are an expression of the enormous strength of electrostatic interactions that enforce electroneutrality. Even atomic scale systems, active sites of enzymes or pores in channel proteins where dimensions of 1Å are significant, have deviations much less than 10^{-3}.

Statistical mechanics arose from the treatment of ideal gases of uncharged particles that hardly

interact.(*25-27*) Statistical mechanics has been extended to deal with simple fluids with great success even when they are nonideal (*3-5*). These nonideal fluids have significant hard core interactions caused by the finite volume of molecules that do not overlap. Statistical mechanics has been less successful in dealing with the experimental properties of ionic solutions (*6-11, 13, 15, 28*). Theories of even the fundamental property of solutions (the free energy per mole of each component) have not been particularly successful (illustrated in Fig. XX of Ref; Fig YY see (*28*) for references) even in solutions of one salt (e.g., NaCl in water). In mixed solutions, like those of living systems, success is even more limited and descriptions used in technological applications (which have to get their predictions right!) often involve large numbers of empirical parameters.(*15, 16, 29-31*)

Molecular dynamics simulations have not escaped these difficulties since their force fields are nearly always calibrated under ideal conditions of zero concentration. The force fields of molecular dynamics are not designed to deal with finite concentrations of ions, or mixtures of different types of ions. When atomic scale simulations are used to compute macroscopic systems, they must be calibrated (*32*) to show that they compute properties actually measured in the nonideal solutions of chemical and biological interest.(*33*)

We thought a variational approach designed to deal with strong interactions might be a useful alternative approach to the historical tradition (*34, 35*) Ionic solutions in fact are a relatively simple complex fluid in some ways, because their microelements are hard spheres (Na^+, K^+, Ca^{2+}) or nearly hard spheres Cl^- in the most important biological cases. Water can often be successfully described as a continuum, as it is in implicit solvent models of ionic solutions (also called 'the primitive model') and proteins.(REFERENCES) The theory of complex fluids has dealt with systems with complex microelements: liquid crystals, polymeric fluids (*36, 37*), colloids and suspensions (*38, 39*) and electrorheological fluids (*40, 41*); magnetohydrodynamics systems (*42*); systems with deformable electrolyte droplets that fission and fuse (*38, 43*); and suspensions of ellipsoids. The theory deals also interfacial properties of these complex mixtures, such as surface tension and the Marangoni effects of 'oil on water' and 'tears of wine' (*38, 39, 44, 45*).

We want to see how well the theory of complex fluids can deal the properties of ionic solutions of sodium, potassium, calcium, and chloride ions, because these solutions are (nearly) the extracellular solutions of living systems. Living solutions are not all that simple. Real extracellular solutions contain other components and the molecular detail of water can be important. Living solutions inside cells also contain proteins, nucleic acids, lipids, and organic ions (like free amino acids), that are complex

microelements, that form the macromolecules of life. It will be interesting to see if the theory of complex fluids can extended to them (in (*34, 35*) and forthcoming work involving membrane (Ryham, personal communication) and tissue (Mori, personal communication) structures.

Here we apply this approach to a simple system chosen to illustrate interactions. We deal with a particular phenomenon that arises from the interaction of ions and a charged wall. Ions have charge and finite diameter. They do not overlap. Thus, when ions are near a charged wall, complex distributions occur if the ions have different charge and/or diameter. These complex distributions near walls have historically been important in characterizing nonideal behavior of solutions and theories. They also have technological importance as the source of the strength of cement.(*46*) The complex distributions are closely related to distributions in and near proteins and lipid membranes.(*47-49*) Here we use a variational approach to try catch the essential property of interaction near a wall in as general a way as we can. We are not concerned yet with the molecular details so well described in a recent paper from Pettitt's group (*50*). Rather, we refer to that paper and Boda's work (*51-54*) for historical and chemical detail and apologize to the many authors whose work we do not know well enough about to cite properly.

1.   B. Hille, *Ionic Channels of Excitable Membranes*.   (Sinauer Associates Inc., Sunderland, ed. 3rd, 2001), pp. 1-814.

