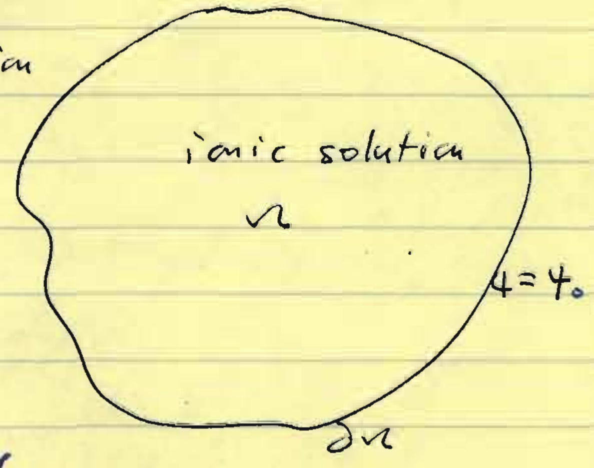
The Poisson-Boltzmann Equation

2. Variational approach. Mathematical theory. size effect, etc.

<u>Notation</u>

$c_i = c_i(x)$ ... local ionic concentration of the ith species at x.



$\rho_f : \Omega \to \mathbb{R}$. fixed charge density. [Known]

[This can be some surface charge density, and/or charges from proteins — like point charges].

$\varepsilon(x)$ ... "dielectric coefficient."

$\varepsilon(x) = \varepsilon_r(x)\,\varepsilon_0$ $\quad$ $\varepsilon_r(x)$ ... relative permittivity (dielectric coefficient)

ε_0 ... vaccum permittivity

[Known]

$\psi = \psi(x)$ ... electrostatic potential

$\rho = \rho(x)$ ... total charge density

z_i ... valence of ions of ith species

e ... elementary charge

$q_i = z_i e$. $\quad i = 1, \cdots, M$ $\quad$ [Known]

$\psi_0 = \psi_0(x)$: boundary data [Known]

$\beta = (k_B T)^{-1}$

μ_j ... chemical potential

Λ ... de Broglie length

A mean-field electrostatic free-energy functional

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

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

$$\begin{cases} \nabla\cdot\varepsilon(x)\nabla\psi = -\rho & \text{in } \Omega \\ \psi = \psi_0 & \text{on } \partial\Omega. \end{cases}$$

$\int_\Omega \frac{1}{2}\rho\psi\, dV$ .... the potential energy.

$-\beta^{-1}\int_\Omega \ldots$ ... the entropy

Given $c = (c_1, \ldots, c_M)$:

$\longrightarrow \rho = \rho_f + \sum_j q_j c_j$

$\longrightarrow$ Poisson's eq: ψ

$\longrightarrow F[c]$.

We calculate: $\delta F[c]$ and $\delta^2 F[c]$.

Assume for simplicity: $\psi_0(x) = 0$ on $\partial\Omega$

Denote by $\psi = \mathcal{L}(\rho)$ the unique solution to

$$\begin{cases} \nabla\cdot\varepsilon(x)\nabla\psi = -\rho & \text{in } \Omega \\ \psi = 0 & \text{on } \partial\Omega \end{cases}$$

⊙ $\mathcal{L}$ is like the inverse of $-\Delta$ w.r.t. to the B.C. $\psi = 0$ on $\partial\Omega$

⊙ $\mathcal{L}$ is linear! ⊙ $\mathcal{L}$ is symmetric

$$F[c] = \int_\Omega \left\{ \frac{1}{2}\left(\rho_f + \sum_j q_j c_j\right)\mathcal{L}\left(\rho_f + \sum_j q_j c_j\right) + \beta^{-1}\sum_{j=1}^{M} c_j\left[\log(\Lambda^3 c_j) - 1\right] - \sum_{j=1}^{M}\mu_j c_j \right\} dV$$

$$= \int_\Omega \Big\{ \frac{1}{2} \rho_f \mathcal{L}(\rho_f) + \frac{1}{2}\Big(\sum_j q_j c_j\Big)\mathcal{L}(\rho_f) + \frac{1}{2}\rho_f \mathcal{L}\Big(\sum_j q_j c_j\Big)$$

