Modeling and Simulation of Charged Molecules with Legendre-Transformed Poisson-Boltzmann Electrostatic Free Energy Functional

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Outline

1. Legendre-Transformed (LT) Poisson-Boltzmann (PB) functional
2. Applications to interface problem
3. Numerical methods and results
4. Conclusions

Legendre-Transformed Poisson-Boltzmann functional

Classical Poisson-Boltzmann energy functional

$$I[\phi] = \int_\Omega [-\frac{\epsilon}{2}|\nabla\phi|^2 + f\phi - B(\phi)]dx$$

- $\Omega \subseteq \mathbb{R}^3$: bounded region
- $\phi : \Omega \to \mathbb{R}$: electrostatic potential
- $\epsilon : \Omega \to \mathbb{R}$: dielectric coefficient
- $f : \Omega \to \mathbb{R}$: fixed charge density
- $B : \mathbb{R} \to \mathbb{R}$: strictly convex, $B(0) = 0$ and $B(\infty) = \infty$. E.g. $B(\phi) = \cosh(\phi)$

The Euler-Lagrange equation of $I[\phi]$ is

$$\text{PBE} : \qquad \nabla \cdot \epsilon\nabla\phi - B'(\phi) = -f$$

Legendre-Transformed Poisson-Boltzmann functional

Legendre Transform: For function B, $\forall \xi \in \mathbb{R}$, $B^*(\xi) = \sup_{s\in\mathbb{R}}(s\xi - B(s))$

LT PB energy functional (Maggs, 2012)

$$J[D] = \int_\Omega [\frac{1}{2\epsilon}|D|^2 + B^*(f - \nabla \cdot D)]dx + \int_{\partial\Omega} gD \cdot ndS$$

$D : \Omega \to \mathbb{R}^3$, $D = -\epsilon\nabla\phi$

Equivalence between two functionals (Ciotti & Li, 2018)

$\forall \phi \in H^1_g(\Omega), \forall D \in H(div, \Omega)$, we have $I[\phi] \leq J[D]$

- $H^1_g(\Omega) = \{u \in H^1(\Omega) : u = g \text{ on } \partial\Omega\}$
- $H(div, \Omega) = \{D \in [L^2(\Omega)]^3 : \nabla \cdot D \in L^2(\Omega)\}$

Moreover, we have $D_B = -\epsilon\nabla\phi_B$ and

$$I[\phi_B] = \max_{\phi\in H^1_g(\Omega)} I[\phi] = \min_{D\in H(div,\Omega)} J[D] = J[D_B]$$

Applications to interface problem

Classical PB energy functional:

$$I_\Gamma[\phi] = \int_\Omega [-\frac{\epsilon_\Gamma}{2}|\nabla\phi|^2 + f\phi - \chi_+ B(\phi)]dx$$

$$\epsilon_\Gamma = \begin{cases} \epsilon_+ & \text{in} \quad \Omega_+ \\ \epsilon_- & \text{in} \quad \Omega_- \end{cases}$$

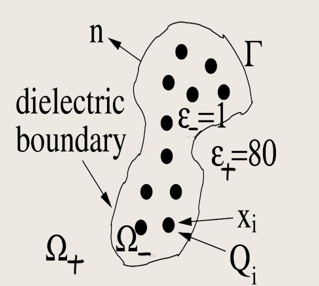


Figure 1: Interface problem

LT PB energy functional:

$$J_\Gamma[D] = \int_\Omega [\frac{1}{2\epsilon_\Gamma}|D|^2 + \chi_+ B^*(f - \nabla\cdot D)]dx + \int_{\partial\Omega} gD\cdot ndS, \forall D \in V_\Gamma$$

$$V_\Gamma = \{D \in H(div, \Omega) : \nabla\cdot D = f \quad \text{in} \quad \Omega_-\}$$

Applications to interface problem

Equivalence between two functionals (Ciotti & Li, 2018)

$\forall \phi \in H_g^1(\Omega), \forall D \in V_\Gamma$, we have

$$I_\Gamma[\phi] \leq J_\Gamma[D]$$

Moreover, we have

$$I_\Gamma[\phi_\Gamma] = \max_{\phi \in H_g^1(\Omega)} I_\Gamma[\phi] = \min_{D \in V_\Gamma} J_\Gamma[D] = J_\Gamma[D_\Gamma]$$

Here, $D_\Gamma = -\epsilon_\Gamma \nabla \phi_\Gamma$.

