The Poisson–Boltzmann Theory of Electrostatics

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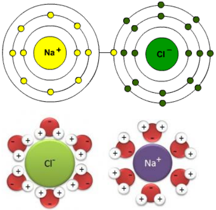
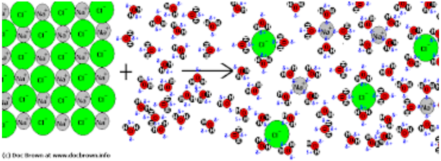
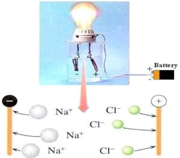
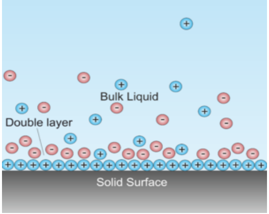
Ions and Ionic Solution



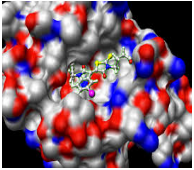


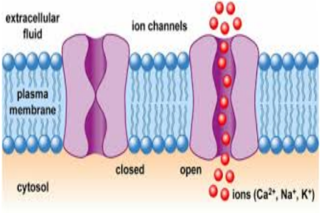


Electric Double Layer

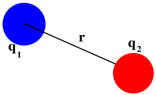


Biological Molecules





Coulomb's Law



- Potential: $U_{21} = \dfrac{1}{4\pi\varepsilon}\dfrac{q_1 q_2}{r}$
- Force: $\mathbf{F}_{21} = -\nabla U_{21}(r) = -\dfrac{1}{4\pi\varepsilon}\dfrac{q_1 q_2}{r^2}\mathbf{r}_{21}$

Poisson's Equation: $\nabla \cdot \varepsilon \nabla \psi = -\rho$

- ε : permittivity
- ψ : electrostatic potential
- ρ : charge density

The Poisson–Boltzmann (PB) Equation (PBE)

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

- Poisson's equation $\nabla \cdot \varepsilon \nabla \psi = -\left(f + \sum_{j=1}^{M} q_j c_j \right)$
- Boltzmann's distributions: $c_j = c_j^{\infty} e^{-\beta q_j \psi} \quad (j = 1, \dots, M)$

Questions: Derivation, solution formula, PDE analysis, numerical analysis, generalizations, applications, limitations, etc.

Outline

1. **The Classical PB Theory**
   and the Legendre-Transformed PB Energy
2. **Generalization: Ionic Size Effects**
3. **Generalization: Dielectric Decrement**
4. **Application of PB Theory in Molecular Solvation**
5. **Conclusions and Discussions**

1. The Classical PB Theory and the Legendre-Transformed PB Energy

PBE: $\nabla \cdot \varepsilon \nabla \psi + \sum_{j=1}^{M} q_j c_j^{\infty} e^{-\beta q_j \psi} = -f \quad \text{in } \Omega$

- $\psi : \Omega \to \mathbb{R}$: electrostatic potential
- $\varepsilon : \Omega \to \mathbb{R}$: dielectric permittivity
- $q_j = z_j e$: charge of an ion of jth species (z_j: valence, and e: elementary charge)
- c_j^{∞} : bulk concentration of jth ionic species
- β : inverse thermal energy ($\beta = 1/k_{\mathrm{B}} T$)
- $f : \Omega \to \mathbb{R}$: given, fixed charge density

The Debye–Hückel approximation (linearized PBE) with κ : the inverse Debye screening length given by $\kappa^2 = (\beta/\varepsilon) \sum_{j=1}^{M} q_j^2 c_j^{\infty}$

$$\nabla \cdot \varepsilon \nabla \psi - \varepsilon \kappa^2 \psi = -f$$

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

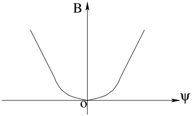
$$\nabla \cdot \varepsilon \nabla \psi - 2 c_1^{\infty} \sinh(\beta \psi) = -f$$

PBE $\quad \nabla \cdot \varepsilon \nabla \psi - B'(\psi) = -f$

$$B(\psi) = \beta^{-1} \sum_{j=1}^{M} c_j^{\infty} \left(e^{-\beta q_j \psi} - 1 \right)$$

Define $\quad \mathcal{A}[\phi] = \int_{\Omega} \left[\frac{\varepsilon}{2} |\nabla \phi|^2 - f\phi + B(\phi) \right] dV$

$$H_g^1(\Omega) = \{ u \in H^1(\Omega) : u = g \text{ on } \partial\Omega \}$$



Theorem (Li, SIMA 2009 and Li, Cheng & Zhang, SIAP 2011)

- The functional $\mathcal{A} : H_g^1(\Omega) \to \overline{\mathbb{R}}$ has a unique minimizer ψ.
- The minimizer is the unique solution to the PBE.

Proof. *Step 1.* Existence and uniqueness by the direct method.
Step 2. Key: The L^∞-bound. A comparison argument.

$$\psi_\lambda(x) := \begin{cases} -\lambda & \text{if } \psi(x) < -\lambda, \\ \psi(x) & \text{if } |\psi(x)| \le \lambda, \\ \lambda & \text{if } \psi(x) > \lambda. \end{cases}$$

It follows from $\mathcal{A}[\psi] \le \mathcal{A}[\psi_\lambda]$, $|\nabla \psi_\lambda| \le |\nabla \psi|$, and the convexity of B that $|\{|\psi| > \lambda\}| = 0$ for large λ.

