

Poisson Fermi Theory of Ionic Solutions

Bob Eisenberg

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Illinois Institute of Technology: Applied Math
Rush University: Physiology and Biophysics
Chicago

劉晉良



Jinn-Liang Liu

*discovered role of
SATURATION*

using

*Fermi Distribution
and Yukawa Potential in
Theories of Ionic Solutions*

We couple the
Screened Coulomb (Yukawa) Potential*
and
Far Field Poisson Electrostatics

***to avoid the Lennard Jones Combining Rules
that are
Badly defined in Experiments
and
Simulations of Liquids**

Lennard Jones potentials are troublesome

**because they have combining rules that are ill defined in experiments,
whether Lorentz-Berthelot or Kong.**

Combining parameters are likely to depend on ionic species, concentration and perhaps other variables.

It is dangerous to have a model that depends sensitively on parameters that are unknown experimentally.

Yukawa Screened Coulomb Potential

We use Yukawa potential $Y(\mathbf{r} - \mathbf{r}')$ to describe Bjerrum/Debye Screening

$$Y(\mathbf{r} - \mathbf{r}') = \frac{\exp(-|\mathbf{r}-\mathbf{r}'|/\lambda)}{4\pi|\mathbf{r}-\mathbf{r}'|} \quad (1)$$

Yukawa potential $Y(\mathbf{r} - \mathbf{r}')$ satisfies the differential equation

$$-\nabla^2 Y(\mathbf{r} - \mathbf{r}') + \frac{1}{\lambda^2} Y(\mathbf{r} - \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \quad (2)$$

$Y(\cdot)$ is the lowest order amplitude term in a general expansion of interaction of a pair of fermions

The effective dielectric function of $Y(\rho)$ is $\exp(-\rho/\lambda)$

λ is the Fermi-Thomas screening wave vector.

Definition

LOCAL POTENTIAL

$\tilde{\phi}(\mathbf{r})$ is defined by Poisson equation as

$$-\varepsilon_s \varepsilon_0 \nabla^2 \tilde{\phi}(\mathbf{r}) = \rho_I(\mathbf{r}) \stackrel{\text{def}}{=} \sum_1^K q_i c_i(\mathbf{r}) \quad (4)$$

Local Potential and Yukawa interaction must be joined to create a long range global potential to deal with correlations in high field or crowded conditions in which the size and valence of ions and the polarization of water play significant roles.

Ions are often crowded where they are important

Local Potential and Yukawa interaction
are joined
to create a long range
Global Potential

Global Potential is needed to deal with Correlations
in high field or crowded conditions
in which the size and valence of ions
and the polarization of water
are important.

Ions are often crowded where they are important:
DNA, ion channels, enzymes, binding proteins, electrodes, batteries, supercapacitors

We introduce a
GLOBAL POTENTIAL
 $\phi(\mathbf{r})$

that is a convolution of Yukawa screened Coulomb potential and the Poisson local potential $\tilde{\phi}$

$$\phi(\mathbf{r}) = \int \frac{1}{\lambda^2} Y(\mathbf{r} - \mathbf{r}') \tilde{\phi}(\mathbf{r}') d\mathbf{r}' \quad (5)$$

Multiply the Yukawa potential $Y(\mathbf{r} - \mathbf{r}')$ in its defining differential equation (2) by the local Poisson potential $\tilde{\phi}(\mathbf{r})$ and integrate to smooth the product, reducing the detail (and resolution) of the result.

The smoothed global potential $\phi(\mathbf{r})$ allows easier computation in a differential equation we will now use.

GLOBAL POTENTIAL

$$\phi(\mathbf{r})$$

is a convolution of the Yukawa screened Coulomb potential and the local Poisson potential

The global potential is a convolution eq. (5) and also a solution of the differential equation

$$\lambda^2 \nabla^2 \phi(\mathbf{r}) + \phi(\mathbf{r}) = \tilde{\phi}(\mathbf{r}) \quad (6)$$

ϕ becomes approximate when we impose a finite domain for computation

See Xie and Volkmer (2015) Comm Computational Physics 13:174-194.

also Hildebrandt et al (2004) Phys. Rev. Lett. **93**, 108104;

Xie, Liu, and Eisenberg, Phys. Rev. E (2016) **94**, 012114;

using numerical methods in Xie, et al, (2012) 34:B107-B126.

