Include Ionic Excluded-Volume (Size) Effects in Mean-Field Models of Electrostatics

Consider an ionic solution that occupies a bounded region $\Omega \subset \mathbb{R}^3$. Assume there are $M (\geq 1)$ ionic species.

Denote

$c_j(x)$ ... local concentration of jth ionic species

z_j ... valence of jth ionic species

$q_j = z_j e$

e ... elementary charge

a_j ... linear size of an ion of jth species
More precisely: a_j^3 = volume of ion of jth species

a_0 ... linear size of a solvent molecule
more precisely: a_0^3 = volume of a solvent molecule

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

k_B ... the Boltzmann constant

T ... temperature

μ_j ... chemical potential of ~~jth~~ ions of jth species

$c_0(x)$ ... local concentration of solvent molecules

The mean-field, electrostatic free-energy functional is ($c = (c_1, \cdots, c_M)$)

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

starts from $j=0$

$$a_0^3 c_0(x) = 1 - \sum_{j=1}^{M} a_j^3 c_j(x).$$

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

ρ_f is the fixed charge.

$$(*) \quad \begin{cases} \nabla\cdot\varepsilon\nabla\psi = -\rho & \Omega \\ \psi = 0 & \partial\Omega \end{cases}$$

Note: we can use also a more general boundary condition $\psi = \psi_0$ on $\partial\Omega$ for a fixed function ψ_0 on $\partial\Omega$.

Again, we use $\mathcal{L}$ to denote the operator defined by $(*)$ above. $\psi = \mathcal{L}(\rho)$

$$F[c] = \int_\Omega \Big\{ \frac{1}{2}\Big(\rho_f + \sum_{j=1}^{M} q_j c_j\Big) \mathcal{L}\Big(\rho_f + \sum_{j=1}^{M} q_j c_j\Big) + \beta^{-1} c_0\big[\log(a_0^3 c_0) - 1\big] + \beta^{-1}\sum_{j=1}^{M} c_j\big[\log(a_j^3 c_j) - 1\big] - \sum_{j=1}^{M} \mu_j c_j \Big\} dV$$

$$= \int_\Omega \Big\{ \frac{1}{2}\Big(\sum_{i=1}^{M} q_i c_i\Big) \mathcal{L}\Big(\sum_{j=1}^{M} q_j c_j\Big) + \Big(\sum_{j=1}^{M} q_j c_j\Big)\mathcal{L}(\rho_f) + \cancel{\beta^{-1} c_0\big[\log(a_0^3 c_0) - 1\big] + \beta^{-1}\sum_{j=1}^{M}}$$
$$+ \beta^{-1} a_0^{-3}\Big(1 - \sum_{j=1}^{M} a_j^3 c_j\Big)\Big[\log\Big(1 - \sum_{j=1}^{M} a_j^3 c_j\Big) - 1\Big] + \beta^{-1}\sum_{j=1}^{M} c_j\big[\log(a_j^3 c_j) - 1\big] - \sum_{j=1}^{M} \mu_j c_j \Big\} dV + \int_\Omega \frac{1}{2}\rho_f \mathcal{L}(\rho_f)\, dV$$

<u>Convexity</u>. Need only to check the entropic part

Give $a_0 > 0, \ldots, a_M > 0$.

Define $g: (0,1)^M \to \mathbb{R}$ by

$$g(u) = a_0^{-3}\Big(1 - \sum_{j=1}^{M} u_j\Big)\Big[\log\Big(1 - \sum_{j=1}^{M} u_j\Big) - 1\Big] + \sum_{j=1}^{M} a_j^{-3} u_j\big[\log u_j - 1\big].$$

HW: Prove that g is convex. and there exists a unique minimizer $u = (u_1, \ldots, u_M)$ of g over $(0,1)^M$.

$$\partial_j g = a_0^{-3}(-1)\left[\log\left(1-\sum_{i=1}^{M} u_i\right)-1\right]$$
$$+ a_0^{-3}\left(1-\sum_{i=1}^{M} u_i\right)\frac{(-1)}{1-\sum_{i=1}^{M} u_i}$$
$$+ \sum_{i=1}^{M}\left[a_i^{-3}\left(\log u_i - 1\right) + a_i^{-3} u_i \cdot \frac{1}{u_i}\right]$$
$$= -a_0^{-3}\log\left(1-\sum_{i=1}^{M} u_i\right) + \sum_{i=1}^{M} a_i^{-3}\log u_i$$

$$\partial_{jk} g = -a_0^{-3}\frac{(-1)}{1-\sum_{i=1}^{M} u_i} + a_k^{-3}\frac{1}{u_k}$$
$$= \frac{a_0^{-3}}{1-\sum_{i=1}^{M} u_i} + a_k^{-3}\frac{1}{u_k}$$

The Hessian is

$$\nabla^2 g = \left[\partial_{jk} g\right] = \frac{1}{a_0^3\left(1-\sum^{M} u_i\right)} e\otimes e + \operatorname{diag}\left(\frac{1}{a_1^3 u_1}, \cdots, \frac{1}{a_M^3 u_M}\right)$$

Symmetric positive definite!