Step 3. Routine calculations: PBE = EL-equation for I. **Q.E.D.**

Electrostatic free-energy functional

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

$$\rho = f + \sum_{j=1}^M q_j c_j$$

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

BC: $\psi = \psi_0$ or $\partial_n \psi = 0$ on $\partial\Omega$

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

Equilibrium conditions

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

Minimum electrostatic free-energy **(Note the sign!)**

$$G_{\min} = \int_\Omega \left[-\frac{\varepsilon}{2} |\nabla \psi|^2 + f\psi - B(\psi) \right] dV$$

PBE: $\quad \nabla \cdot \varepsilon \nabla \psi - B'(\psi) = -f$

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

Theorem (Li, SIMA 2009)

- The functional G has a unique minimizer $c = (c_1, \dots, c_M)$.
- There exist $\theta_1, \theta_2 > 0$ s.t. $\theta_1 \le c_j(x) \le \theta_2$ a.e. $x \in \Omega$ for all j.
- All c_j are given by the Boltzmann distributions.
- The corresponding potential is the unique solution to the PBE.

Observe: (1) G is strictly convex;
(2) $s \mapsto s \ln s$ is bounded below and superlinear at ∞.

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

- L^1 weak compactness of a minimizing sequence;
- L^1 conververgence of convex combinations of the sequence;
- Sequential weak lower semi-continuity and Fatou's lemma;
- A lemma (cf. next slide). **Q.E.D.**

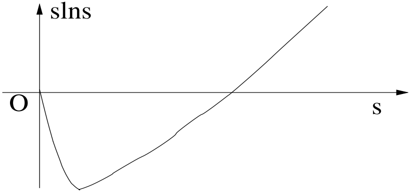
$$G[c] = \int_\Omega \left\{ \frac{1}{2}\rho\psi + \beta^{-1} \sum_{j=1}^{M} c_j \left[\ln(\Lambda^3 c_j) - 1 \right] - \sum_{j=1}^{M} \mu_j c_j \right\} dV$$

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

- $\hat{c}$ is close to c in $L^1 \cap H^{-1}$;
- $G[\hat{c}] \le G[c]$;
- there exist constants $\theta_1 > 0$ and $\theta_2 > 0$ such that

$$\theta_1 \le \hat{c}_j(x) \le \theta_2 \quad \text{a.e. } x \in \Omega \ \forall j = 1, \ldots, M.$$

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



The Legendre-Transformed PB (LTPB) Energy

The PB energy functional $I : H_g^1(\Omega) \to \overline{\mathbb{R}}$:

$$I[\phi] = \int_\Omega \left[-\frac{\varepsilon}{2} |\nabla \phi|^2 + f\phi - B(\phi) \right] dV.$$

Recall: $\exists\, !\ \hat{\phi} = \text{argmax}_{H_g^1(\Omega)} I[\cdot]$, the soln to the PBE.

The LTPB functional $J : H(\text{div}, \Omega) \to \overline{\mathbb{R}}$ (Maggs, EPL 2012):

$$J[D] = \int_\Omega \left[\frac{1}{2\varepsilon} |D|^2 + B^*(f - \nabla \cdot D) \right] dx + \int_{\partial\Omega} gD \cdot n \, dS.$$

- $H(\text{div}, \Omega) = \{ D \in L^2(\Omega, \mathbb{R}^3) : \nabla \cdot D \in L^2(\Omega) \}$: Hilbert space.

  $$\langle D_1, D_2 \rangle = \int_\Omega [D_1 \cdot D_2 + (\nabla \cdot D_1)(\nabla \cdot D_2)] \, dV.$$

  If $D \in H(\text{div}, \Omega)$ then $D \cdot n \in L^2(\partial\Omega)$, and

  $$\int_\Omega (\nabla \cdot D)\, \eta \, dV = -\int_\Omega D \cdot \nabla \eta \, dV + \int_{\partial\Omega} (D \cdot n)\, \eta \, dS \quad \forall \eta \in H^1(\Omega).$$

- B^* is the Legendre transform of B:
  $B(\xi) = \sup_{a \in \mathbb{R}} [\xi a - B(a)] = \xi s - B(s)$ with $B'(s) = \xi$.

Theorem (Ciotti & Li, SIAP 2018)

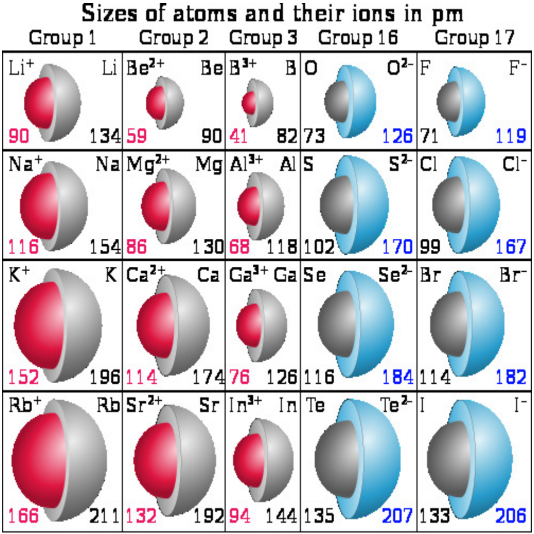
- $\hat{D} := -\varepsilon \nabla \hat{\phi} \in H(\mathrm{div}, \Omega)$ is the unique minimizer of J.
- Duality: $\max_{H_g^1(\Omega)} I[\cdot] = \min_{H(\mathrm{div},\Omega)} J[\cdot]$.

