A New Poisson-Boltzmann Equation for two types of ion species with different size

Chiun-Chang Lee

chlee@mail.nhcue.edu.tw / Applied Mathematics, NHCUE

This is a joint work with Professors T.C. Lin & Chun Liu

Workshop on Analysis and Its Applications in Biology and Physiology

Center for Advanced Study in Theoretical Sciences (CASTS)

Dec. 26-31. 2014

Outline

- Review on Modified Poisson-Boltzmann (MPB) equations with steric effects
- PB_ns equations: a new Poisson-Boltzmann equation with steric effects
- Limiting behavior of 1-D solutions of the PB_ns equation
- Asymptotic analysis and comparison with MPB equations

Review on Modified Poisson-Boltzmann (MPB) equations with steric effects

MPB equation

Two counterions with the same size a (cf. [1])

$$\epsilon^2 w'' = \frac{c_b(e^{q_1 w} - e^{-q_2 w})}{(1-\nu) + \frac{\nu}{q_1+q_2}(q_2 e^{q_1 w} + q_1 e^{-q_2 w})}$$

$\omega = \frac{e_0 \phi}{k_B T}$; ϕ: electrostatic potential

e_0: elementary charge

$k_B T$: thermal energy

c_b: bulk concentration

ϵ^2: dielectric constant

$-q_1$: the valence of the negative ion

$+q_2$: the valence of the positive ion

$\nu \sim (q_1 + q_2) c_b a^3 \ll 1$

[1] Borukhov, Andelman and Orland (1997) ***Steric Effects in Electrolytes: A Modified Poisson-Boltzmann Equation***, PRL

MPB equation

Two counterions with the same size a (cf. [1])

$\epsilon^2 u$ **Poisson's equation**: $\epsilon^2 \omega'' = q_1 n - q_2 p$

Boltzmann distri.: $q_1 n = \theta e^{q_1 w}, q_2 p = \theta e^{-q_2 w}$

Electroneutrality

Standard Poisson-Boltzmann equation

$$\epsilon^2 w'' = \theta \left(e^{q_1 w} - e^{-q_2 w} \right)$$

MPB equation

Two counterions with the same size a (cf. [1])

$$\epsilon^2 w'' = \frac{c_b(e^{q_1 w} - e^{-q_2 w})}{(1-\nu) + \frac{\nu}{q_1+q_2}(q_2 e^{q_1 w} + q_1 e^{-q_2 w})}$$

Standard Poisson-Boltzmann equation

$$\epsilon^2 w'' = \theta(e^{q_1 w} - e^{-q_2 w})$$

$$\theta = \theta(w) = \frac{1}{(1-\nu) + \frac{\nu}{q_1+q_2}(q_2 e^{q_1 w} + q_1 e^{-q_2 w})}$$

MPB equation

Two counterions with the same size a (cf. [1])

$$\epsilon^2 w'' = \frac{c_b(e^{q_1 w} - e^{-q_2 w})}{(1-\nu) + \frac{\nu}{q_1+q_2}(q_2 e^{q_1 w} + q_1 e^{-q_2 w})}$$

Free Energy $F = U - TS$

$$U = \int \left(-\frac{\epsilon^2}{2} |\mathrm{w}'|^2 + (q_1 e_0 c^- - q_2 e_0 c^+) w \right) dx$$

$$-TS = \frac{k_B T}{a^3} \int c^+ a^3 \log(c^+ a^3) + c^- a^3 \log(c^- a^3) + (1 - c^+ a^3 - c^- a^3) \log(1 - c^+ a^3 - c^- a^3)\ dx$$

$\frac{\delta F}{\delta w} = 0 \implies -\epsilon^2 w'' = -q_1 e_0 c^- + q_2 e_0 c^+$: **Poisson's Equation**

$\frac{\delta F}{\delta c^\pm} = \mu^\pm(\text{chemical potential})$: **Modified Boltzmann distribution**

MPB equation

Modified Boltzmann distribution (continued)

$$c^- = \frac{e_0 c_b e^{\frac{q_1 e_0}{k_B T} w}}{(1-\nu) + \frac{\nu\left(q_2 e^{\frac{q_1 e_0}{k_B T} w} + q_1 z e^{-\frac{q_2 e_0}{k_B T} w}\right)}{q_1 + q_2}},$$

$$c^+ = \frac{e_0 c_b e^{-\frac{q_2 e_0}{k_B T} w}}{(1-\nu) + \frac{\nu\left(q_2 e^{\frac{q_1 e_0}{k_B T} w} + q_1 z e^{-\frac{q_2 e_0}{k_B T} w}\right)}{q_1 + q_2}}.$$