Let $v = (v_1, \cdots, v_M)^T \neq 0$.

$$v\cdot\nabla^2 g\, v = \frac{1}{a_0^3\left(1-\sum_i^{M} u_i\right)}(e\cdot v)^2 + \sum_{k=1}^{M}\frac{1}{a_k^3 u_k} v_k^2 > 0$$

So, the functional $F[c]$ is (still) convex!

$$\delta F[c][d] = \frac{d}{dt}\Big|_{t=0} F[c+td]$$
$$= \frac{d}{dt}\Big|_{t=0}\int_\Omega\left\{\frac{1}{2}\left(\sum_{j=1}^{M} q_j c_j + t\sum_{j=1}^{M} q_j d_j\right)\mathcal{L}\left(\sum_{j=1}^{M} q_j c_j + t\sum_{j=1}^{M} q_j d_j\right)\right.$$
$$+ \mathcal{L}(\rho_f)\left(\sum_{j=1}^{M} q_j c_j + t\sum_{j=1}^{M} q_j d_j\right)$$
$$+ \beta^{-1} a_0^{-3}\left(1-\sum_{j=1}^{M} a_j^3 c_j - t\sum_{j}^{M} a_j^3 d_j\right)\left[\log\left(1-\sum_{j=1}^{M} a_j^3 c_j - t\sum_{j=1}^{M} a_j^3 d_j\right)-1\right]$$
$$\left. + \beta^{-1}\sum_{j=1}^{M}(c_j + t d_j)\left[\log(a_j^3 c_j + t a_j^3 d_j) - 1\right] - \sum_{j=1}^{M} \mu_j c_j - t\sum_{j=1}^{M}\mu_j d_j\right\} dx$$

$$= \int_\Omega\left\{\left(\sum_{j=1}^{M} q_j d_j\right)\mathcal{L}\left(\sum_{i=1}^{M} q_i c_i\right) + \left(\sum_{j=1}^{M} q_j d_j\right)\mathcal{L}(\rho_f)\right.$$

$$+\beta^{-1} a_0^{-3}\left(-\sum_{j=1}^{M} a_j^3 d_j\right)\left[\log\left(1-\sum_{j=1}^{M} a_j^3 c_j\right)-1\right]$$

$$+\beta^{-1} a_0^{-3}\left(1-\sum_{j=1}^{M} a_j^3 c_j\right)\frac{-\sum_{j=1}^{M} a_j^3 d_j}{1-\sum_{j=1}^{M} a_j^3 c_j}$$

$$+\beta^{-1}\sum_{j=1}^{M}\left\{d_j\left[\log(a_j^3 c_j)-1\right]+\beta^{-1}\cancel{\sum_{j=1}^{M}} c_j\,\frac{a_j^3 d_j}{a_j^3 c_j}\right\}-\sum_{j=1}^{M}\mu_j d_j\Big\}\,dV$$

$$=\int_\Omega\Big\{\left(\sum_{j=1}^{M} q_j d_j\right)\psi-\beta^{-1}a_0^{-3}\left(\sum_{j=1}^{M} a_j^3 d_j\right)\log\left(1-\sum_{j=1}^{M} a_j^3 c_j\right)$$

$$+\beta^{-1}\sum_{j=1}^{M} d_j\log(a_j^3 c_j)-\sum_{j=1}^{M}\mu_j d_j\Big\}\,dV$$

Equilibrium conditions: $\delta F[c]=0$.

Fix k $(1\le k\le M)$ $\quad d=(0,\dots,0,d_k,0,\dots,0)$.

$$q_k\psi-\beta^{-1}a_0^{-3}a_k^3\log\left(1-\sum_{j=1}^{M}a_j^3c_j\right)+\beta^{-1}\log(a_k^3c_k)-\mu_k=0$$

Denote $a_0^3c_0=1-\sum_{j=1}^{M}a_j^3c_j$.

$$\boxed{\left(\frac{a_k}{a_0}\right)^3\log(a_0^3c_0)-\log(a_k^3c_k)=\beta(q_k\psi-\mu_k)\qquad k=1,\dots,M}$$