Proof. $I[\phi] \le J[D] \ \forall (\phi, D)$ and $I[\hat{\phi}] = J[\hat{D}]$. **Q.E.D.**

$$
\begin{aligned}
I[\phi] &= \int_\Omega \left[-\frac{\varepsilon}{2} |\nabla \phi|^2 + f\phi - B(\phi) \right] dV \\
&\le \int_\Omega \left[-\frac{\varepsilon}{2} |\nabla \phi|^2 + f\phi - B(\phi) + \frac{1}{2\varepsilon} |D + \varepsilon \nabla \phi|^2 \right] dx \\
&= \int_\Omega \left[\frac{1}{2\varepsilon} |D|^2 + f\phi - B(\phi) + D \cdot \nabla \phi \right] dx \\
&= \int_\Omega \left[\frac{1}{2\varepsilon} |D|^2 + (f - \nabla \cdot D)\phi - B(\phi) \right] dV + \int_{\partial\Omega} g D \cdot n \, dS \\
&\le \int_\Omega \left[\frac{1}{2\varepsilon} |D|^2 + B^*(f - \nabla \cdot D) \right] dV + \int_{\partial\Omega} g D \cdot n \, dS \\
&= J[D] \quad \forall \phi \in H_g^1(\Omega) \ \forall D \in H(\mathrm{div}, \Omega).
\end{aligned}
$$

2. Generalization: Ionic Size Effects

Ions can have different sizes: Sodium: 3.34 Å, Chloride: 2.32 Å.



A generalized electrostatic free-energy functional

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

$$\rho = f + \sum_{j=1}^{M} q_j c_j$$

$$\nabla \cdot \varepsilon \nabla \psi = -\rho \quad (+\text{ BC, e.g., } \psi = 0 \text{ on } \partial\Omega)$$

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

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

Bikerman, Philos. Mag. 1942

Eigen & Wicke, J. Phys. Chem. 1954

Kralj-Iglic & Iglic, J. Phys. (II) 1996

Borukhov, Andelman, & Orland, Phys. Rev. Letters 1997

Li, Nonlinearity 2009

Theorem (Li, Nonlinearity 2009) The functional G has a unique minimizer $(c_1, \ldots, c_M)$, characterized by the following conditions:

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

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

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

$$\left(\frac{a_j}{a_0}\right)^3 \ln\left(a_0^3 c_0\right) - \ln\left(a_j^3 c_j\right) = \beta\left(q_j \psi - \mu_j\right) \quad \forall j = 1, \ldots, M,$$

  where ψ is the electrostatic potential corresponding to $(c_1, \ldots, c_M)$.

Proof. Similar to the case without the size effect with more delicate constructions of comparison concentrations. **Q.E.D.**

$$\left(\frac{a_j}{a_0}\right)^3 \ln\left(a_0^3 c_0\right) - \ln\left(a_j^3 c_j\right) = \beta\left(q_j\psi - \mu_j\right) \quad (j = 1, \ldots, M)$$

$$\sum\nolimits_{j=0}^{M} a_j^3 c_j = 1 \qquad \text{in } \Omega$$

A special case: uniform size. $a_0 = a_1 = \cdots = a_M = a$.
The generalized Boltzmann distributions and PBE

$$c_j = \frac{c_j^\infty e^{-\beta q_j \psi}}{1 + a^3 \sum_{i=1}^{M} c_i^\infty \left(e^{-\beta q_i \psi} - 1\right)}, \quad c_j^\infty = \frac{a^{-3} e^{\beta \mu_j}}{1 + \sum_{j=1}^{M} e^{\beta \mu_j}}$$

$$\nabla \cdot \varepsilon \nabla \psi + \frac{\sum_{j=1}^{M} q_j c_j^\infty e^{-\beta q_j \psi}}{1 + a^3 \sum_{j=1}^{M} c_j^\infty \left(e^{-\beta q_j \psi} - 1\right)} = -f$$

A variational principle: ψ minimizes the *convex* functional

$$K[\phi] = \int_\Omega \left[\frac{\varepsilon}{2}|\nabla\phi|^2 - f\phi + \beta^{-1} a^{-3} \ln\left(1 + \sum\nolimits_{j=1}^{M} a^3 c_j^\infty e^{-\beta q_j \phi}\right)\right] dV$$

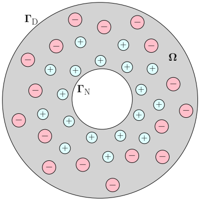
$$\left(\frac{a_j}{a_0}\right)^3 \ln\left(a_0^3 c_0\right) - \ln\left(a_j^3 c_j\right) = \beta\left(q_j\psi - \mu_j\right) \quad (j = 1, \dots, M)$$

$$\sum_{j=0}^{M} a_j^3 c_j = 1$$

The general case: nonuniform ionic sizes. Explicit formulas of $c_j = c_j(\psi)$ are unavailable!

- For any $\psi \in \mathbb{R}$, there exists a unique solution $(c_1, \dots, c_M)$ with all $c_j = c_j(\psi) > 0$ $(j = 1, \dots, M)$. Implicit Boltzmann distributions: $c_j(x) = c_j(\psi(x))$ for $x \in \Omega$ and $j = 1, \dots, M$.
- Define $B(\phi) = -\sum_{j=1}^{M} q_j \int_0^{\phi} c_j(\xi)\, d\xi$ and assume the charge neutrality $\sum_{j=1}^{M} q_j c_j(0) = 0$. Then, the function B is smooth, strictly convex, minimized at 0, and $B(\pm\infty) = \infty$.
- An implicit PBE: $\quad \nabla \cdot \varepsilon \nabla \psi - B'(\psi) = -f.$

How to find ψ and $c_1, \dots, c_M$?



Constrained Optimization

(Zhou, Wang & Li, PRE 2011)

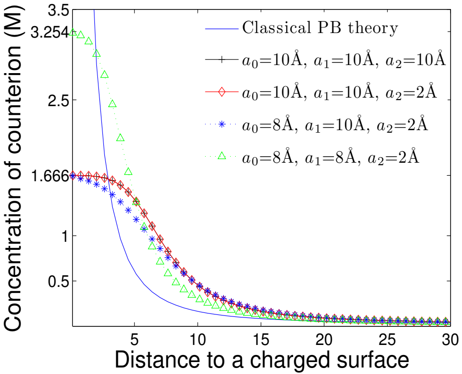
Minimize the free-energy functional

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

subject to the constraints

$$\begin{cases} \text{Conservation of mass} & \int_\Omega c_j \, dV = N_j, \quad j = 1, \dots, M \\ \text{Charge neutrality} & \sum_{j=1}^{M} N_j q_j + \int_\Omega f \, dV + \int_\Gamma \sigma \, dS = 0 \\ \text{Poisson's Equation} & -\nabla \cdot \varepsilon \nabla \psi = f + \sum_{j=1}^{M} q_j c_j \quad \text{in } \Omega \\ \text{Boundary condition} & -\varepsilon \partial_n \psi = \sigma \quad \text{on } \Gamma \end{cases}$$

Example 1. $M = 2,\ z_1 = -1,\ z_2 = 1,\ N_1 = 2Z,\ N_2 = Z = 60,$
$R = 14$ Å, $L = 160$ Å, $256 \times 256 \times 256$ grid points.