If the size of two ions are not the same, then c^+ and c^- satisfy a coupled system of nonlinear algebraic equations

$$\frac{\delta F}{\delta c^+} = \mu^+, \quad \frac{\delta F}{\delta c^-} = \mu^-,$$

which cannot be solved explicitly. [2]

[2] Li, Liu, Xu, Zhou (2013) ***Generalized Boltzmann Distributions, Counterion Stratification, and Modified Debye Length*** Nonlinearity

A New Poisson-Boltzmann equations with steric effects

The **PB_ns E**quation

[3] Y. Hyon, B. Eisenberg and C. Liu (2010-2012 JCP, CMS, DCDS-A)

[4] T.C. Lin and B. Eisenberg (2014 CMS)

COMMUN. MATH. SCI.
Vol. 12, No. 1, pp. 149–173

A NEW APPROACH TO THE LENNARD-JONES POTENTIAL AND A NEW MODEL: PNP-STERIC EQUATIONS*

TAI-CHIA LIN† AND BOB EISENBERG‡

Abstract. A class of approximate Lennard-Jones (LJ) potentials with a small parameter is found whose Fourier transforms have a simple asymptotic behavior as the parameter goes to zero. When the LJ potential is replaced by the approximate LJ potential, the total energy functional becomes simple and exactly the same as replacing the LJ potential by a delta function. Such a simple energy functional can be used to derive the Poisson-Nernst-Planck equations with steric effects (PNP-steric equations), a new mathematical model for the LJ interaction in ionic solutions. Using formal asymptotic analysis, stability and instability conditions for the 1D PNP-steric equations with the Dirichlet boundary conditions for one anionic and cationic species are expressed by the valences, diffusion constants, ionic radii, and coupling constants. This is the first step to study the dynamics of solutions of the PNP-steric equations.

The **PB_ns E**quation

- Repulsive free energy for electrolyte solutions

$$E_\sigma[c_1, \dots, c_N, \phi] = E_{PB}[c_1, \dots, c_N, \phi] + \frac{1}{2}\int \sum_{i,j} g_{ij} c_i c_j dx$$

$$g_{ij} \sim \left(a_i + a_j\right)^3$$

- $E_{PB}[c_1, \dots, c_N, \phi] = \int \left(\ k_B T \sum_i c_i \mathrm{lo\,g} c_i + \frac{1}{2} \sum_i z_i e_0 c_i \, \phi \right) dx$

a_i*:* radius of *i*th ion species

$\varepsilon_{i,j}$'s are positive energy constants due to ion-ion interaction

The **PB_ns E**quation

- The variation of E_σ gives our PB_ns equatoin

$$k_B T \log c_i + z_i e_0 \phi + \sum_j g_{ij} c_j = \mu_i$$

$$-\nabla \cdot (\epsilon^2 \nabla \phi) = \sum_j z_j e_0 c_j$$

The **PB_ns** Equation

- The variation of E_σ gives our PB_ns equatoin

$$k_B T \log c_i + z_i e_0 \phi + \sum_j g_{ij} c_j = \mu_i$$

$$-\nabla \cdot (\epsilon^2 \nabla \phi) = \sum_j z_j e_0 c_j$$

Main study: Focus on the model with one cation and one anion species (e.g. NaCl or $CaCl_2$)

(i) Consider the case of $g_{11} = g_{22} = g_{12} > 0$ and compare the PB_ns equation with the MPB equation as $\epsilon \downarrow 0$.

(ii) Analyze the uniqueness result for the two component of algebraic equations.

