Continuum Electrostatics for Ionic Solutions with Nonuniform Ionic Sizes

Bo Li
Department of Mathematics and
Center for Theoretical Biological Physics (CTBP)
University of California, San Diego, USA

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Discussions with J. Che, V. Chu, J. Dzubiella, and B. Lu

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References

[1] B. Li, SIAM J. Math. Anal., 40, 2536–2566, 2009.

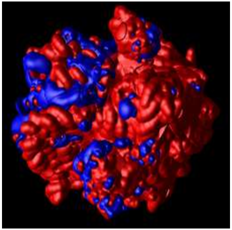
[2] B. Li, Nonlinearity, 22, 811–833, 2009

[3] B. Li, unpublished notes, 2009.

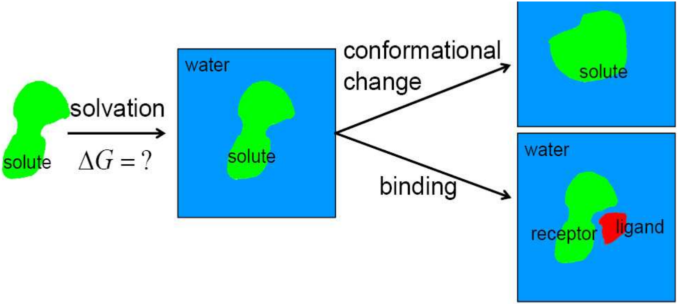
1. Introduction

Electrostatic interactions

- charges in biomolecules
- solvent polarization, ions
- long range
- main part of solvation free energy
  $\Delta G = G_2 - G_1$

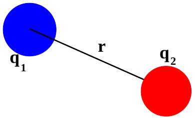


(McCammon's work)



Coulomb's law

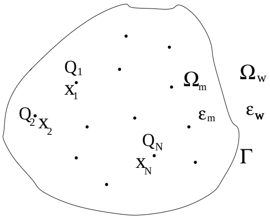
- potential
  $$U_{21} = \frac{1}{4\pi\varepsilon}\frac{q_1 q_2}{r}$$
- force
  $$\mathbf{F}_{21} = -\nabla U_{21}(r) = -\frac{1}{4\pi\varepsilon}\frac{q_1 q_2}{r^2}\mathbf{r}_{21}$$



Poisson's equation

$$\nabla \cdot \varepsilon \nabla \psi = -4\pi\rho$$

- ψ: electrostatic potential
- ρ: charge density
- ε: dielectric coefficient



Implicit-solvent models

Main issue: the electrostatics of induced ions.

2. The Classical Poisson–Boltzmann Theory

Consider an ionic solution occupying a region Ω.

- $\rho_f : \Omega \to \mathbb{R}$: given, fixed charge density
- $c_j : \Omega \to \mathbb{R}$: concentration of jth ionic species
- c_j^∞ : bulk constant concentration of jth ionic species
- q_j: charge of jth ionic species
- β: inverse thermal energy

Poisson's equation:	$\nabla \cdot \varepsilon(x) \nabla \psi(x) = -4\pi\rho(x)$
Charge density:	$\rho(x) = \rho_f(x) + \sum_{j=1}^{M} q_j c_j(x)$
Boltzmann distributions:	$c_j(x) = c_j^\infty e^{-\beta q_j \psi(x)}$

The Poisson–Boltzmann equation (PBE)

$$\boxed{\nabla \cdot \varepsilon \nabla \psi + 4\pi \sum_{j=1}^{M} q_j c_j^\infty e^{-\beta q_j \psi} = -4\pi\rho_f}$$

PBE $$\nabla \cdot \varepsilon \nabla \psi + 4\pi \sum_{j=1}^{M} q_j c_j^{\infty} e^{-\beta q_j \psi} = -4\pi \rho_f$$

- Linearized PBE (the Debye–Hückel approximation)

$$\boxed{\nabla \cdot \varepsilon \nabla \psi - \varepsilon \kappa^2 \psi = -4\pi \rho_f}$$

Here $\kappa > 0$ is the ionic strength or the inverse Debye–Hückel screening length, defined by

$$\kappa^2 = \frac{4\pi\beta \sum_{i=1}^{M} q_j^2 c_j^{\infty}}{\varepsilon}$$

"Derivation": use the Taylor expansion and

Electrostatic neutrality: $\sum_{j=1}^{M} q_j c_j^{\infty} = 0$

- The sinh PBE for 1:1 salt ($q_2 = -q_1$, $c_2^{\infty} = c_1^{\infty}$)

$$\boxed{\nabla \cdot \varepsilon \nabla \psi - 8\pi q c_1^{\infty} \sinh(\beta q \psi) = -4\pi \rho_f}$$