Special Case $\quad a_0=a_1=\cdots=a_M=a$

$$\log(a^3c_0)-\log(a^3c_k)=\beta(q_k\psi-\mu_k)$$

$$\cancel{c_k c_0^{-1}=e^{\beta q_k\psi}e^{-\beta\mu_k}}$$

$$\cancel{c_k=c_0^{-1}e^{\beta q_k\psi}}$$

$$c_k=c_0a^3c_k^{\infty}e^{-\beta q_k\psi}$$

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

$$a^3 c_k = c_0 a^6 c_k^\infty e^{-\beta q_k \psi}$$

$$1 - \sum_1^M a^3 c_k = 1 - c_0 a^6 \sum_1^M c_k^\infty e^{-\beta q_k \psi}$$

$$\shortparallel$$

$$a^3 c_0 = 1 - a^6 c_0 \sum_1^M c_k^\infty e^{-\beta q_k \psi}$$

$$a^3 c_0 \left(1 + a^3 \sum_1^M c_k^\infty e^{-\beta q_k \psi}\right) = 1$$

$$c_0 = \frac{1}{a^3\left(1 + a^3 \sum_1^M c_k^\infty e^{-\beta q_k \psi}\right)}$$

$$c_k = c_0 a^3 c_k^\infty e^{-\beta q_k \psi}$$

$$c_k = \frac{c_k^\infty e^{-\beta q_k \psi}}{1 + a^3 \sum_{j=1}^M c_j^\infty e^{-\beta q_j \psi}} \quad (k = 1, \ldots, M)$$

$$\boxed{\begin{array}{l} \text{The generalized PB equation.} \\ \nabla \cdot \varepsilon(x) \nabla \psi + \sum_{j=1}^M \dfrac{q_j c_j^\infty e^{-\beta q_j \psi}}{1 + a^3 \sum_{k=1}^M c_k^\infty e^{-\beta q_k \psi}} = -\rho_f . \end{array}}$$

$\cancel{I[\psi] =}$

$$\min F = \int_\Omega \left\{ -\frac{\varepsilon}{2} |\nabla \psi|^2 + \rho_f \psi - \beta^{-1} a^{-3} \left[1 + \log\left(1 + \sum_{i=1}^M a^3 c_i^\infty e^{-\beta q_i \psi}\right)\right]\right\} dV$$

Variational principle.

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

$\min I[\psi] \Longrightarrow$ The generalized PBE.

The general case.

$$\left(\frac{a_k}{a_0}\right)^3 \log\left(a_0^3 c_0\right) - \log\left(a_k^3 c_k\right) = \beta\left(q_k \psi - \mu_k\right) \qquad k=1,\cdots,M$$

where

$$a_0^3 c_0 = 1 - \sum_{j=1}^{M} a_j^3 c_j .$$

A system of M nonlinear equations of M unknowns $c_1,\cdots,c_M$.

Hard to find a formula of the solution.

<u>Lemma</u> The above system has a unique solution $(c_1,\cdots,c_M)$ with $a_j^3 c_j \in (0,1)$, $j=1,\cdots,M$.

~~See~~ <u>Pf</u>. Let $D_M = \left\{ u=(u_1,\cdots,u_M)\in \mathbb{R}^M : u_1>0,\cdots,u_M>0, \text{ and } \sum_{i=1}^{M} a_i^3 u_i < 1 \right\}$.

$D_M \subset \prod_1^M (0, a_i^{-3})$

For $u=(u_1,\cdots,u_M)\in D_M$, let

$$u_0 = a_0^{-3}\left(1 - \sum_1^M a_i^3 u_i\right).$$

Define $\hat{f} = (\hat{f}_1,\cdots,\hat{f}_M) : D_M \to \mathbb{R}^M$ by

$$\hat{f}_i(u) = \left(\frac{a_i}{a_0}\right)^3 \log\left(a_0^3 u_0\right) - \log\left(a_i^3 u_i\right).$$

$$\forall u=(u_1,\cdots,u_M), \quad i=1,\cdots,M.$$

We <u>claim</u>: $\hat{f} : D_M \to \mathbb{R}^M$ is C^∞ and bijective.

That "$\hat{f}$ is C^∞" is clear.

Now, $\nabla \hat{f}(u) = -\mathrm{diag}\left(\frac{1}{u_1},\cdots,\frac{1}{u_M}\right) - \frac{1}{a_0^3 u_0}\, p \otimes p$

$$p = \begin{bmatrix} a_1^3 \\ \vdots \\ a_M^3 \end{bmatrix}.$$

$$\det \nabla \hat{f}(u) = \frac{(-1)^M}{u_1 \cdots u_M}\left(1 + \frac{1}{a_0^3 u_0}\sum_{i=1}^{M} a_i^6 u_i\right) \neq 0$$

$\Rightarrow \hat{f} : D_M \to \mathbb{R}^M$ is injective.