The **PB_ns E**quation

- **Simple case: NaCl Solution with $\boldsymbol{g_{11} = g_{22} = g_{12}}$**

$$k_B T \log c_1 - e_0 \phi + g_{12}(c_1 + c_2) = 0$$

$$k_B T \log c_2 + e_0 \phi + g_{12}(c_1 + c_2) = 0$$

$$\nabla \cdot (\epsilon^2 \nabla \phi) = e_0 c_1 - e_0 c_2$$

The **PB_ns** Equation

- **Simple case: NaCl Solution with $g_{11} = g_{22} = g_{12}$**

$$k_B T \log c_1 - e_0 \phi + g_{12}(c_1 + c_2) = 0$$

$$k_B T \log c_2 + e_0 \phi + g_{12}(c_1 + c_2) = 0$$

$$\nabla \cdot (\epsilon^2 \nabla \phi) = e_0 c_1 - e_0 c_2$$

- $c_1 = \theta e^{\frac{e_0 \phi}{k_B T}}, c_2 = \theta e^{-\frac{e_0 \phi}{k_B T}}$

Standard Poisson-Boltzmann equation

$$\begin{cases} \nabla \cdot (\epsilon^2 \nabla \phi) = e_0 \theta \left(e^{\frac{e_0 \phi}{k_B T}} - e^{-\frac{e_0 \phi}{k_B T}} \right) \\ \dfrac{\log \theta}{\theta} = -\dfrac{g_{12}}{k_B T} \left(e^{\frac{e_0 \phi}{k_B T}} + e^{-\frac{e_0 \phi}{k_B T}} \right) \end{cases}$$

The **PB_ns E**quation

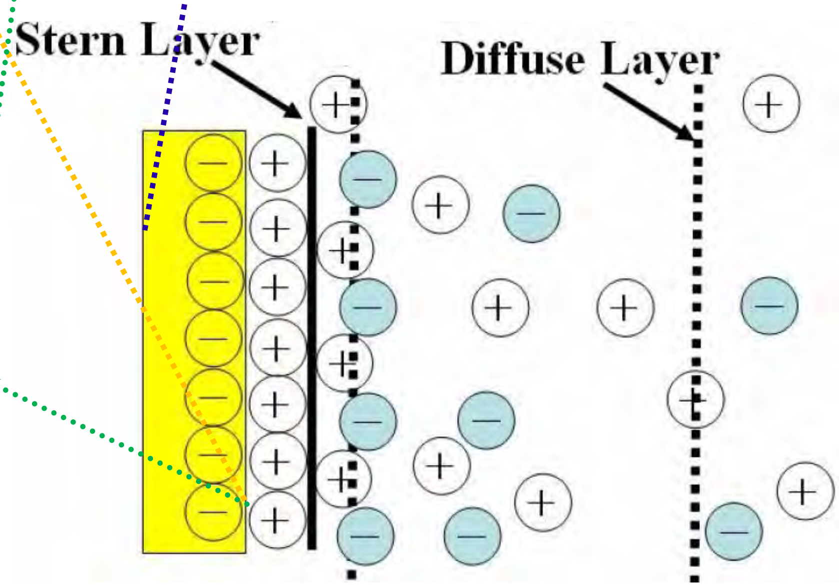
Boundary condition

- The capacitance effect of the electric double layer gives

$$\phi + \eta \frac{\partial \phi}{\partial \nu}\Big|_{\partial\Omega} = \varphi_{\mathrm{bd}} \quad \text{(Gauss's law in electrostatics)}$$

$\eta > 0$: thickness of Stern layer

Normal electric field at the surface



The **PB_ns** Equation

Existence and Uniqueness

$$\begin{cases} \epsilon^2 \phi'' = e_0 \theta \left(e^{\frac{e_0 \phi}{k_B T}} - e^{-\frac{e_0 \phi}{k_B T}} \right) \\ \dfrac{\log\theta}{\theta} = -\dfrac{g_{12}}{k_B T} \left(e^{\frac{e_0 \phi}{k_B T}} + e^{-\frac{e_0 \phi}{k_B T}} \right) \end{cases} \quad \text{in} \quad \Omega$$

$$\phi + \eta \frac{\partial \phi}{\partial \nu}\bigg|_{\partial\Omega} = \varphi_{\mathrm{bd}}$$

$$c_1(\phi) = \theta(\phi) e^{\frac{e_0 \phi}{k_B T}} \qquad c_2(\phi) = \theta(\phi) e^{-\frac{e_0 \phi}{k_B T}}$$