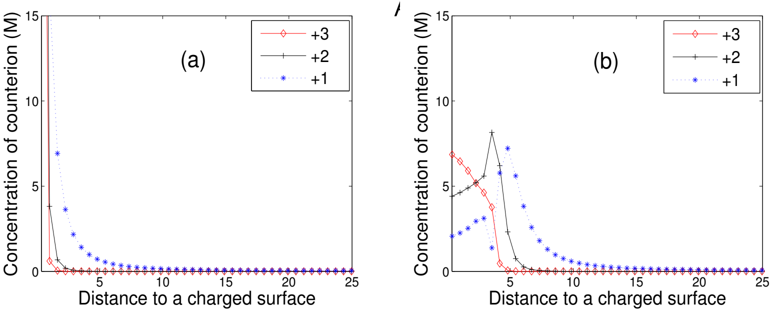


Concentration of counterions. Note that $1/a_1^3 = 1.666$ M when $a_1 = 10$ Å and $1/a_1^3 = 3.254$ M when $a_1 = 8$ Å.

Observation: Maximal packing!

Example 2. $M = 3,\ z_1 = +3,\ z_2 = +2,\ z_3 = +1,\ Z = -200,$

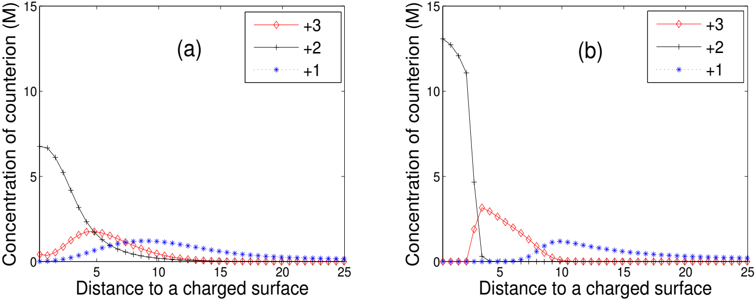
$$z_1 N_1 = z_2 N_2 = z_3 N_3 = -Z/3,$$



(a) The classical PB solution: no size effect.

(b) The size effect with $a_0 = a_1 = a_2 = a_3 = 5\,\text{Å}$.

Observation: nonmonotonocity and stratification!



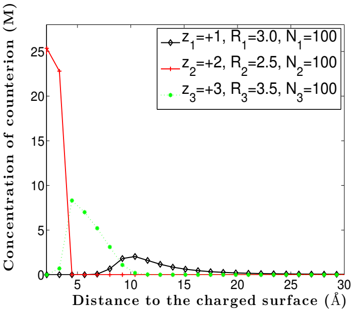
Denote $\alpha_i = z_i / a_i^3$ $(i = 1, \ldots, M)$, the valence-to-volume ratios.

(a) $a_0 = 2\,\text{Å}$, $a_{+3} = 7\,\text{Å}$, $a_{+2} = 6\,\text{Å}$, $a_{+1} = 5\,\text{Å}$.
$\alpha_{+2} : \alpha_{+3} : \alpha_{+1} = 1.163 : 1.088 : 1.$

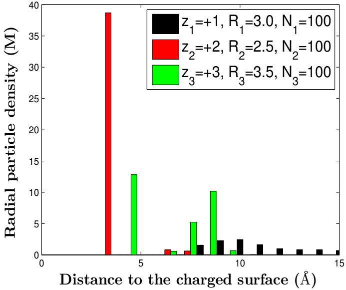
(b) $a_0 = 2\,\text{Å}$, $a_{+3} = 7\,\text{Å}$, $a_{+2} = 5\,\text{Å}$, $a_{+1} = 6\,\text{Å}$.
$\alpha_{+2} : \alpha_{+3} : \alpha_{+1} = 3.478 : 1.891 : 1.$

Observation: The valence-to-volume ratios are key parameters!

Comparison between the generalized PB theory for ionic size effect and Monte Carlo simulations



Size-modified PB theory
(Zhou, Wang & Li, PRE 2011)



Monte Carlo simulations
(Wen, Zhou, Xu, & Li, PRE 2012)

Assume valence-to-volume ratios satisfy

$$\frac{z_{-l}}{a_{-l}^3} < \cdots < \frac{z_{-1}}{a_{-1}^3} < \frac{z_0}{a_0^3} = 0 < \frac{z_1}{a_1^3} < \cdots < \frac{z_m}{a_m^3}.$$

Theorem (Li, Liu, Xu, & Zhou. Nonlinearity 2013).