Numerical methods and results

Problem

Convex optimization problem with constraint:

$$\begin{cases} min\ J_\Gamma[D] \\ \text{s.t. } \nabla \cdot D = f \quad \text{in} \quad \Omega_- \end{cases}$$

Penalty method

Given a penalty coefficient μ, we need to minimize the following:

$$J_{\Gamma,\mu}[D] = J_\Gamma[D] + \frac{1}{\mu}\int_{\Omega_-}(\nabla \cdot D - f)^2 dx$$

$$= \int_\Omega [\frac{1}{2\epsilon_\Gamma}|D|^2 + \chi_+ B^*(f - \nabla \cdot D) + \frac{1}{\mu}\chi_-(\nabla \cdot D - f)^2]dx + \int_{\partial\Omega} gD \cdot ndS$$

One good optimization algorithm is the limited-memory BFGS method.

Numerical methods and results

$$J_{\Gamma,\mu}[D] = J_{\Gamma}[D] + \frac{1}{\mu}\int_{\Omega_-}(\nabla\cdot D - f)^2 dx$$

$$= \int_{\Omega}[\frac{1}{2\epsilon_{\Gamma}}|D|^2 + \chi_+ B^*(f - \nabla\cdot D) + \frac{1}{\mu}\chi_-(\nabla\cdot D - f)^2]dx + \int_{\partial\Omega} gD\cdot ndS$$

Convergence theorem of penalty method

1. For each μ, there exists a unique $D_{\Gamma,\mu}$ which minimizes $J_{\Gamma,\mu}[D]$
2. min $J_{\Gamma,\mu}[D] \to \min_{D\in V_{\Gamma}} J_{\Gamma}[D]$ as $\mu \to 0$
3. $D_{\Gamma,\mu} =$ argmin $J_{\Gamma,\mu}[D] \to \text{argmin}_{D\in V_{\Gamma}} J_{\Gamma}[D] = D_{\Gamma}$ as $\mu \to 0$

Numerical methods and results

Computational region $\Omega = [-1, 1]^3$.

Particular solution

For Γ which is a sphere in $\mathbb{R}^3$, one particular solution $D_{\Gamma,\mu}$ is given by

$$D_{\Gamma,\mu}(r) = \begin{cases} \frac{\epsilon_+ \exp(-\lambda r)(\lambda r + 1)}{r^3} \boldsymbol{v} & \text{in } \Omega_+ \\ -2C\epsilon_- \boldsymbol{v} & \text{in } \Omega_- \end{cases}$$

Here $\boldsymbol{v} = (x, y, z)$, r is the distance to the origin, C is a constant to be decided in terms of μ, $\lambda = \sqrt{\frac{1}{\epsilon_+}}$ is also a constant.

Numerical methods and results

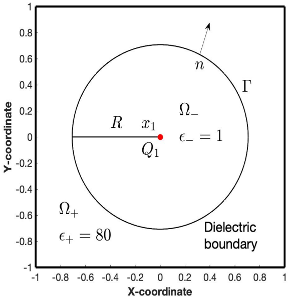


Figure 2: Computational domain

In numerical test, constants include

- Radius $R = 1/\sqrt{2}$
- Tolerance for the norm of the gradient $= 3 * 10^{-6}$

Parameters include

- Number of intervals on each direction N
- Penalty coefficient μ

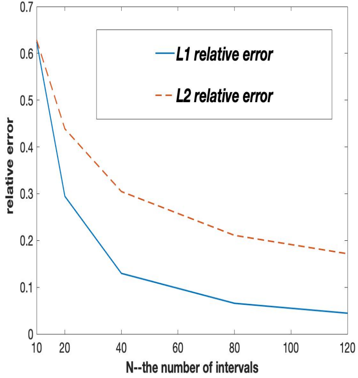
Result for $\mu = 1$, change N

N	L1 rel. error	L2 rel. error	Time	Epoch	Order
10	0.6250	0.6286	5s	1131	-
20	0.2944	0.4386	1m	1910	0.6119
40	0.1296	0.3046	20m	3867	0.5858
80	0.0657	0.2110	2h	5895	0.5564
120	0.0445	0.1716	14h	8439	0.5222

Table 1: Result for $\mu = 1$

The minimal value of the functional is approximately $1.23 * 10^4$. The order of convergence is approximately 0.5.