Recall

$$k_B T \log c_1 - e_0 \phi + g_{12}(c_1 + c_2) = 0$$

$$k_B T \log c_2 + e_0 \phi + g_{12}(c_1 + c_2) = 0$$

The **PB_ns** Equation

Existence and Uniqueness

$$\begin{cases} \epsilon^2 \phi'' = e_0 \theta \left(e^{\frac{e_0 \phi}{k_B T}} - e^{-\frac{e_0 \phi}{k_B T}} \right) \\ \dfrac{\log\theta}{\theta} = -\dfrac{g_{12}}{k_B T} \left(e^{\frac{e_0 \phi}{k_B T}} + e^{-\frac{e_0 \phi}{k_B T}} \right) \end{cases} \quad \text{in} \quad \Omega \tag{1.1}$$

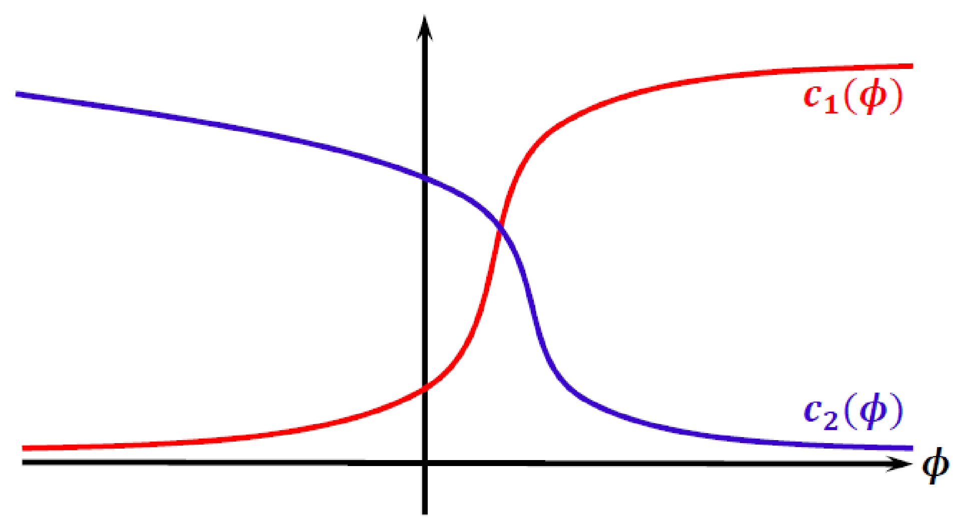
$$\phi + \eta \frac{\partial \phi}{\partial \nu}\Big|_{\partial\Omega} = \ _{\mathrm{bd}} \tag{1.2}$$

- $\dfrac{dc_1}{d\phi} > 0 > \dfrac{dc_2}{d\phi}$
- $\dfrac{d^2 c_1}{d\phi^2} > 0 > \dfrac{d^2 c_2}{d\phi^2}$ as $\phi \in (-\infty, \phi^*)$; $\dfrac{d^2 c_1}{d\phi^2} < 0 < \dfrac{d^2 c_2}{d\phi^2}$ as $\phi \in (\phi^*, \infty)$

Recall

$$k_B T \log c_1 - e_0 \phi + g_{12}(c_1 + c_2) = 0$$

$$k_B T \log c_2 + e_0 \phi + g_{12}(c_1 + c_2) = 0$$



The **PB_ns E**quation

Existence and Uniqueness

$$\begin{cases} \epsilon^2 \phi'' = e_0 \theta \left(e^{\frac{e_0 \phi}{k_B T}} - e^{-\frac{e_0 \phi}{k_B T}} \right) \\ \dfrac{\log \theta}{\theta} = -\dfrac{g_{12}}{k_B T} \left(e^{\frac{e_0 \phi}{k_B T}} + e^{-\frac{e_0 \phi}{k_B T}} \right) \end{cases} \text{in} \quad \Omega \tag{1.1}$$

$$\phi + \eta \frac{\partial \phi}{\partial \nu}\Big|_{\partial \Omega} = \ _{\mathrm{bd}} \tag{1.2}$$

- Energy functional $\mathrm{E}[\phi] = \int_\Omega \frac{\epsilon^2}{2} |\nabla \phi|^2 + \underbrace{\mathrm{G}\left(e^{\frac{e_0 \phi}{k_B T}} + e^{-\frac{e_0 \phi}{k_B T}} \right)}_{\text{strictly convex}} dx + \int_{\partial \Omega} \frac{\epsilon^2}{2\eta} (\phi - \varphi_{\mathrm{bd}})^2 dS$