2.   M. H. Jacobs, *Diffusion Processes*.   (Springer Verlag, New York, 1967), pp. 160.

3.   J.-P. Hansen, I. R. McDonald, *Theory of Simple Liquids*.   (Academic Press, New York, ed. Third Edition, 2006), pp. 416.

4.   S. A. Rice, P. Gray, *Statistical Mechanics of Simple Fluids*.   (Interscience (Wiley), New York, 1965), pp. 582.

5.   J. Barker, D. Henderson, *Reviews of Modern Physics* **48**, 587 (1976).

6.   L. Vrbka *et al.*, *The Journal of chemical physics* **131**, 154109 (2009).

7.   I. Kalcher, J. Dzubiella, *The Journal of chemical physics* **130**, 134507 (2009).

8.   I. S. Joung, T. E. Cheatham, *The Journal of Physical Chemistry B*,   (2009).

9.   Z. Abbas, E. Ahlberg, S. Nordholm, *The Journal of Physical Chemistry B* **113**, 5905 (2009).

10.   L. L. Lee, *Molecular Thermodynamics of Electrolyte Solutions*.   (World Scientific Singapore, 2008).

11.   W. R. Fawcett, *Liquids, Solutions, and Interfaces: From Classical Macroscopic Descriptions to Modern Microscopic Details*.   (Oxford University Press, New York, 2004), pp. 621.

12.   S. Durand-Vidal, J.-P. Simonin, P. Turq, *Electrolytes at Interfaces*.   (Kluwer, Boston, 2000).

13.   J. Barthel, H. Krienke, W. Kunz, *Physical Chemistry of Electrolyte Solutions: Modern Aspects*.   (Springer, New York, 1998).

14.   S. Durand-Vidal, P. Turq, O. Bernard, C. Treiner, L. Blum, *Physica A* **231**, 123 (1996).

15.   K. S. Pitzer, *Thermodynamics*.   (McGraw Hill, New York, ed. 3rd, 1995), pp. 626.

16.   K. S. Pitzer, *Activity Coefficients in Electrolyte Solutions*.   (CRC Press, Boca Raton FL USA, 1991).

17.   J.-C. Justice, in *Comprehensive Treatise of Electrochemistry Volume 5 Thermondynbamic and Transport Properties of Aqueous and Molten Electrolytes,* B. E. Conway, J. O. M. Bockris, E. Yaeger, Eds. (Plenum, New York, 1983),   pp. 223-338.

18.   H. L. Friedman, *Ionic Solution Theory*.   (Interscience Publishers, New York, 1962).

19.   R. A. Robinson, R. H. Stokes, *Electrolyte Solutions*.   (Butterworths Scientific Publications, London, ed. Second, 1959).

20.   H. S. Harned, B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*.   (Reinhold Publishing Corporation, New York, ed. Third, 1958).

21.   A. Singer, Z. Schuss, R. S. Eisenberg, *Journal of   Statistical Physics* **119**, 1397 (2005).

22.   L. Pauling, *Nature of the Chemical Bond*.   (Cornell University Press, New York, ed. Third Edition, 1960), pp. 664.

23. J. R. Henderson, in *Fundamentals of Inhomogeneous Fluids,* D. Henderson, Ed. (Marcel Dekker, New York, 1992), pp. 23-84.

24. P. A. Martin, *Reviews of Modern Physics* **60**, 1076 (1988).

25. S. G. Brush, *The Kind of Motion We Call Heat*. (North Holland, New York, 1986).

26. E. Garber, S. G. Brush, C. W. F. Everitt, Eds., *Maxwell on Molecules and Gases*, (MIT Press, Cambridge MA, 1986).

27. L. Boltzmann, *Lectures on Gas Theory*. S. Brush, Ed., (University of California, Berkely CA, 1964).

28. D. Fraenkel, *Molecular Physics: An International Journal at the Interface Between Chemistry and Physics* **108**, 1435 (2010).

29. J. V. Sengers, R. F. Kayser, C. J. Peters, H. J. White, Jr., *Equations of State for Fluids and Fluid Mixtures (Experimental Thermodynamics)* (Elsevier, New York, 2000), pp. 928.