$$+ \frac{1}{2}\Big(\sum_j q_j c_j\Big)\mathcal{L}\Big(\sum_i q_i c_i\Big)$$

$$\boxed{\int_\Omega \mathcal{L}(\rho_f)\Big(\sum_j q_j c_j\Big) dV = \int_\Omega \rho_f \mathcal{L}\Big(\sum_j q_j c_j\Big) dV} \qquad + \beta^{-1} \sum_j c_j \left[\log(\Lambda^3 c_j) - 1\right] - \sum_{j=1}^{M} \mu_j c_j \Big\} dV$$

$$= \int_\Omega \Big\{ \frac{1}{2}\Big(\sum_j q_j c_j\Big)\mathcal{L}\Big(\sum_i q_i c_i\Big) + \Big(\sum_j q_j c_j\Big)\mathcal{L}(\rho_f)$$

$$+ \beta^{-1} \sum_j c_j \left[\log(\Lambda^3 c_j) - 1\right] - \sum_{j=1}^{M} \mu_j c_j \Big\} dV$$

$$+ \underbrace{\int_\Omega \frac{1}{2} \rho_f \mathcal{L}(\rho_f) \, dV}_{\text{a constant w.r.t. } c.}$$

Denote it by E_0.

$$F[c] = \int_\Omega \Big\{ \frac{1}{2}\Big(\sum_j q_j c_j\Big)\mathcal{L}\Big(\sum_i q_i c_i\Big) + \Big(\sum_j q_j c_j\Big)\mathcal{L}(\rho_f)$$

$$+ \beta^{-1} \sum_j c_j \left[\log(\Lambda^3 c_j) - 1\right] - \sum_{j=1}^{M} \mu_j c_j \Big\} dV + E_0.$$

Equilibrium conditions.

Fix i $(1 \le i \le M)$. Let $e_i = (0, \dots, 0, \overset{i\text{th component}}{1}, 0, \dots, 0) \in \mathbb{R}^M$

$$\delta F[c][d] = \frac{d}{dt}\Big|_{t=0} F[c + t d]$$

$$= \frac{d}{dt}\Big|_{t=0} \int_\Omega \Big\{ \frac{1}{2} \sum_j \left(q_j c_j + t q_j d_j\right) \mathcal{L}\Big(\sum_i \left(q_i c_i + t q_i d_i\right)\Big)$$

$$+ \sum_j \left(q_j c_j + t q_j d_j\right) \mathcal{L}(\rho_f)$$

$$+ \beta^{-1} \sum_j \left[(c_j + t d_j) \log(\Lambda^3 c_j + \Lambda^3 t d_j) - 1 \right]$$

$$- \sum_j \left(\mu_j c_j + t \mu_j d_j\right) \Big\} dV$$

$$= \int_\Omega \Big\{ \frac{1}{2} \Big(\sum_j q_j d_j\Big) \mathcal{L}\Big(\sum_i q_i c_i\Big) + \frac{1}{2} \Big(\sum_j q_j c_j\Big) \mathcal{L}\Big(\sum_i q_i d_i\Big)$$

$$+ \Big(\sum_j q_j d_j\Big) \mathcal{L}(\rho_f)$$

$$+ \beta^{-1} \sum_j \Big[d_j \big(\log(\Lambda^3 c_j) \cancel{-1}\big) + c_j \frac{\Lambda^3 d_j}{\Lambda^3 c_j} \Big]$$

$$- \sum_j \mu_j d_j \Big] dV$$

Not rigorous! But fine. Will fix it later

$$= \int_\Omega \Big\{ \Big(\sum_j q_j d_j\Big) \mathcal{L}\Big(\sum_i q_i c_i\Big) + \Big(\sum_j q_j d_j\Big) \mathcal{L}(\rho_f)$$

$$+ \beta^{-1} \sum_j \Big[d_j \log(\Lambda^3 c_j) \underbrace{- d_j + d_j}_{=0} \Big] - \sum_j \mu_j d_j \Big\} dV$$

Fix k. Let $d_j(x) \equiv 0$ if $j \neq k$.