The **PB_ns** Equation

Existence and Uniqueness

$$\begin{cases} \epsilon^2 \phi'' = e_0 \theta \left(e^{\frac{e_0 \phi}{k_B T}} - e^{-\frac{e_0 \phi}{k_B T}} \right) \\ \frac{\log \theta}{\theta} = -\frac{g_{12}}{k_B T} \left(e^{\frac{e_0 \phi}{k_B T}} + e^{-\frac{e_0 \phi}{k_B T}} \right) \end{cases} \quad \text{in} \quad \Omega \tag{1.1}$$

$$\phi + \eta \frac{\partial \phi}{\partial \nu}\Big|_{\partial \Omega} = \quad_{\mathrm{bd}} \tag{1.2}$$

- Energy functional $\mathrm{E}[\phi] = \int_{\Omega} \frac{\epsilon^2}{2} |\nabla \phi|^2 + \underbrace{\mathrm{G}\left(e^{\frac{e_0 \phi}{k_B T}} + e^{-\frac{e_0 \phi}{k_B T}} \right)}_{\text{strictly convex}} dx + \int_{\partial \Omega} \frac{\epsilon^2}{2\eta} (\phi - \varphi_{\mathrm{bd}})^2 dS$

Theorem 1

Assume that Ω is a bounded domain with $\partial\Omega \in C^2$. *Let* $\epsilon > 0$ *and* $\eta \geq 0$. *Then the equation (1.1) with the boundary condition (1.2) has a unique solution*

$$\phi \in C^2(\overline{\Omega}) \cap C^\infty(\Omega).$$

The **PB_ns** Equation

Limiting behavior ($\epsilon \downarrow 0$): 1-dimensional case

Theorem 2

(i) *There exist C and M independent of* ϵ *such that*

$$|\phi'(x)| \le \frac{C}{\epsilon}\left(e^{-\frac{M(1+x)}{\epsilon}} + e^{-\frac{M(1-x)}{\epsilon}}\right) \; for\ x \in [-1,1].$$

(ii) $\big(\phi(x), \theta(x)\big) \to (\phi^*, \theta^*)$ *in* $(-1,1)$ *as* $\epsilon \downarrow 0$, *where*

$$\phi^* = 0, \frac{\log\theta^*}{\theta^*} = -\frac{2g_{12}}{k_B T}.$$

(iii) $\epsilon\phi'(\pm 1) \to \phi_\pm$ *as* $\epsilon \downarrow 0$, *where* $\phi_\pm$ *is determined by*

$$\sqrt{\frac{g_{12}}{\gamma^2}(\varphi_{\mathrm{bd}}(\pm 1) - \phi_\pm)^2 + \left(1 + \frac{2g_{12}}{k_B T}\theta^*\right)^2} -$$

$$\left(e^{\phi_\pm} + e^{-\phi_\pm}\right) \times e^{\sqrt{\frac{g_{12}}{\gamma^2}(\varphi_{\mathrm{bd}}(\pm 1) - \phi_\pm)^2 + \left(1 + \frac{2g_{12}}{k_B T}\theta^*\right)^2}} = 1.$$

Here we assume $\frac{e_0}{k_B T} = 1$ *and* $\frac{\eta}{\epsilon} \to \gamma$ *as* $\epsilon \downarrow 0$.

The **PB_ns E**quation

Limiting behavior ($\epsilon \downarrow 0$): 1-dimensional case

$$\begin{cases} \epsilon^2 \phi'' = e_0 \theta \left(e^{\frac{e_0 \phi}{k_B T}} - e^{-\frac{e_0 \phi}{k_B T}} \right) \\ \dfrac{\log\theta}{\theta} = -\dfrac{g_{12}}{k_B T} \left(e^{\frac{e_0 \phi}{k_B T}} + e^{-\frac{e_0 \phi}{k_B T}} \right) \end{cases} \text{ in } (-1,1)$$

$$\phi(\pm 1) \pm \eta \phi'(\pm 1) = \varphi_{\mathrm{bd}}(\pm 1)$$

$$\log\theta = \log \frac{\theta}{\theta^*} + \log \theta^* \sim \frac{\theta}{\theta^*} - 1 + \log \theta^*$$

$$\Rightarrow \quad \theta \sim \frac{\theta^*}{(1-\mu^*) + \mu^* \cosh \dfrac{e_0 \phi}{k_B T}}$$