Electrostatic free-energy functional of ionic concentrations

$$G[c] = \int_\Omega \left\{ \frac{1}{2}\rho\psi + \beta^{-1}\sum_{j=1}^{M} c_j \left[\ln(\Lambda^3 c_j) - 1\right] - \sum_{j=1}^{M} \mu_j c_j \right\} dV$$

$$\rho(x) = \rho_f(x) + \textstyle\sum_{j=1}^{M} q_j c_j(x)$$

$$\psi = L\rho: \ \nabla\cdot\varepsilon\nabla\psi = -4\pi\rho \ \text{ and } \ \psi = 0 \text{ on } \partial\Omega$$

- Λ : the thermal de Broglie wavelength
- μ_j: chemical potential for the jth ionic species

Equilibrium conditions

$$(\delta G[c])_j = q_j\psi + \beta^{-1}\ln(\Lambda^3 c_j) - \mu_j = 0 \Longleftrightarrow \text{ Boltzmann distributions}$$

Minimum electrostatic free-energy

$$G_{min} = \int_\Omega \left[-\frac{\varepsilon}{8\pi}|\nabla\psi|^2 + \rho_f\psi - \beta^{-1}\sum_{j=1}^{M} c_j^\infty \left(e^{-\beta q_j \psi} - 1\right) \right] dV$$

$$G[c] = \int_\Omega \left\{ \frac{1}{2}\rho\psi + \beta^{-1} \sum_{j=1}^{M} c_j \left[\ln(\Lambda^3 c_j) - 1 \right] - \sum_{j=1}^{M} \mu_j c_j \right\} dV$$

Theorem (B.L. 2009).

- The functional G has a unique minimizer $c = (c_1, \dots, c_M)$ which is also the unique equilibrium.
- $\exists\, \theta_1 > 0,\ \theta_2 > 0 : \theta_1 \le c_j(x) \le \theta_2$ a.e. $x \in \Omega$, $j = 1, \dots, M$.
- The equilibrium concentrations $c_1, \dots, c_M$ and corresponding potential ψ are related by the Boltzmann distributions.
- The potential ψ is the unique solution to the PBE.

Remark. Bounds are not physical! A drawback of the PB theory.

Proof. By the direct method in the calculus of variations, using:

- convexity: $G[\lambda u + (1-\lambda)v] \le \lambda G[u] + (1-\lambda) G[v]$;
- lower boundedness of $s \mapsto s(\log s - \alpha)$ with $\alpha \in \mathbb{R}$;
- superlinearity of $s \mapsto s \log s$;
- a lemma (cf. next slide). **Q.E.D.**

$$G[c] = \int_\Omega \left\{ \frac{1}{2}\rho L\rho + \beta^{-1}\sum_{j=1}^{M} c_j \left[\ln(\Lambda^3 c_j) - 1\right] - \sum_{j=1}^{M} \mu_j c_j \right\} dV$$

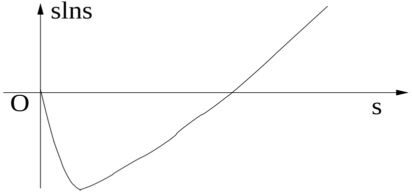
$$\rho(x) = \rho_f(x) + \textstyle\sum_{j=1}^{M} q_j c_j(x)$$

$$\psi = L\rho : \ \nabla \cdot \varepsilon \nabla \psi = -4\pi\rho \text{ and } \psi = 0 \text{ on } \partial\Omega$$

Lemma (B.L. 2009). Given c. There exists $\hat{c}$ satisfying:

- $\hat{c}$ is close to c;
- $G[\hat{c}] \leq G[c]$;
- $\exists\, \theta_1 > 0,\ \theta_2 > 0 : \theta_1 \leq \hat{c}_j(x) \leq \theta_2 \quad \text{a.e. } x \in \Omega,\ j = 1, \dots, M.$

Proof. By construction using the fact that the entropic change is very large for $c_j \approx 0$ and $c_j \gg 1$. **Q.E.D.**