$\delta F[c][d] = 0$:

$$\int_\Omega \Big\{ q_k d_k \mathcal{L}\Big(\sum_i q_i c_i\Big) + q_k d_k \mathcal{L}(\rho_f)$$

$$+ \beta^{-1} d_k \log(\Lambda^3 c_k) - \mu_k d_k \Big\} = 0 \quad \forall d_k.$$

$$\int_\Omega d_k \{ \cdots \} dV = 0$$

$$\Longrightarrow \{ \cdots \} = 0$$

$$\boxed{q_k \mathcal{L}\Big(\sum_i q_i c_i\Big) + q_k \mathcal{L}(\rho_f) + \beta^{-1} \log(\Lambda^3 c_k) - \mu_k = 0. \quad k = 1, 2, \ldots M}$$

Let $\psi = \psi(x)$ be defined by

$$\psi = \mathcal{L}\left(\rho_f + \sum_i q_i c_i\right)$$

i.e.
$$\begin{cases} \nabla \cdot \varepsilon(x) \nabla \psi = -\left(\rho_f + \sum_i q_i c_i\right) & \text{in } \Omega \\ \psi = 0 & \text{on } \partial\Omega \end{cases}$$

ψ is the electrostatic potential corresponding to the equilibrium concentrations $c = (c_1, \cdots, c_M)$.

$$q_k \psi + \beta^{-1} \log(\Lambda^3 c_k) - \mu_k = 0$$

$$\boxed{c_k(x) = c_k^\infty e^{-\beta q_k \psi(x)} \qquad k = 1, \cdots, M}$$

$$c_k^\infty = \Lambda^{-3} e^{\beta \mu_k}$$

The Boltzmann distributions!

$$\Longrightarrow \quad \nabla \cdot \varepsilon \nabla \psi = \rho_f + \sum_k c_k^\infty e^{-\beta q_k \psi(x)} \quad \underline{\underline{\text{The PBE!}}}$$

<u>Remark</u> If $\psi_0 \neq 0$ on $\partial\Omega$. Then the Boltzmann distributions become

$$c_k(x) = c_k^\infty e^{-\beta q_k [\psi(x) - \hat{\psi}_0(x)]} \qquad k = 1, \cdots, M$$

where
$$\begin{cases} \nabla \cdot \varepsilon(x) \nabla \hat{\psi}_0 = 0 & \text{in } \Omega, \\ \hat{\psi}_0 = \psi_0 & \text{on } \partial\Omega. \end{cases}$$

Next, $\delta^2 F[c]$. to see the convexity!

Recall (from middle of p. $\boxed{30}$)

$$F[c] = \int_\Omega \left\{ \frac{1}{2}\left(\sum_j q_j c_j\right) \mathcal{L}\left(\sum_i q_i c_i\right) + \left(\sum_j q_j c_j\right) \mathcal{L}(\rho_f) + \beta^{-1} \sum_j c_j \left[\log(\Lambda^3 c_j) - 1\right] - \sum_j \mu_j c_j \right\} dV$$

$\mathcal{L}$: symmetric, elliptic (= positive definite)

... $\frac{1}{2}\left(\sum_j q_j c_j\right) \mathcal{L}\left(\sum_i q_i c_i\right)$ quadratic in c. positive definite.

... $\left(\sum_j q_j c_j\right) \mathcal{L}(\rho_f)$, $-\sum_j \mu_j c_j$: linear

... $\frac{d}{dc_j}\left(c_j \log c_j\right)' = \log c_j + 1$

$\frac{d^2}{dc_j^2}\left(c_j \log c_j\right) = \frac{1}{c_j} > 0$ not so rigourous. But ok!

From $\boxed{p\ 31}$

$$\delta F[c][d] = \int_\Omega \left\{ \left(\sum_j q_j d_j\right) \mathcal{L}\left(\sum_i q_i c_i\right) + \left(\sum_j q_j d_j\right) \mathcal{L}(\rho_f) + \beta^{-1} \sum_j d_j \log(\Lambda^3 c_j) - \sum_j \mu_j d_j \right\} dV$$

Definition $\delta^2 F[c][d,e] = \left.\frac{d}{dt}\right|_{t=0} \delta F[c+te][d]$

$$= \left.\frac{d}{dt}\right|_{t=0} \int_\Omega \left\{ \left(\sum_j q_j d_j\right) \mathcal{L}\left(\sum_i (q_i c_i + q_i t e_i)\right) + \beta^{-1} \sum_j d_j \log\left(\Lambda^3 (c_j + t e_j)\right) \right\} dV$$

only perturb c_j, so, d_j terms alone become 0.

$$= \int_\Omega \left\{ \left(\sum_j q_j d_j\right) \mathcal{L}\left(\sum_i q_i e_i\right) + \beta^{-1} \sum_j \frac{d_j e_j}{c_j} \right\} dV$$

$\delta^2 F[c] : X \times X \to \mathbb{R}$ a bi-linear form.