$0 < \mu^* = \dfrac{\frac{2 g_{12}}{k_B T} \theta^*}{1 + \frac{2 g_{12}}{k_B T} \theta^*} < 1$ is related to the total bulk volume fraction of ions

The **PB_ns E**quation

Limiting behavior ($\epsilon \downarrow 0$): 1-dimensional case

$$\epsilon^2 \phi'' = e_0 \theta \left(e^{\frac{e_0 \phi}{k_B T}} - e^{-\frac{e_0 \phi}{k_B T}} \right)$$

$$= \frac{2 e_0 \theta^* \sinh \frac{e_0 \phi}{k_B T}}{(1-\mu^*) + \mu^* \cosh \frac{e_0 \phi}{k_B T}} + o(\phi)$$

The **PB_ns** Equation

Limiting behavior ($\epsilon \downarrow 0$): 1-dimensional case

$$\epsilon^2 \phi'' = e_0 \theta \left(e^{\frac{e_0 \phi}{k_B T}} - e^{-\frac{e_0 \phi}{k_B T}} \right)$$

$$= \frac{2 e_0 \theta^* \sinh \frac{e_0 \phi}{k_B T}}{(1-\mu^*) + \mu^* \cosh \frac{e_0 \phi}{k_B T}} + o(\phi)$$

Same with Andelman's MPB equation

MPB Equation with $q_1 = q_2 = 1$

$$\epsilon^2 w'' = \frac{c_b (e^{q_1 w} - e^{-q_2 w})}{(1-\nu) + \frac{\nu}{q_1 + q_2} (q_2 e^{q_1 w} + q_1 e^{-q_2 w})}$$

The **PB_ns E**quation

Limiting behavior ($\epsilon \downarrow 0$): 1-dimensional case

$$\begin{cases} \epsilon^2 \phi'' = e_0 \theta \left(e^{\frac{e_0 \phi}{k_B T}} - e^{-\frac{e_0 \phi}{k_B T}} \right) \\ \dfrac{\log \theta}{\theta} = -\dfrac{g_{12}}{k_B T} \left(e^{\frac{e_0 \phi}{k_B T}} + e^{-\frac{e_0 \phi}{k_B T}} \right) \end{cases} \text{ in } (-1,1)$$

is equivalent to the equation

$$\epsilon^2 \phi'' = e_0 e^{1 - \frac{e_0}{k_B T} \sqrt{g_{12} (\epsilon^2 \phi'^2 - 2 C_\epsilon)}} \left(e^{\frac{e_0 \phi}{k_B T}} - e^{-\frac{e_0 \phi}{k_B T}} \right),$$

Conclusion: When $g_{11} = g_{22} = g_{12}$, the PB_ns equation and the MPB equation have same asymptotic behavior at interior points, however, have different asymptotic behavior at boundary points.

The **PB_ns E**quation

Limiting behavior ($\epsilon \downarrow 0$): 1-dimensional case

PB_ns equation

$$\epsilon^2 \phi''(x) = q_1 c_1(\phi(x)) - q_2 c_2(\phi(x)) \quad \text{for} \quad x \in (-1,1),$$

$$\log c_1 = q_1 \phi - (g_{11} c_1 + g_{12} c_2),$$

$$\log c_2 = -q_2 \phi - (g_{12} c_1 + g_{22} c_2).$$

$$\phi(\pm 1) \pm \eta \phi'(\pm 1) = \varphi_{\mathrm{bd}}(\pm 1)$$

MPB equation

$$\epsilon^2 w'' = \frac{c_b (e^{q_1 w} - e^{-q_2 w})}{(1-\nu) + \frac{\nu}{q_1+q_2}(q_2 e^{q_1 w} + q_1 e^{-q_2 w})}$$

$$w(\pm 1) \pm \eta w'(\pm 1) = \varphi_{\mathrm{bd}}(\pm 1) - \frac{1}{q_1+q_2} \log \frac{q_2}{q_1}$$