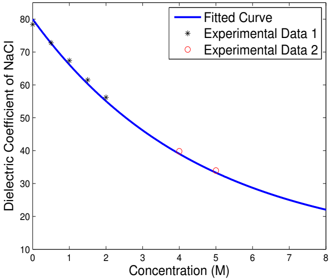
- *Monotonicity:* $c_{-l}'(\phi) > 0$ and $c_m'(\phi) < 0$ for all $\phi \in \mathbb{R}$.
- *Asymptotic behavior:*

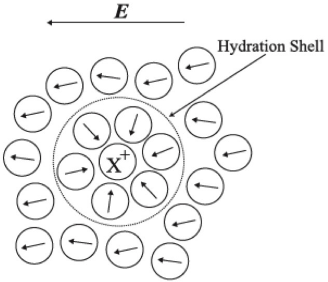
$$a_{-l}^3 c_{-l}(\phi) \to 1 \quad \text{and} \quad c_i(\phi) \to 0 \quad (i \neq -l) \quad \text{as } \phi \to \infty,$$
$$a_m^3 c_m(\phi) \to 1 \quad \text{and} \quad c_i(\phi) \to 0 \quad (i \neq m) \quad \text{as } \phi \to -\infty.$$

In particular, $\sum_i q_i c_i(\phi)$ grows linearly at $\phi = \pm\infty$.

3. Generalization: Dielectric Decrement

Experiment and heuristics





$$\varepsilon(\bar{c}) = 70e^{-0.22\bar{c}} + 10.$$

Hasted, Riston, & Collie, JCP 1948.

Lyashchenko & Zasetsky, J. Molecular Liquids 1998.

Ben-Yaakov, Andelman, & Podgornik, JCP 2011.

Electrostatic free-energy functional

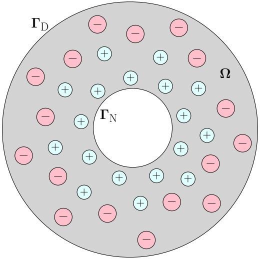
(Ben-Yaakov, Andelman, & Podgornik, JCP 2011)

$$F[c] = \int_\Omega \frac{1}{2}\rho\psi\, dV + \int_{\Gamma_{\rm N}} \frac{1}{2}\sigma\psi\, dS + \beta^{-1}\sum_{i=1}^M \int_\Omega c_i \left[\log(\Lambda^3 c_i) - 1\right] dV - \sum_{i=1}^M \mu_i \int_\Omega c_i\, dV.$$

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

$$\begin{cases} \nabla\cdot\varepsilon(\bar{c})\nabla\psi = -\rho & \text{in } \Omega \\ \varepsilon(\bar{c})\dfrac{\partial\psi}{\partial n} = \sigma & \text{on } \Gamma_{\rm N} \\ \psi = 0 & \text{on } \Gamma_{\rm D} \end{cases}$$

$$\bar{c} = \sum_{i=1}^M c_i$$



First variations

$$\delta F[c][d] = \lim_{t \to 0} \frac{F[c+td] - F[c]}{t}$$

Theorem (Li, Wen & Zhou, CMS 2016) Let $c = (c_1, \ldots, c_M) \in L^2(\Omega, \mathbb{R}^M)$. Assume $\exists \delta_1, \delta_2 > 0$ s.t. $\delta_1 \le c_i \le \delta_2$ a.e. Ω for all i. Let $d = (d_1, \ldots, d_M) \in L^\infty(\Omega, \mathbb{R}^M)$. Then

$$\delta F[c][d] = \sum_{i=1}^{M} \int_\Omega d_i \, \delta_i F[c] \, dV,$$

where $\delta_i F[c] : \Omega \to \mathbb{R}$ is given by

$$\delta_i F[c] = q_i \psi(c) - \frac{1}{2} \varepsilon'(\bar{c}) |\nabla \psi(c)|^2 + \beta^{-1} \log \left(\Lambda^3 c_i \right) - \mu_i.$$

Generalized Boltzmann distributions

$$c_i = c_i^\infty \exp \left\{ -\beta \left[q_i \psi(c) - \frac{1}{2} \varepsilon'(\bar{c}) |\nabla \psi(c)|^2 \right] \right\}$$

Second variations

$$\delta^2 F[c][a,b] = \lim_{t\to 0} \frac{\delta F[c+ta][b] - \delta F[c][b]}{t}$$

Define $\Psi(c,a)$:

$$\begin{cases} -\nabla \cdot \varepsilon(\bar{c})\nabla\Psi(c,a) = \sum_{i=1}^{M} a_i \left[q_i + \nabla\cdot\varepsilon'(\bar{c})\nabla\psi(c)\right] & \text{in } \Omega \\ \varepsilon(\bar{c})\dfrac{\partial\Psi(c,a)}{\partial n} = -\dfrac{\varepsilon'(\bar{c})}{\varepsilon(\bar{c})}\sigma & \text{on } \Gamma_{\mathrm{N}} \\ \Psi(c,a) = 0 & \text{on } \Gamma_{\mathrm{D}} \end{cases}$$

Theorem (Li, Wen & Zhou, CMS 2016) Same assumptions for $c = (c_1, \dots, c_M)$, and $a, b \in L^\infty(\Omega, \mathbb{R}^M)$:

$$\delta^2 F[c][a,b] = \int_\Omega \Big[\varepsilon(\bar{c})\nabla\Psi(c,b)\cdot\nabla\Psi(c,a) \\ - (1/2)\bar{a}\bar{b}\varepsilon''(\bar{c})|\nabla\psi(c)|^2 + (1/\beta)\textstyle\sum_{i=1}^M a_i b_i / c_i\Big]\, dV.$$

Nonconvexity of the free-energy functional

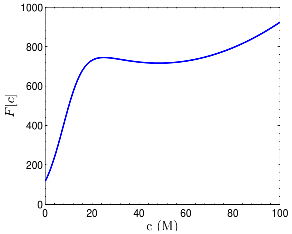
Let σ, β, λ, $\mu \in \mathbb{R}$ with $\beta > 0$, $\lambda > 0$. Consider

$$F[c] = \int_0^1 \frac{1}{2} c\psi dx + \frac{1}{2}\sigma\psi(0) + \int_0^1 \left[\beta^{-1} c \log(\lambda c) - \mu c\right] dx.$$

$$\begin{cases} (\varepsilon(c(x))\psi'(x))' = -c(x) & \text{for } x \in (0,1) \\ \psi(1) = 0, & \\ \varepsilon(c(0))\psi'(0) = -\sigma & \end{cases}$$

$$\varepsilon(c) = 70e^{-0.22c} + 10$$

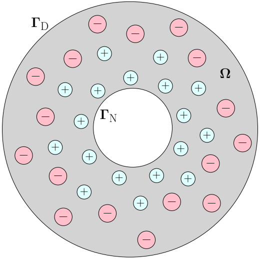
For constant $c > 0$: $F[c] = \frac{c^2+3c\sigma+3\sigma^2}{6\varepsilon(c)} + \beta^{-1} c \log\left(\frac{c}{c^\infty}\right)$.