30. Y. Lin, K. Thomen, J.-C. d. Hemptinne, *American Institute of Chemical Engineers AICHE Journal* **53**, (2007).

31. R. T. Jacobsen, S. G. Penoncello, E. W. Lemmon, R. Span, in *Equations of State for Fluids and Fluid Mixtures,* J. V. Sengers, R. F. Kayser, C. J. Peters, H. J. White, Jr., Eds. (Elsevier, New York, 2000), pp. 849-882.

32. D. E. Post, L. G. Votta, *Physics Today* **58**, 35 (2005).

33. B. Eisenberg, *Physics Today* **58**, p.13 (Letter to the Editor) (2005).

34. B. Eisenberg, Y. Hyon, C. Liu, *Preprint# 2317 of the reprint series of the Institute for Mathematics and its Applications (IMA, University of Minnesota, Minneapolis)* *http://www.ima.umn.edu/preprints/jun2010/jun2010.html*, (2010).

35. Y. Hyon, B. Eisenberg, C. Liu, *Preprint# 2318 of the reprint series of the Institute for Mathematics and its Applications (IMA, University of Minnesota, Minneapolis)* *http://www.ima.umn.edu/preprints/jun2010/jun2010.html*, (2010).

36. R. B. Bird, R. C. Armstrong, O. Hassager, *Dynamics of Polymeric Fluids, Fluid Mechanics*. (Wiley, New York, 1977), vol. Volume 1, pp. 672.

37. R. B. Bird, O. Hassager, R. C. Armstrong, C. F. Curtiss, *Dynamics of Polymeric Fluids, Kinetic Theory* (Wiley, New York, 1977), vol. Volume 2, pp. 437.

38. P. Yue, J. J. Feng, C. Liu, J. Shen, *Journal of Fluid Mechanics* **515**, 293 (2004).

39. P. Yue, J. J. Feng, C. Liu, J. Shen, *Journal of Fluid Mechanics* **540**, 427 (2005).

40. P. Sheng, J. Zhang, C. Liu, *Progress of Theoretical Physics Supplement No. 175*, 131 (2008).

41. J. Zhang, X. Gong, C. Liu, W. Wen, P. Sheng, *Physical Review Letters* **101**, 194503 (2008).

42. C. Liu, *Energetic Variational Approaches in Complex Fluids*. (Beijing University, 2008).

43. R. Ryham, C. Liu, L. Zikatanov, *Discrete Contin. Dyn. Syst.-Ser. B* **8**, 649 (2007).

44. B. Franklin, W. Brownrigg, M. Farish, *Philosophical Transactions of the Royal Society of London* **64**, 445 (1774).

45. M. G. Velarde, *Interfacial Phenomena and the Marangoni Effect*. Interfacial Phenomena and the Marangoni Effect (Springer, New York, 2003).

46. B. Jönsson, A. Nonat, C. Labbez, B. Cabane, H. Wennerström, *Langmuir* **21**, 9211 (2005).

47. R. S. Eisenberg, in *New Developments and Theoretical Studies of Proteins,* R. Elber, Ed. (World Scientific, Philadelphia, 1996), vol. 7, pp. 269-357. Published in the Physics ArXiv as arXiv:0807.0715.

48. R. S. Eisenberg, *Journal of Membrane Biology* **171**, 1 (1999).

49. B. Eisenberg, *Physica Status Solidi (c)* **5**, 708 (2008).

50. J. J. Howard, J. S. Perkyns, B. M. Pettitt, *The Journal of Physical Chemistry B* **114**, 6074 (2010).

51. D. Boda, K.-Y. Chan, D. Henderson, *The Journal of chemical physics* **109**, 7362 (1998).

52. D. Gillespie, M. Valisko, D. Boda, *Journal of Physics: Condensed Matter* **17**, 6609 (2005).

53. M. Valisko, D. Boda, D. Gillespie, *Journal of Physical Chemistry C* **111**, 15575 (2007).

54. D. Henderson, D. Boda, *Phys Chem Chem Phys* **11**, 3822 (May 28, 2009).