Theorem 3

Assume that q_1 and q_2 are positive constants and $g_{11} = g_{22} = g_{12}$. For $\epsilon > 0$ and $\eta \geq 0$, let ϕ be the unique classical solution of the PB_ns equation (1.1) with the boundary condition (1.5), and let w be the unique classical solution of the MPB equation (1.9) with the boundary condition (1.14). Then for any compact subset K of the interval (-1,1), both w and $\phi - \frac{1}{q_1+q_2} \log \frac{q_2}{q_1}$ uniformly converge to zero in K as ϵ goes to zero. Moreover, we have

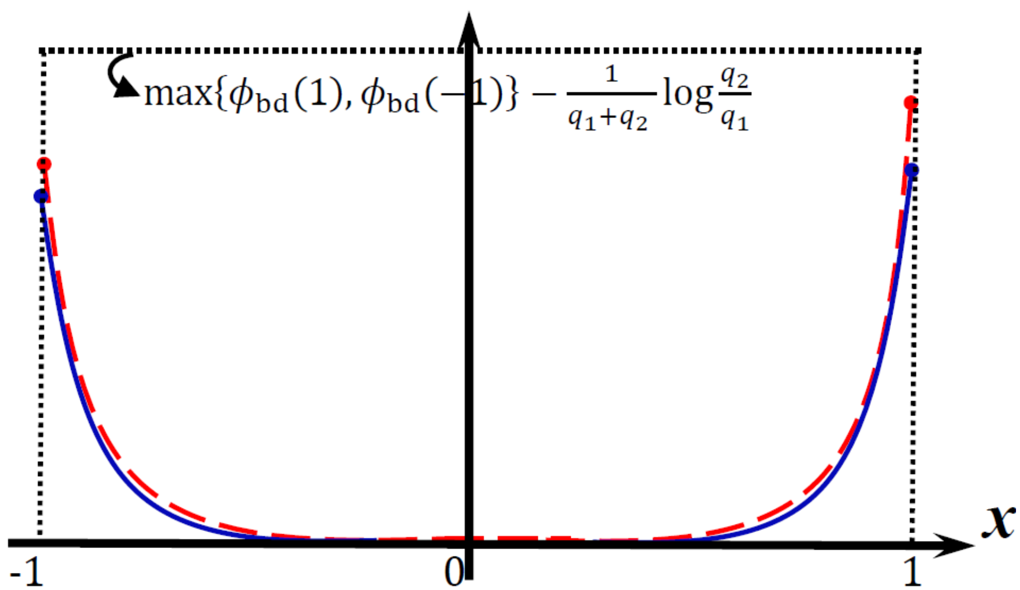
The Main Results (continued)

(i) If $\frac{1}{q_1+q_2}\log\frac{q_2}{q_1} < \min\{\phi_{\rm bd}(1), \phi_{\rm bd}(-1)\}$, *then both* ϕ *and* w *are* ***convex*** *on* $(-1,1)$, *and*

$$0 \le \phi(x) - \frac{1}{q_1+q_2}\log\frac{q_2}{q_1} \le w(x) \le M^*, \quad \text{for} \quad x \in [-1,1], \tag{1.27}$$

where $M^* = \max\{\phi_{\rm bd}(1), \phi_{\rm bd}(-1)\} - \frac{1}{q_1+q_2}\log\frac{q_2}{q_1}$.

(i) The case of $\frac{1}{q_1+q_2}\log\frac{q_2}{q_1} < \min\{\phi_{\rm bd}(1), \phi_{\rm bd}(-1)\}$.



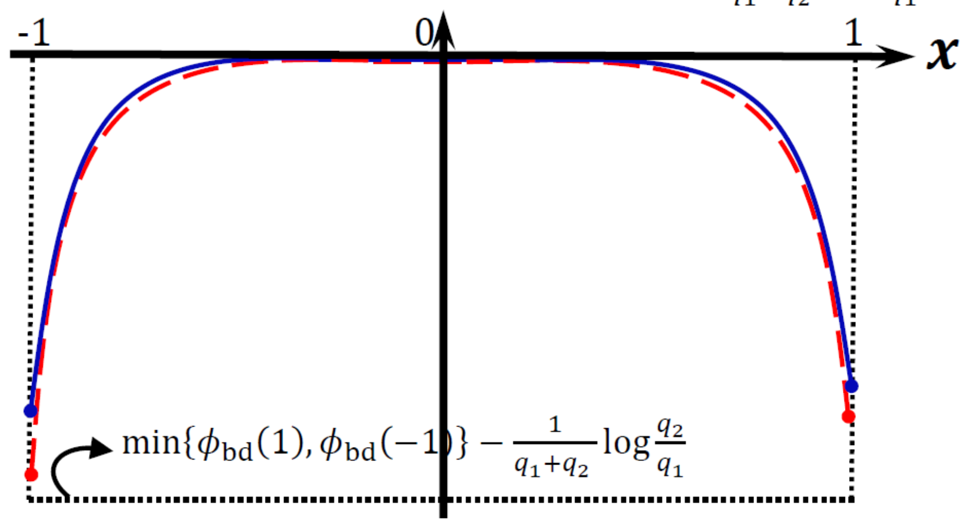
The Main Results (continued)