3. A Size-Modified Poisson–Boltzmann Theory

Electrostatic free-energy functional of ionic concentrations

$$G[c] = \int_\Omega \left\{ \frac{1}{2}\rho\psi + \beta^{-1}\sum_{j=0}^{M} c_j \left[\ln(a_j^3 c_j) - 1\right] - \sum_{j=1}^{M} \mu_j c_j \right\} dV$$

$$\rho(x) = \rho_f(x) + \textstyle\sum_{j=1}^{M} q_j c_j(x)$$

$$L\rho = \psi : \ \nabla \cdot \varepsilon \nabla \psi = -4\pi\rho \ \text{ and } \ \psi = 0 \text{ on } \partial\Omega.$$

$$c_0(x) = a_0^{-3}\left[1 - \textstyle\sum_{i=1}^{M} a_i^3 c_i(x)\right]$$

- a_j $(1 \le j \le M)$: linear size of ions of jth species
- a_0: linear size of a solvent molecule
- c_0: local concentration of solvent

$$G[c] = \int_\Omega \left\{ \frac{1}{2}\rho L \rho + \beta^{-1} \sum_{j=0}^{M} c_j \left[\ln(a_j^3 c_j) - 1 \right] - \sum_{j=1}^{M} \mu_j c_j \right\} dV$$

$$\rho = \rho_f + \sum_{i=1}^{M} q_i c_i$$

Theorem (B.L. 2009). The functional G has a unique minimizer $c = (c_1, \ldots, c_M)$ which is also the unique local minimizer. It is characterized by the following two conditions:

- Bounds. There exist $\theta_1, \theta_2 \in (0,1)$ such that

$$\theta_1 \le a_j^3 c_j(x) \le \theta_2 \quad \text{a.e.} x \in \Omega, \; j = 0, 1, \ldots, M;$$

- Equilibrium conditions (i.e.,$(\delta G[c])_j = 0$ for $j = 1, \ldots, M$)

$$a_j^3 a_0^{-3} \log\left(a_0^3 c_0\right) - \log\left(a_j^3 c_j\right) = \beta\left(q_j \psi - \mu_j\right) \quad \text{a.e.}\, \Omega, \, j = 1, \ldots, M.$$

Remark. The bounds are non-physical microscopically!

Proof. Similar. Use the convexity and a lemma. **Q.E.D.**

The convexity.

$$h(u_1,\dots,u_M)=\left(1-\sum_{k=1}^{M}a_k^3u_k\right)\left[\log\left(1-\sum_{k=1}^{M}a_k^3u_k\right)-1\right]$$

$$\sum_{i,j=1}^{M}\partial_{u_i}\partial_{u_j}h(u)v_iv_j=\frac{\left(\sum_{i=1}^{M}a_i^3v_i\right)^2}{1-\sum_{k=1}^{M}a_k^3u_k}\geq 0\quad\forall v_1,\dots,v_M\in\mathbb{R}$$

Lemma (B.L. 2009). Given $c=(c_1,\dots,c_M)$. There exists $\hat{c}=(\hat{c}_1,\dots,\hat{c}_M)$ that satisfies the following:

- $\hat{c}$ is close to c;
- $G[\hat{c}]\leq G[c]$;
- there exist θ_1 and θ_2 with $0<\theta_1<\theta_2<1$ such that

$$\theta_1\leq a_j^3\hat{c}_j(x)\leq\theta_2\qquad \text{a.e.} x\in\Omega,\ j=0,1,\dots,M.$$

Proof. By construction. First, treat $c_0=a_0^{-3}(1-\sum_{i=1}^{M}a_i^3c_i)$. Then, treat c_j $(j=1,\dots,M)$. **Q.E.D.**

Uniform size: Generalized Boltzmann distributions

Assume: $a_0 = a_1 = \cdots = a_M =: a$.

- Equilibrium conditions: $c_j = c_0 a^3 c_j^\infty e^{-\beta q_j \psi}$ $(j = 1, \ldots, M)$
- Definition of c_0: $a^3 \sum_{j=0}^M c_j = 1$

The generalized Boltzmann distributions

$$\boxed{c_j = \frac{c_j^\infty e^{-\beta q_j \psi}}{1 + a^3 \sum_{i=1}^M c_i^\infty e^{-\beta q_i \psi}}, \quad j = 1, \ldots, M}$$

The generalized PBE

$$\boxed{\nabla \cdot \varepsilon \nabla \psi + 4\pi \frac{\sum_{j=1}^M q_j c_j^\infty e^{-\beta q_j \psi}}{1 + a^{-3} \sum_{i=1}^M c_i^\infty e^{-\beta q_i \psi}} = -4\pi \rho_f}$$

A variational principle: ψ minimizes the **convex** functional

$$I[\phi] = \int_\Omega \left[\frac{\varepsilon}{8\pi} |\nabla \phi|^2 - \rho_f \phi + \beta^{-1} a^{-3} \log \left(1 + \sum_{i=1}^M a^3 c_i^\infty e^{-\beta q_i \phi} \right) \right] dx$$