Result for $\mu = 1$, change N



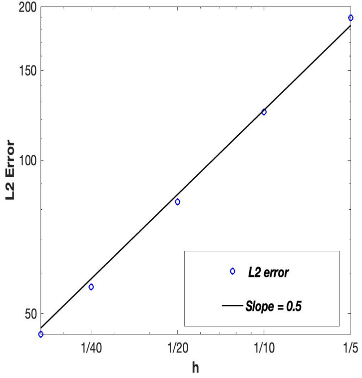


Figure 3: Result for $\mu = 1$

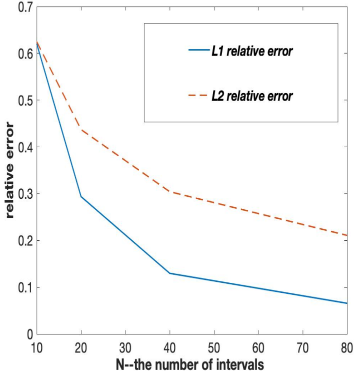
Result for $\mu = 10^{-2}$, change N

N	L1 rel. error	L2 rel. error	Time	Epoch	Order
10	0.6209	0.6250	30s	10983	-
20	0.2938	0.4371	13m	23582	0.6068
40	0.1298	0.3043	3.5h	56498	0.5818
80	0.0657	0.2109	3d8h	128958	0.5551

Table 2: Result for $\mu = 10^{-2}$

The minimal value of the functional is approximately $1.19 * 10^4$. The order of convergence is approximately 0.5.

Result for $\mu = 10^{-2}$, change N



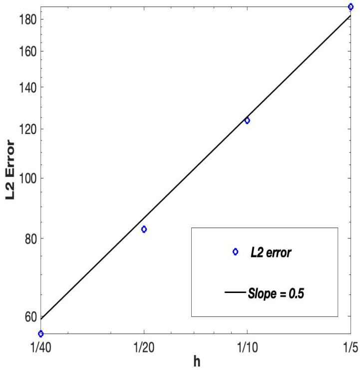


Figure 4: Result for $\mu = 10^{-2}$

Result for $\mu = 10^{-5}$, change N

N	L1 rel. error	L2 rel. error	Time	Epoch	Order
10	0.6209	0.6250	2m	5576	-
20	0.2938	0.4371	40m	80235	0.6067
40	0.1298	0.3043	5d	928830	0.5817

Table 3: Result for $\mu = 10^{-5}$

The minimal value of the functional is approximately $1.15 * 10^4$. The order of convergence is approximately 0.5.

Result for $\mu = 10^{-5}$, change N

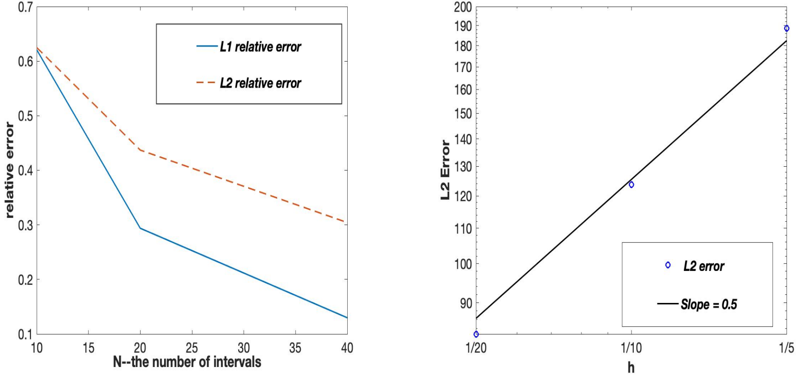


Figure 5: Result for $\mu = 10^{-5}$

Result for $N = 40$, change μ

μ	L1 rel. error	L2 rel. error	Time	Epoch	Value
10^5	1.4923	2.4879	30m	2150	2.92*10^7
10^4	0.9509	1.5560	10m	3018	2.92*10^6
10^3	0.3119	0.5732	10m	3003	3.02*10^5
10^2	0.1456	0.3360	5m	2588	4.05*10^4
10	0.1296	0.3077	10m	2520	1.44*10^4
1	0.1296	0.3046	20m	3867	1.18*10^4
10^{-1}	0.1297	0.3043	1h	11960	1.15*10^4
10^{-2}	0.1298	0.3043	3h30m	56498	1.15*10^4
10^{-5}	0.1298	0.3043	5d	928830	1.15*10^4

Table 4: Result for $N = 40$

Test for constraint

Numerical quadrature in Ω_-

As $\mu \to 0$,

$$E(D) = \int_{\Omega_-} (\nabla \cdot D - f)^2 dx \to 0$$

N	μ	E(D)	Min Value of LT PB functional
20	1	262.2015	$1.1317*10^4$
20	10^{-2}	0.0262	$1.1039*10^4$
20	10^{-5}	$2.6250*10^{-8}$	$1.1036*10^4$

Table 5: Result for numerical quadrature in Ω_-

Conclusions

1. LT PB functional: A novel convex functional for electrostatic energy.
2. Penalty method converges: Theoretical proof and numerical test.
3. Further improvement: Combine the model with the level-set method for molecular dynamics.