(ii) If $\frac{1}{q_1+q_2}\log\frac{q_2}{q_1} > \max\{\phi_{\text{bd}}(1), \phi_{\text{bd}}(-1)\}$, *then both* ϕ *and* w *are* ***concave*** *on* $(-1,1)$, *and*

$$m^* \le w(x) \le \phi(x) - \frac{1}{q_1+q_2}\log\frac{q_2}{q_1} \le 0, \quad \text{for} \quad x \in [-1,1], \tag{1.28}$$

where $m^* = \min\{\phi_{\text{bd}}(1), \phi_{\text{bd}}(-1)\} - \frac{1}{q_1+q_2}\log\frac{q_2}{q_1}$.

(ii) The case of $\max\{\phi_{\text{bd}}(1), \phi_{\text{bd}}(-1)\} < \frac{1}{q_1+q_2}\log\frac{q_2}{q_1}$.



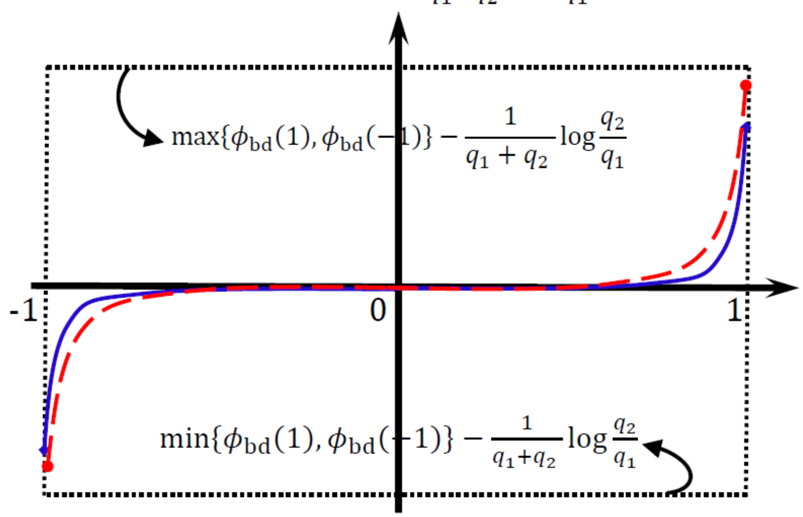
The **Main** Results (continued)

(iii) If $\phi_{\mathrm{bd}}(-1) < \phi_{\mathrm{bd}}(1)$ and $\phi_{\mathrm{bd}}(-1) \le \frac{1}{q_1+q_2}\log\frac{q_2}{q_1} \le \phi_{\mathrm{bd}}(1)$, then both ϕ and w are monotonically increasing on $(-1,1)$, and there exists $x_{0,\epsilon} \in (-1,1)$ such that

$$m^* \le w(x) \le \phi(x) - \frac{1}{q_1+q_2}\log\frac{q_2}{q_1}, \quad \text{for} \quad x \in [-1, x_{0,\epsilon}), \tag{1.29}$$

$$\phi(x) - \frac{1}{q_1+q_2}\log\frac{q_2}{q_1} \le w(x) \le M^*, \quad \text{for} \quad x \in (x_{0,\epsilon}, 1]. \tag{1.30}$$

(iii) The case of $\min\{\phi_{\mathrm{bd}}(1), \phi_{\mathrm{bd}}(-1)\} \le \frac{1}{q_1+q_2}\log\frac{q_2}{q_1} \le \max\{\phi_{\mathrm{bd}}(1), \phi_{\mathrm{bd}}(-1)\}$.



Thank you for your attention