① symmetric $\delta^2 F[c][d,e] = \delta^2 F[c][e,d]$

~~$\delta^2 F[c]$~~ ② positive-definite: $\delta^2 F[c][d,d] > 0$ (if $d \neq 0$)

Check ②:

$$\delta^2 F[c][d,d] = \int_\Omega \left\{ \left(\sum_j q_j d_j\right) \mathcal{L}\left(\sum_j q_j d_j\right) + \beta^{-1} \sum_j \frac{d_j^2}{c_j} \right\} dV$$

Let $u = \sum_j q_j d_j$. $\phi = \mathcal{L}\left(\sum_j q_j d_j\right)$

$$\begin{cases} \nabla \cdot \varepsilon \nabla \phi = -u & \text{in } \Omega \\ \phi = 0 & \text{on } \partial\Omega \end{cases}$$

$$\int_\Omega u \phi \, dV = \int_\Omega (-\nabla \cdot \varepsilon \nabla \phi) \phi \, dV$$

$$= \int_\Omega \varepsilon |\nabla \phi|^2 dV - \int_{\partial\Omega} \varepsilon \frac{\partial \phi}{\partial n} \overset{=0}{\phi} \, dV$$

$$= \int_\Omega \varepsilon |\nabla \phi|^2 dV \geq 0$$

$$\int_\Omega u \phi \, dV = 0 \implies \nabla \phi = 0 \implies \phi = 0 \text{ in } \Omega$$

since $\phi = 0$ on $\partial\Omega$.

Expected: $\exists !$ a unique minimizer

$c = (c_1, \cdots, c_M)$: $\min_c F[c]$.

$F[c]$ is convex in c.

Need a rigorous proof to avoid $c \approx 0$.

~~Consequence~~.

See p. $\boxed{40}$ for an expression of

$F_{min} = \min F[c]$

We continue our discussions on the mean-field electrostatic free-energy functional

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

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

$$\nabla\cdot\varepsilon(x)\nabla\psi = -\rho \quad \text{in } \Omega \qquad \Bigg\| \quad \psi = \mathcal{L}(\rho).$$
$$\psi = 0 \quad \text{on } \partial\Omega$$

Formal calculations:

(1) $\delta F[c][d] = 0 \iff$ Boltzmann's distributions

$$c_k(x) = c_k^{\infty} e^{-\beta q_k \psi(x)}, \quad k = 1, \cdots, M.$$

(2) $$\delta^2 F[c][d,d] = \int_\Omega \left[\left(\sum_{j=1}^{M} q_j d_j\right) \mathcal{L}\left(\sum_j q_j d_j\right) + \beta^{-1}\sum_{j=1}^{M}\frac{d_j^2}{c_j}\right] dV$$
$$\geq 0 \quad \forall d.$$

$$\cdots = 0 \iff \text{all } d_j = 0 \iff d = 0.$$

Convexity!

We now show that for equilibrium concentrations $c_1, \cdots, c_M$ there are bounds.

$$0 < \theta_1 \leq c_j(x) \leq \theta_2 \qquad x \in \Omega, \ j = 1, \cdots, M.$$

where θ_1, θ_2 are constants.

<u>Theorem</u>. For any $c = (c_1, \cdots, c_M)$, there exists $\hat{c} = (\hat{c}_1, \cdots, \hat{c}_M)$ such that

(a) $\| c - \hat{c} \| << 1$

(b) $\exists\ 0 < \theta_1 < \theta_2$ s.t.

$$\theta_1 \le \hat{c}_j(x) \le \theta_2 \quad \text{for } x \in \Omega,\ j = 1, \cdots, M.$$

(c) $F[\hat{c}] \le F[c]$.