GLOBAL POTENTIAL $\phi(\mathbf{r})$

combines Yukawa Screened Coulomb and Poisson Far Field

$$-\varepsilon_s \varepsilon_0 \nabla^2 \tilde{\phi}(\mathbf{r}) = \rho_I(\mathbf{r}) \stackrel{\text{def}}{=} \sum_1^K q_i C_i(\mathbf{r}) \quad (4)$$

$$\lambda^2 \nabla^2 \phi(\mathbf{r}) + \phi(\mathbf{r}) = \tilde{\phi}(\mathbf{r}) \quad (6)$$

Eq. (4) and (6) give the fourth order equation

$$\lambda^2 \varepsilon_s \varepsilon_0 \nabla^4 \phi(\mathbf{r}) + \varepsilon_s \varepsilon_0 \nabla^2 \phi(\mathbf{r}) = \rho_I(\mathbf{r}) \quad (7)$$

which is best solved as a pair of second order differential equations, *we think*

Liu and Eisenberg (2015) Phys Rev E 92: 012711, also <https://arxiv.org/pdf/011506.005953>

Liu and Eisenberg (2018) J Chem Phys 148:054501, also <https://arxiv.org/abs/1801.03470>

We move from the potential
to

Free energy

using a functional formulation
but not yet dissipation

Free energy formulation with functionals

$$F(\mathbf{C}, \phi) = F_{el}(\mathbf{C}, \phi) + F_{en}(\mathbf{C}), \quad (8)$$

$$F_{el}(\mathbf{C}, \phi) = \frac{1}{2} \int \rho_I \phi \, d\mathbf{r} + \frac{1}{2} \int \rho_I L^{-1} \phi \, d\mathbf{r} \quad (9)$$

$$F_{en}(\mathbf{C}) = k_B T \int \left\{ \sum_1^K q_i C_i(\mathbf{r}) \left(\ln \frac{C_i(\mathbf{r})}{C_i^B} - \mathbf{1} \right) + \frac{\Gamma(\mathbf{r})}{v_0} \left(\ln \frac{\Gamma(\mathbf{r})}{\Gamma^B} - \mathbf{1} \right) \right\} d\mathbf{r} \quad (10)$$

Here $F_{en}(\mathbf{C})$ is our (saturating) entropy functional embodying the entropy of all species C_i **and their steric interactions**; $F_{el}(\mathbf{C}, \phi)$ is our electrostatic functional; the sum over index i is

$$\text{Average Volume} \stackrel{\text{def}}{=} v_0 = \frac{1}{K+1} \sum_1^{K+1} v_i \quad (11)$$

And L^{-1} is the inverse of the fourth order self adjoint positive linear operator

$$\text{Fourth Order Operator} \quad L = \lambda^2 \varepsilon_s \varepsilon_0 \nabla^4 \phi(\mathbf{r}) + \varepsilon_s \varepsilon_0 \nabla^2 \phi(\mathbf{r}) \quad (12)$$

It is usually best numerically to rewrite the L operator as a pair of second order operators.

Taking the variation of $F(\mathbf{C}, \phi)$ at ϕ
recovers previous

Crucial Multiscale Equation that links Atomic and Macroscales of Potential

$$\lambda^2 \varepsilon_s \varepsilon_0 \nabla^4 \phi(\mathbf{r}) + \varepsilon_s \varepsilon_0 \nabla^2 \phi(\mathbf{r}) = \rho_I(\mathbf{r}) \quad (13)$$

with $\phi(\mathbf{r}) = \mathbf{0}$ on the boundary.

This equation is converted to two second order differential equations
to make numerical treatments easier and more accurate.

Saturation Phenomena

Crucial in crowded systems,
Near electrodes, DNA,
in ion channels, binding proteins,
Enzyme active sites,
Batteries, Electrodes, Supercapacitors

Ions are often crowded where they are most important

Much less important in homogeneous bulk solutions

Volume in our Hard Sphere Model

Spherical Ions are Species 1, 2, 3 ... K
Spherical 'Water' is Species $K + 1$
Voids* are Species $K + 2$

$$\text{Volume } V \equiv \underbrace{\sum_1^{K+1} v_i N_i}_{\text{Ions + Water}} + \underbrace{V_{K+2}}_{\text{Voids}} \quad (14)$$

The volume of each sphere $v_i = \frac{4}{3}a_i^3$ where a_i is the radius of the i^{th} species
 N_i is the total number of spheres in the volume V .