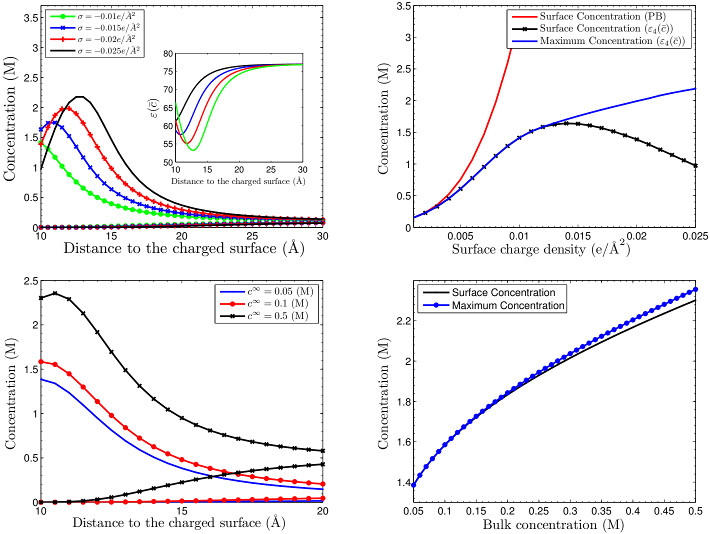
Parameters
$\sigma = -0.04$
$\beta^{-1} = 1$
$c^\infty = \lambda^{-1} e^{\beta\mu} = 0.1$
Two local minima at
$c = 0$ and $c \approx 48.4$.

Numerical Study of a Model Problem

Parameters
$R_{\mathrm{N}} = 10$ Å
$R_{\mathrm{D}} = 60$ Å
$\sigma \approx -0.005$ to -0.025 e/Å^2
$k_{\mathrm{B}}T$ is the units of energy

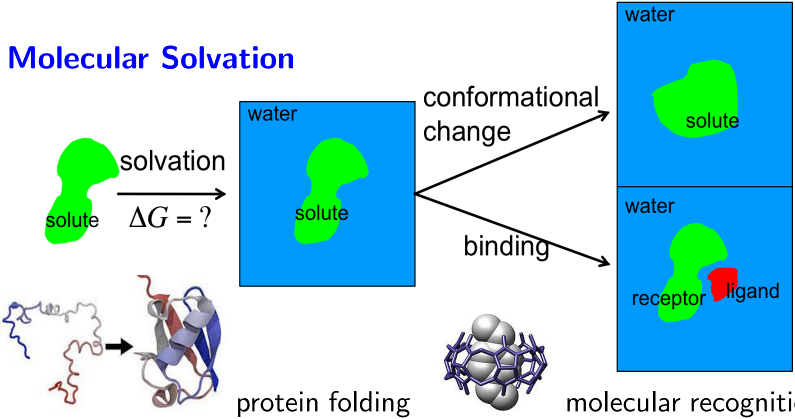


System I: $Z_1 = 1$, $Z_2 = -1$, $c_1^\infty = c_2^\infty = 0.1$ M.
System II: $Z_1 = 2$, $Z_2 = 1$, $Z_3 = -2$, $c_1^\infty = c_2^\infty = 0.1$ M, $c_3^\infty = 0.15$ M.


$\sigma = -0.01e/\AA^2$
$\sigma = -0.015e/\AA^2$
$\sigma = -0.02e/\AA^2$
$\sigma = -0.025e/\AA^2$
Concentration (M)
Distance to the charged surface (Å)
$\varepsilon(\bar{c})$
Distance to the charged surface (Å)
Surface Concentration (PB)
Surface Concentration ($\varepsilon_4(\bar{c})$)
Maximum Concentration ($\varepsilon_4(\bar{c})$)
Concentration (M)
Surface charge density (e/Å^2)
$c^\infty = 0.05$ (M)
$c^\infty = 0.1$ (M)
$c^\infty = 0.5$ (M)
Concentration (M)
Distance to the charged surface (Å)
Surface Concentration
Maximum Concentration
Concentration (M)
Bulk concentration (M)

4. Application of the PB Theory in Molecular Solvation

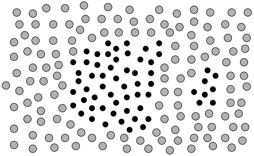
Molecular Solvation



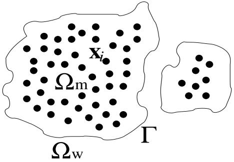
protein folding

molecular recognition

explicit solvent

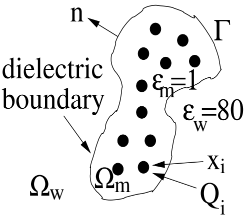


implicit solvent



Variational Implicit-Solvent Model (VISM)

(Dzubiella, Swanson & McCammon, PRL & JCP 2006)



Solvation free-energy functional

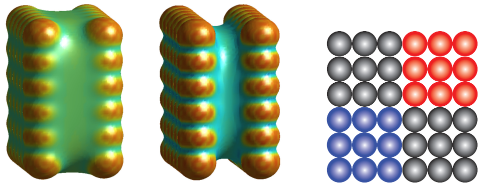
$$G_{\text{total}}[\Gamma] = P\,\text{Vol}\,(\Omega_{\text{m}}) + \gamma_0 \int_\Gamma (1 - 2\tau H)\, dS + \rho_{\text{w}} \int_{\Omega_{\text{w}}} U_{\text{vdW}}\, dV + G_{\text{ele}}[\Gamma]$$