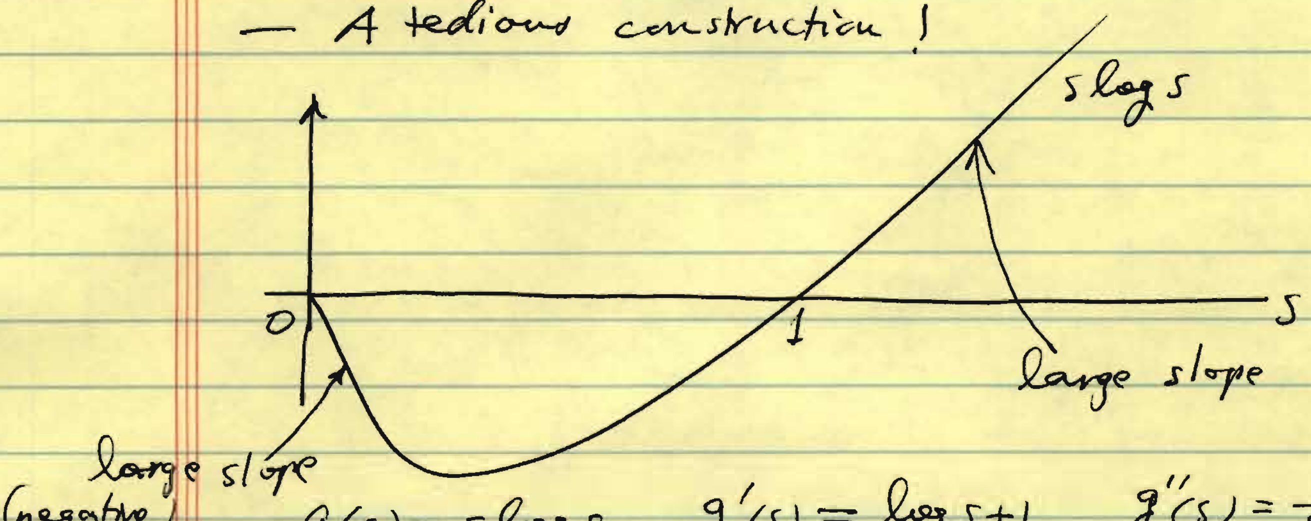
In particular, equilibrium concentrations are always bounded away from 0 and bounded above.

<u>The idea of proof</u>

$$F[c] = \int_\Omega \Big[\overbrace{\Big(\sum_j q_j c_j\Big) \mathcal{L}\Big(\sum_i q_i c_i\Big)}^{\text{quadratic in } c} + \sum_j \underbrace{a_j(x)}_{\text{a nice, bded function}} c_j(x) + \beta^{-1} \sum_{j=1}^{M} c_j \log c_j \Big] dx$$

$\hat{c} = c +$ some small perturbation

— A tedious construction!



$g(s) = s \log s.$ $\quad g'(s) = \log s + 1,$ $\quad g''(s) = \frac{1}{s} > 0.$

$\hat{c}_j = c_j + \alpha.$ $\qquad (c_j + \alpha)^2 - c_j^2 = 2\alpha c_j + \alpha^2$

$$a_j(c_j + \alpha) - a_j c_j = a_j \alpha.$$

$$(c_j + \alpha)\log(c_j + \alpha) - c_j \log c_j \approx (\log c_j + 1)\,\alpha.$$

If $c_j \approx 0$ then $\log c_j$ is very negative.
If $c_j >> 1$ then $\log c_j$ is very positive. Then use $-\alpha$.

$$\hat{c}_j = \begin{cases} c_j + \alpha & \text{at } x \text{ where } c_j(x) \gtrsim 0 \\ c_j - \alpha & \text{at } x \text{ where } c_j(x) >> 1. \end{cases} \qquad \square$$

<u>Corollary</u> The PBE has a unique solution ψ where $c_k(x) = c_k^\infty e^{-\beta q_k \psi(x)}$ are the equilibrium concentrations.