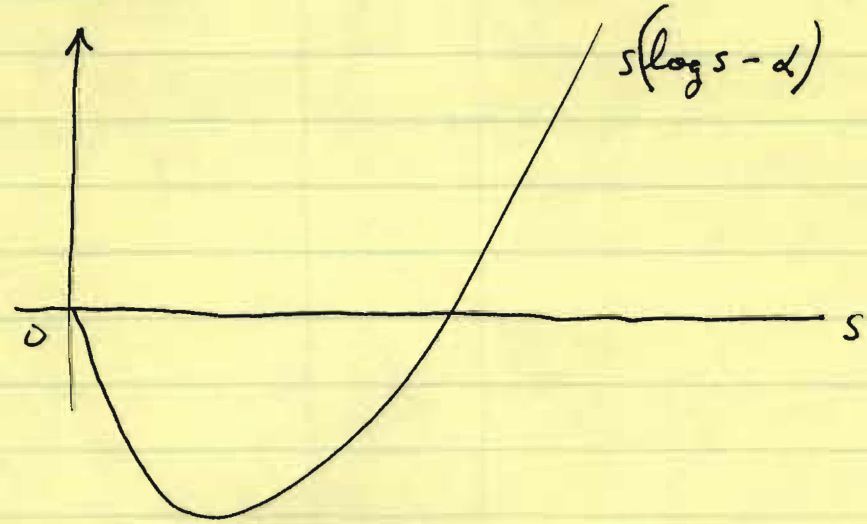
Now we prove that $\hat{f} : D_M \longrightarrow \mathbb{R}^M$ is surjective.

Let $r = (r_1, \cdots, r_M) \in \mathbb{R}^M$. We prove $\exists\, u = (u_1, \cdots, u_M) \in D_M$ s.t. $\hat{f}(u) = r$.

Define $\hat{F} : D_M \to \mathbb{R}$ by

$$\hat{F}(u) = \frac{1}{a_0^3}\left(1 - \sum_{j=1}^{M} a_j^3 u_j\right)\left[\log\left(1 - \sum_{j=1}^{M} a_j^3 u_j\right) - 1\right] + \sum_{j=1}^{M} u_j\left[\log(a_j^3 u_j) - 1\right] - \sum_{j=1}^{M} r_j u_j \quad \forall u \in D_M$$

Clearly, $\hat{F} \in C^\infty(D_M)$. Notice that if $\exists j$. $(1 \le j \le M)$ s.t. when u_i are fixed $(1 \le i \le M, i \ne j)$ and $u_j \to 0$ or $\frac{1}{a_j^3}$ then $\hat{F}(u)$ ~~increases~~. More precisely, ~~as $u_j \to 0^+$~~ for any u_j, if u_j is close to 0, then by perturbing u_j to $u_j + \delta$, we can reduce $\hat{F}$. Similarly, if u_j is close to $\frac{1}{a_j^3}$, we can perturb it to $u_j - \delta$ $(0 < \delta \ll 1)$ to reduce $\hat{F}$. The latter reduction is done through the $u_0 \log(a_0^3 u_0)$ part.



Therefore a minimum value of $\hat{F}$ can only be achieve by some u in the interior of D_M. Since $\hat{F}: D_M \to R$ is bded below $\hat{F}$ achieves its min. value in D_M. Hence, $\nabla_u \hat{F} = 0$. This proves $\hat{F}(u) = r$. □

Now the equilibrium conditions

$$\left(\frac{a_k}{a_0}\right)^3 \log(a_0^3 c_0) - \log(a_k^3 c_k) = \beta(q_k \psi - \mu_k), \quad k = 1, \cdots, M$$

where $a_0^3 c_0 = 1 - \sum_{j=1}^{M} a_j^3 c_j$

define the implicit Boltzmann distributions

$$c_j = B_j(\psi). \quad j = 1, \cdots, M$$

Define

$$V(\phi) = -\sum_{i=1}^{M} q_i \int_0^{\phi} B_i(s)\, ds.$$

Clearly $V'(\psi) = -\sum_1^M q_i B_i(\psi) = -\left(\sum_1 q_i c_i\right)$ is the negative ionic charge density.

Assume the charge neutrality $\sum_{i=1}^{M} q_i B_i(0) = 0$

Then, one can show that

$$V''(\psi) > 0. \quad \text{so, } V \text{ is convex}$$

In fact, we can show also

$$V'(\phi) = \begin{cases} > 0 & \text{if } \phi > 0 \\ = 0 & \text{if } \phi = 0 \\ < 0 & \text{if } \phi < 0 \end{cases}$$

Moreover, $V(\phi) > V(0) = 0$ for all $\phi \neq 0$. $V(\pm\infty) = \infty$.

~~Ge~~ The implicit PBE is:

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

It cannot predict the wall-mediated like-charge attraction!