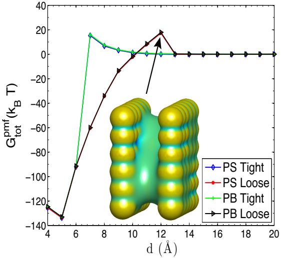
$$U_{\text{vdW}}(x) = \sum_{i=1}^{N} U_{\text{LJ}}^{(i)}(|x - x_i|)$$

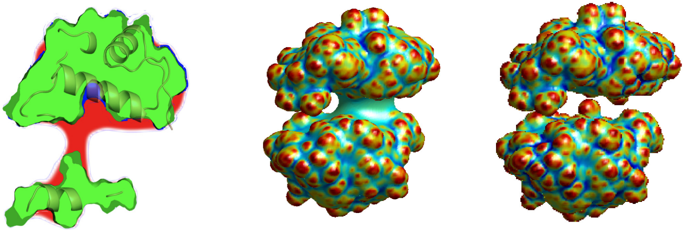
The level-set method: $V_n = -\delta_\Gamma G_{\text{total}}[\Gamma]$

$$\delta_\Gamma G_{\text{total}}[\Gamma] = P + 2\gamma_0 (H - \tau K) - \rho_{\text{w}} U_{\text{vdW}} + \delta_\Gamma G_{\text{ele}}[\Gamma]$$

Level-Set Computation





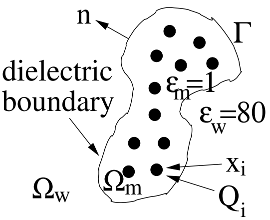


Cheng, Z. Wang, S. Zhou, Z. Zhang, S. Liu, Ricci, Che, Dzubiella, Li, McCammon, et al. JCP 2007, 2009, 2016, & 2021; JCTC 2009, 2012–2014, & 2021; JPCB 2014 & 2018; PRL 2009; J. Comput. Phys. 2010, 2018, & 2023; JCC 2015; PNAS 2019.

Dielectric Boundary Force (DBF)

Dielectric coefficient

$$\varepsilon_\Gamma = \begin{cases} \varepsilon_{\rm m} & \text{in } \Omega_{\rm m} \\ \varepsilon_{\rm w} & \text{in } \Omega_{\rm w} \end{cases}$$



Typical: $\varepsilon_{\rm m} = \varepsilon_0$ and $\varepsilon_{\rm w} = 80\varepsilon_0$.

Write $G = G_{\rm ele}$.

PBE $$\nabla \cdot \varepsilon_\Gamma \nabla \psi - \chi_{\rm w} B'(\psi) = -f$$

PB free energy $$G[\Gamma] = \int_\Omega \left[-\frac{\varepsilon_\Gamma}{2} |\nabla \psi|^2 + f\psi - \chi_{\rm w} B(\psi) \right] dV$$

Define DBF: $\Gamma \Longrightarrow \Gamma_t \Longrightarrow \psi_{\Gamma_t} \Longrightarrow G[\Gamma_t]$

$$\Longrightarrow \delta_\Gamma G[\Gamma] := \left.\frac{d}{dt}\right|_{t=0} G[\Gamma_t] \Longrightarrow F_n := -\delta_\Gamma G[\Gamma]$$

Let $V \in C_c^\infty(\mathbb{R}^3, \mathbb{R}^3)$. Define $x : [0, \infty) \times \mathbb{R}^3 \to \mathbb{R}^3$ by

$$\begin{cases} \dot{x} = V(x) & \text{for } t > 0, \\ x(0, X) = X. \end{cases}$$

Then $T_t(X) := x(t, X) \approx X + tV(X)$ if $|t| \ll 1$. Define

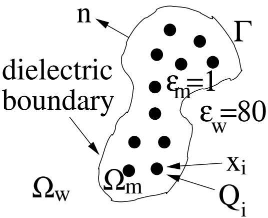
$$\delta_{\Gamma,V} G[\Gamma] = \lim_{t \to 0} \frac{G[\Gamma_t] - G[\Gamma]}{t} = \int_\Gamma w(X)[V(X) \cdot n(X)]\, dS_X$$

for some $w : \Gamma \to \mathbb{R}$ by the Structure Theorem.

Shape derivative $\quad \delta_\Gamma G[\Gamma](X) = w(X) \qquad \forall X \in \Gamma$

Theorem (Li, Cheng & Zhang, SIAP 2011; Li, Zhang & Zhou, J. Nonlinear Sci. 2021) Let ψ be the unique solution to the boundary-value problem of PBE. Then

$$\delta_\Gamma G[\Gamma] = \frac{1}{2}\left(\frac{1}{\varepsilon_m} - \frac{1}{\varepsilon_w}\right)|\varepsilon_\Gamma \nabla\psi \cdot n|^2 + \frac{1}{2}(\varepsilon_w - \varepsilon_m)\,|(I - n\otimes n)\nabla\psi|^2 + B(\psi).$$



Corollary. If $\varepsilon_w > \varepsilon_m$, then $-\delta_\Gamma G[\Gamma] < 0$.

B. Chu, Molecular Forces Based on the Baker Lectures of Peter J. W. Debye, John Wiley & Sons, 1967:

"Under the combined influence of electric field generated by solute charges and their polarization in the surrounding medium which is electrostatic neutral, an additional potential energy emerges and drives the surrounding molecules to the solutes."