The PBE.

$$\begin{cases} \nabla \cdot \varepsilon(x) \nabla \psi + \sum_{j=1}^{M} q_j c_j^\infty e^{-\beta q_j \psi} = -\rho_f & \text{in } \Omega \\ \psi = \psi_0 & \text{on } \partial\Omega \end{cases}$$

Let.

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

$$B(\psi) = \beta^{-1} \sum_{j=1}^{M} c_j^\infty e^{-\beta q_j \psi}. \quad B \text{ is convex!}$$

The PBE is the Euler-Lagrange equation of $I : H^1_{\psi_0}(\Omega) \to \mathbb{R} \cup \{+\infty\}$.

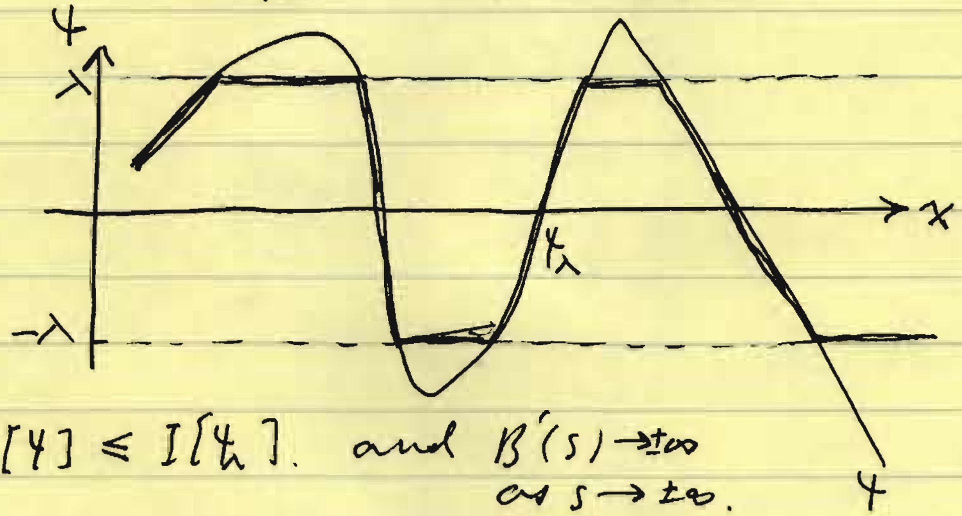
$$H^1_{\psi_0}(\Omega) = \{ u \in H^1(\Omega) : u = \psi_0 \text{ on } \partial\Omega \}$$

Use the ~~meth~~ direct method in the calculus of variations to show that there exists a unique minimizer $\psi \in H^1_{\psi_0}(\Omega)$ of $I : H^1_{\psi_0}(\Omega) \to \mathbb{R} \cup \{+\infty\}$.

Why this minimizer ψ satisfies the Euler-Lagrange equation?

Idea: Let $\lambda > 0$. Define $\psi_\lambda : \Omega \to \mathbb{R}$ by

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



$I[\psi] \le I[\psi_\lambda]$. and $B'(s) \to \pm\infty$ as $s \to \pm\infty$.

More precise calculations:

Assume $\rho_f = 0$.

Otherwise, either absorb $\rho_f \psi$ into $B(\psi)$

or shift ψ to $\psi - \hat{\psi}$ with

$\hat{\psi}$ corresponding to ρ_f: $\nabla \cdot \varepsilon \nabla \hat{\psi} = -\rho_f$.

$I[\psi] \le I[\psi_\lambda]$: $\displaystyle\int_\Omega \left[\frac{\varepsilon(x)}{2} |\nabla\psi|^2 + B(\psi)\right] dV \le \int_\Omega \left[\frac{\varepsilon(x)}{2} |\nabla\psi_\lambda|^2 + B(\psi_\lambda)\right] dV$

But $|\nabla\psi| \ge |\nabla\psi_\lambda|$ in Ω. Hence

$$\int_\Omega B(\psi)\, dV \le \int_\Omega B(\psi_\lambda)\, dV.$$

$$\int_{\{\psi > \lambda\}} B(\psi)\, dV + \int_{\{\psi < -\lambda\}} B(\psi)\, dV + \int_{\{|\psi| \le \lambda\}} B(\psi)\, dV$$

$$\le \int_{\{\psi > \lambda\}} B(\lambda)\, dV + \int_{\{\psi < -\lambda\}} B(-\lambda)\, dV + \int_{\{|\psi| \le \lambda\}} B(\psi)\, dV$$

$$\int_{\{\psi>\lambda\}}[B(\psi)-B(\lambda)]dV+\int_{\{\psi<-\lambda\}}[B(\psi)-B(-\lambda)]dV\le 0$$