Nonuniform size: Implicit Boltzmann distributions

Equilibrium conditions

$$a_j^3 a_0^{-3} \log\left(a_0^3 c_0\right) - \log\left(a_j^3 c_j\right) = \beta\left(q_j\psi - \mu_j\right), \text{ a.e. } \Omega,\ j = 1, \ldots, M.$$

- An implicit Boltzmann distributions:

  $$c_j(x) = B_j(\psi(x)), \quad x \in \Omega,\ j = 1, \ldots, M.$$

- Electrostatic neutrality:

  $$\sum_{j=1}^{M} q_j B_j(0) = 0.$$

- Define $V : \mathbb{R} \to \mathbb{R}$ so that

  $$V'(\psi) = -\sum_{j=1}^{M} q_j c_j = -\sum_{j=1}^{M} q_j B_j(\psi).$$

- Implicit PBE and the related variational principle

  $$\nabla \cdot \varepsilon \nabla \psi - 4\pi V'(\psi) = -4\pi \rho_f,$$

  $$J[\phi] = \int_\Omega \left[\frac{\varepsilon}{8\pi}|\nabla\phi|^2 - \rho_f \phi + V(\phi)\right] dx.$$

Equilibrium conditions

$$a_j^3 a_0^{-3} \log\left(a_0^3 c_0\right) - \log\left(a_j^3 c_j\right) = \beta\left(q_j \psi - \mu_j\right), \text{ a.e. } \Omega, \; j = 1, \ldots, M.$$

Set $D_M = \{u = (u_1, \ldots, u_M) \in \mathbb{R}^M : u_j > 0, \; j = 0, 1, \ldots, M\},$

$$u_0 = a_0^{-3}\left(1 - \sum_{j=1}^M a_j^3 u_j\right),$$

$$f_j(u) = a_j^3 a_0^{-3} \log\left(a_0^3 u_0\right) - \log\left(a_j^3 u_j\right), \quad j = 1, \ldots, M.$$

Lemma (B.L. 2009). The mapping $f : D_M \to R^M$ is C^∞ and bijective.

Proof. It is clear that f is C^∞.

- f is injective: $\det(\nabla f) \neq 0$ by $\det(I + v \otimes w) = 1 + v \cdot w$.
- f is surjective: $f_j(u) = r_j \iff$ all $\partial z / \partial u_j = f_j(u) - r_j = 0$,

where $$z(u) = \sum_{j=0}^M u_j \left[\log\left(a_j^3 u_j\right) - 1\right] + \sum_{j=1}^M r_j u_j.$$

By constructions, $\min_{D_M} z < \min_{\partial D_M} z$. Hence, $\partial z / \partial u_j = 0$ for all $j = 1, \ldots, M$. **Q.E.D.**

Set $g = (g_1, \ldots, g_M) = f^{-1} : \mathbb{R}^M \to D_M,$

$B_j(\phi) = g_j\left(\beta(q_1\phi - \mu_1), \ldots, \beta(q_M\phi - \mu_M)\right),$

$B_0(\phi) = a_0^{-3}\left[1 - \sum_{j=1}^M a_j^3 B_j(\phi)\right].$

Electrostatic neutrality: $\sum_{j=1}^M q_j B_j(0) = 0.$

Define

$$V(\phi) = -\sum_{j=1}^M q_j \int_0^\phi B_j(\xi)\, d\xi \qquad \forall \phi \in \mathbb{R}$$

Lemma (B.L. 2009). The function V is strictly convex. Moreover,

$$V'(\phi) = -\sum_{j=1}^M q_j B_j(\phi) \begin{cases} > 0 & \text{if } \phi > 0, \\ = 0 & \text{if } \phi = 0, \\ < 0 & \text{if } \phi < 0, \end{cases}$$

and $V(\phi) > V(0) = 0$ for all $\phi \in \mathbb{R}$ with $\phi \neq 0$.

Proof. Direct calculations using the Cauchy–Schwarz inequality to show that $V'' > 0$. Also, use the neutrality. **Q.E.D.**

$$G[c] = \int_\Omega \left\{ \frac{1}{2}\rho L \rho + \beta^{-1} \sum_{j=0}^{M} c_j \left[\ln(a_j^3 c_j) - 1 \right] - \sum_{j=1}^{M} \mu_j c_j \right\} dV$$

$$\rho = \rho_f + \sum_{i=1}^{M} q_i c_i$$

Theorem (B.L. 2009).