Proof of Theorem. Let $V \in C_c^\infty(\mathbb{R}^3, \mathbb{R}^3)$ be local, $\Gamma_0 = \Gamma$, and

$$G[\Gamma_t] = G[\Gamma_t, \psi_t] = \max_{\phi \in H_g^1(\Omega)} G[\Gamma_t, \phi].$$

Note $\psi_0 = \psi$. Define $z(t, \phi) = G[\Gamma_t, \phi \circ T_t^{-1}]$. We have

$$G[\Gamma_t] = \max_{\phi \in H_g^1(\Omega)} z(t, \phi).$$

Step 1. Easy to verify that

$$\frac{z(t, \psi_0) - z(0, \psi_0)}{t} \le \frac{G[\Gamma_t] - G[\Gamma]}{t} \le \frac{z(t, \psi_t \circ T_t) - z(0, \psi_t \circ T_t)}{t}.$$

Hence

$$\partial_t z(\xi, \psi_0) \le \frac{G[\Gamma_t] - G[\Gamma]}{t} \le \partial_t z(\eta, \psi_t \circ T_t), \quad \xi, \eta \in [0, t].$$

Step 2. Direct calculations lead to

$$\partial_t z(t,\phi) = \int_\Omega \Big[-\frac{\varepsilon_\Gamma}{2} A'(t)\nabla\phi\cdot\nabla\phi + ((\nabla\cdot(fV))\circ T_t)\phi J_t - \chi_w B(\phi)((\nabla\cdot V)\circ T_t)J_t \Big] dx,$$

where

$$J_t = \det \nabla T_t \quad \text{and} \quad A(t) = J_t(\nabla T_t)^{-1}(\nabla T_t)^{-T}.$$

Replacing t by η and ϕ by $\psi_t \circ T_t$, respectively, we obtain

$$\lim_{t\to 0} \partial_t z(\eta, \psi_t\circ T_t) = \partial_t z(0,\psi_0)$$

and hence

$$\delta_{\Gamma,V} G[\Gamma] = \partial_t z(0,\psi_0),$$

provided that

$$\lim_{t\to 0} \|\psi_t \circ T_t - \psi_0\|_{H^1(\Omega)} = 0.$$

Step 3. The limit

$$\lim_{t \to 0} \|\psi_t \circ T_t - \psi_0\|_{H^1(\Omega)} = 0$$

follows from:

- Weak form of the Euler–Lagrange equation for the maximization of $z(t, \cdot)$ by $\psi_t \circ T_t$ for $t > 0$ and by ψ_0 for $t = 0$, respectively;
- Subtract one from the other;
- Use the properties of $T_t(X)$ and the convexity of B.

Step 4. We now have

$$\delta_{\Gamma,V} G[\Gamma] = \partial_t z(0, \psi_0).$$

Direct calculations, using the properties of ψ_0, complete the proof.
Q.E.D.

5. Conclusions and Discussions

Summary

- PBE and the electrostatic free energy of ionic concentrations: existence, uniqueness, and bounds.
- A generalized PB theory for ionic size effect. Nonuniform sizes: implicit Boltzmann distributions. Constrained optimization! Stratification. Valence-to-volume ratios.
- A generalized PB theory for dielectric decrement. Generalized Boltzmann distributions. Nonconvexity.
- Dielectric boundary force (DBF): an explicit formula. DBF points from the high to low dielectric region.

Discussions

- Derivation of the PB theory from statistical mechanics. Related work: H.-X. Zhou, JCP 1994.
- Linear vs. nonlinear PB. Linear theory works better for lower ionic concentrations but may not capture the entropic effect.

PBE: $\nabla \cdot \varepsilon \nabla \phi = -\rho = -\left(\sum_{j=1}^{M} c_j + f \right)$.

Boltzmann distributions: $c_j = c_j^\infty e^{-\beta q_j \phi}$ $(c_j^\infty = \Lambda^{-3} e^{\beta \mu_j})$.

Set $B(\phi) = \beta^{-1} \sum_{j=1}^{M} c_j^\infty \left(e^{-\beta q_j \phi} - 1 \right)$ and $B'(\phi) = -\sum_{j=1}^{M} q_j c_j$.

Electrostatic free energy:

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

$$= \int_\Omega \left[\frac{1}{2} f \phi + \frac{1}{2} \phi B'(\phi) - B(\phi) \right] dV$$

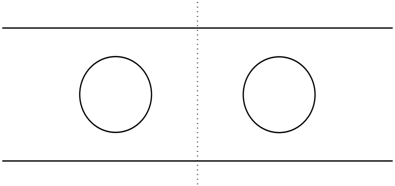
For the linear PB, $B(\phi) = (\kappa^2/2)\phi^2$. So $(1/2)\phi B'(\phi) - B(\phi) = 0$ identically, and no ionic entropy (H.X. Zhou, JCP 1994).

- Charge asymmetry.
  Poisson's equation: $-\nabla \cdot \varepsilon \nabla \phi = \rho$.
  The electrostatic energy: $E = \int \frac{1}{2} \rho \phi \, dV$.
  Same if $\rho \to -\rho$.
  Born's model of the free-energy of the hydration of a single ion of radius R and charge Q:

$$\Delta G = -\frac{Q^2}{8\pi\varepsilon_0 R} \left(\frac{1}{\varepsilon_{\mathrm{m}}} - \frac{1}{\varepsilon_{\mathrm{w}}} \right).$$

  Same for $\pm Q$.
- Limitations of the PB theory. No ion-ion correlations. Efficient, PB-like continuum models including correlations?

PB theory does not predict the like-charge attraction.



$$\Delta\psi = B'(\psi) \text{ inside walls/outside balls}$$
$$\psi = \text{const. on the walls}$$
$$\psi = \text{const. on bdry of balls}$$

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

$\mathbf{F} \cdot$ the unit horizontal vector toward the center < 0.
(Neu, PRL 1999. Sader & Chan, J. Coll. Interface Sci. 1999)

THANK YOU!