Convexity: $B(\psi)-B(\lambda)\ge B'(\lambda)(\psi-\lambda)$

$B(\psi)-B(-\lambda)\ge B'(-\lambda)(\psi+\lambda)$

$B'(s)\to+\infty$ as $s\to+\infty$

$B'(s)\to-\infty$ as $s\to-\infty$

λ large: $$B'(\lambda)\int_{\{\psi>\lambda\}}(\psi-\lambda)dV+\overbrace{[-B'(-\lambda)]}^{>0}\overbrace{\int_{\{\psi<-\lambda\}}(-\psi-\lambda)dV}^{\ge 0}\le 0$$

$$\Longrightarrow\quad |\{\psi>\lambda\}|=0\qquad |\{\psi<-\lambda\}|=0. \qquad \square$$

measure.

Plan ahead:

- Ion-Mediated /Wall-mediated Like-Charge Attractions
  Can the PB theory predict this?

- Adding the ionic size effect in the continuum model
  - Generalized PBE for uniform size
  - Optimization for non-uniform sizes

- (Possibly) The PNP system
  (Poisson-Nernst-Planck)
  diffusion in electrostatic field

The minimum value of the electrostatic free-energy functional

$$F[c] = \int_\Omega \left\{ \frac{1}{2}\left(\rho_f + \sum_j q_j c_j\right)\psi + \beta^{-1}\sum_j c_j\left[\log(\Lambda^3 c_j) - 1\right] - \sum_j \mu_j c_j \right\} dV$$

equilibrium concentrations $c = (c_1, \cdots, c_M)$
(same as the minimizer)
equilibrium electrostatic potential $\psi = \psi(x)$.

$$\begin{cases} -\nabla\cdot\varepsilon(x)\nabla\psi = \rho_f + \sum_j q_j c_j & \Omega \\ \psi = 0 & \partial\Omega \end{cases}$$

Boltzmann's distributions

$$c_j(x) = c_j^\infty e^{-\beta q_j \psi(x)}, \quad j = 1, \cdots, M, \quad x \in \Omega.$$

$$\left[\Lambda^3 c_j^\infty = e^{\beta\mu_j}, \quad j = 1, \cdots, M.\right].$$

$$F_{min} = \min F[\cdot] = F[c]$$

$$= \int_\Omega \left\{ \frac{1}{2}\rho_f\psi + \frac{1}{2}\left(\sum_j q_j c_j\right)\psi + \beta^{-1}\sum_j c_j\left[\underbrace{\log(\Lambda^3 c_j^\infty)}_{=\beta\mu_j} - \beta q_j\psi - 1\right] - \sum_j \mu_j c_j \right\} dV$$

$$= \int_\Omega \left\{ \frac{1}{2}\rho_f\psi - \frac{1}{2}\left(\sum_j q_j c_j\right)\psi - \beta^{-1}\sum_j c_j \right\} dV$$

$$= \int_\Omega \left\{ \cancel{\tfrac{1}{2}}\rho_f\psi - \frac{1}{2}\left(\rho_f + \sum_j q_j c_j\right)\psi - \beta^{-1}\sum_j c_j^\infty e^{-\beta q_j\psi} \right\} dV$$

$$= \int_\Omega \left\{ \cancel{\tfrac{1}{2}}\rho_f\psi + \frac{1}{\cancel{2}}\psi\left(\nabla\cdot\varepsilon(x)\nabla\psi\right) - \beta^{-1}\sum_j c_j^\infty e^{-\beta q_j\psi} \right\} dV$$

$$= \boxed{\int_\Omega \left\{ -\frac{\varepsilon(x)}{2}|\nabla\psi|^2 + \rho_f\psi - \beta^{-1}\sum_j c_j^\infty e^{-\beta q_j\psi} \right\} dV}$$

Concave (not convex) in ψ!