- The equilibrium concentrations $(c_1, \ldots, c_M)$ and corresponding potential ψ are related by the implicit Boltzmann distributions

$$c_j(x) = B_j(\psi(x)) \qquad x \in \Omega, \; j = 1, \ldots, M.$$

- The potential ψ is the unique solution of the boundary-value problem of the implicit PBE

$$\nabla \cdot \varepsilon \nabla \psi - 4\pi V'(\psi) = -4\pi \rho_f.$$

This is the Euler–Lagrange equation of the convex functional

$$J[\phi] = \int_\Omega \left[\frac{\varepsilon}{8\pi} |\nabla \phi|^2 - \rho_f \phi + V(\phi) \right] dx \qquad \forall \phi \in H_0^1(\Omega).$$

4. Application Issues

4.1 Generalized Debye–Hückel approximations

The implicit PBE: $\nabla \cdot \varepsilon \nabla \psi - 4\pi V'(\psi) = -4\pi \rho_f$

- $V'(\phi) \approx V'(0) + V''(0)\phi = V''(0)\phi \quad$ for $|\phi| \ll 1$.
- Electrostatic neutrality $\Longrightarrow V'(0) = -\sum_{j=1}^{M} q_j B_j(0) = 0$.
- It is shown (B.L. 2009)

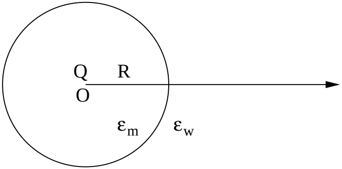
$$V''(0) = \beta \sum_{i=1}^{M} q_i^2 B_i(0) - \frac{\beta \left[\sum_{i=1}^{M} a_i^3 q_i B_i(0)\right]^2}{\sum_{i=0}^{M} a_i^6 B_i(0)}$$

Proposal

- Solve nonlinear algebraic equations to get $B_j(0)$ $(j = 0, 1, \ldots, M)$ and hence $V''(0)$.
- Solve the generalized Debye–Hückel approximation

$$\boxed{\nabla \cdot \varepsilon \nabla \psi - 4\pi V''(0)\psi = -4\pi \rho_f}$$

4.2 Potential monotonicity and charge compensation



$$\varepsilon_w \Delta\psi = V'(\psi) \quad (r > R)$$
$$\psi(R) : \text{ given}$$
$$\psi(\infty) = 0$$

Assume that $V : \mathbb{R} \to \mathbb{R}$ is strictly convex and $V'(0) = 0$.

- Strict monotonicity of the potential:

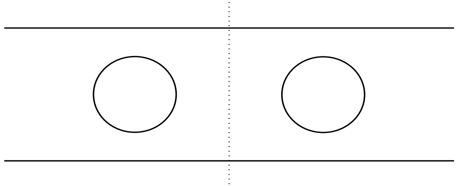
  $$\psi'(r) > 0 \text{ in } (R, \infty) \quad \text{or} \quad \psi'(r) < 0 \text{ in } (R, \infty).$$

- Charge compensation: The induced charge

  $$g(\bar{R}) = \int_{R<|x|<\bar{R}} \sum_{j=1}^{M} q_j c_j(x)\, dV$$

  decreases (if $Q > 0$) or increases (if $Q < 0$) from $g(R) = 0$ to $g(\infty) = -Q\,\mathrm{Vol}(B(0, R))$.

4.3. Wall-mediated like-charge attractions



$$\Delta\psi = V'(\psi) \quad \text{inside walls and outside balls}$$
$$\psi \text{ is a constant on the walls}$$
$$\psi \text{ is a constant on the boundary of balls}$$

Assume that $V : \mathbb{R} \to \mathbb{R}$ is strictly convex and $V'(0) = 0$.

The electrostatic surface force is given by

$$\mathbf{F} = \frac{1}{2} \int_{\partial \text{balls}} (\partial_n \psi)^2 \mathbf{n}\, dS$$

Force repulsive: $\mathbf{F} \cdot \{\text{unit horizontal vector to the center}\} > 0$.

5. Conclusions

Summary

- Electrostatic free-energy minimization provides bonds on concentrations, a limitation of the PB theory.
- A size-modified PB theory is developed. Generalized explicit and implicit Boltzmann distributions are obtained for the case of uniform and nonuniform ionic and molecular sizes, respectively.
- A generalized Debye–Hückel approximation is obtained that can be used for numerical calculations.
- The new theory has the essential features same as the classical one. Thus it is not able to explain the geometry-mediated like-charge attraction.

Outlook

- Bridge the continuum and atomistic models of electrostatics.
- Statistical mechanics basis of the continuum theory with nonuniform ionic sizes.
- Potential monotonicity and charge compensation for general domains.
- The relation between the PB theory and the generalized Born model.

Thank you!