***Voids are needed to fill space
and for actual computations, as we shall see,
spheres cannot fill space.
Leaving out spheres produces contradictions and severe
Numerical difficulties**

Void Volume Fraction $\Gamma(\mathbf{r})$

is a key measure of crowding* in the Fermi Distribution
 \Rightarrow free energy per mole = the activity of voids

$$\Gamma(\text{voids}; \mathbf{r}) \stackrel{\text{def}}{=} \frac{V_{K+2}}{V} = \mathbf{1} - \underbrace{\sum_1^{K+1} v_i C_i(\mathbf{r})}_{\text{Ions + Water}} \quad (15)$$

***Ions are usually crowded where they are important,
Near DNA and Electrodes
Near and in ion channels, binding proteins, enzyme active sites.**

Steric Potential $S^{trc}(\mathbf{r})$

is

Normalized* Activity of Voids[§]

Key parameter in the Fermi Distribution

$$S^{trc}(\mathbf{r}) \stackrel{\text{def}}{=} \ln \left(\Gamma(\mathbf{r}) / \Gamma^{\text{Bulk}} \right) \quad (16)$$

*Normalized with respect to the bulk homogeneous solution Γ^{Bulk} .

[§] Ions are usually crowded where they are important,
near DNA and Electrodes

near and in

Ion Channels, Binding proteins, Enzyme Active Sites

$$\Gamma^{\text{Bulk}} \stackrel{\text{def}}{=} \sum_1^{K+1} \nu_i C_i(\text{Bulk}) \quad \Gamma(\mathbf{r}) \stackrel{\text{def}}{=} \sum_1^{K+1} \nu_i C_i(\mathbf{r}) \quad (17)$$

Steric Potential and the Fermi Distribution*

$$\text{Steric Potential} = S^{trc}(\mathbf{r}) \stackrel{\text{def}}{=} \ln \left(\Gamma(\mathbf{r}) / \Gamma^B \right) \quad (18)$$

$\Gamma^B = \text{reference potential of bulk}$

Determines the

Fermi Distribution of Concentrations*

$$C_i(\mathbf{r}) = C_i^B \exp \left(-\beta_i \phi(\mathbf{r}) + \frac{v_i}{v_0} S^{trc}(\mathbf{r}) \right) \quad \text{where } \beta_i = q_i / k_B T. \quad (19)$$

for **ions** $i = 1, 2, \dots, K.$

and

also **Water** $i = K + 1.$ Water net charge = $q_{K+1} = 0.$

*Fermi distribution saturates!

Saturation Phenomena

can be derived
from the Free Energy Functionals

Taking the variation of $F(\mathbf{C}, \phi)$ at $C_i(\mathbf{r})$, yields saturating, Fermi like distributions that we like to write in terms of the

$$\text{Steric Potential} = S^{trc}(\mathbf{r}) \stackrel{\text{def}}{=} \ln(\Gamma(\mathbf{r})/\Gamma^B); \quad \Gamma^B = \text{reference potential of bulk} \quad (20)$$

that determines the

Fermi Distribution of Concentrations

$$C_i(\mathbf{r}) = C_i^B \exp\left(-\beta_i \phi(\mathbf{r}) + \frac{v_i}{v_0} S^{trc}(\mathbf{r})\right) \quad \text{where } \beta_i = q_i/k_B T \quad (21)$$

for all **ions** $i = 1, 2, \dots, K.$

and also

for **Water** $i = K + 1.$

Water net charge = $q_{K+1} = 0$

Fermi Distribution \Leftrightarrow Saturation

$$C_i(\mathbf{r}) = C_i^B \exp\left(-\beta_i \phi(\mathbf{r}) + \frac{v_i}{v_0} S^{trc}(\mathbf{r})\right) \quad \text{where } \beta_i = q_i/k_B T$$

All concentration functions $C_i(\mathbf{r}) < 1/v_i$

$C_i(\mathbf{r})$ cannot exceed the maximum value $1/v_i$
for any arbitrary (**or even infinite**) potential

Voids

Spheres cannot fill space

Treatments with water as spheres cannot be computed unless voids are included

Proof Follows

Interdisciplinary Confusion

Interdisciplinary Confusion

Physiologists[§] give the following
Saturating Distribution
the name
'Boltzmann'

$$Q(V) = \frac{Q_{max}}{1 + \exp(-Q_{max}(V - V_{1/2})/k_B T)}$$

[§] p.503 of Hodgkin and Huxley. 1952.
'Quantitative description ...' J. Physiol. 117:500-544.

[§] Bezanilla, Villalba-Galea J. Gen. Physiol (2013) 142: 575
'Gating charge ...'

Boltzmann Distribution*
of Physicists
 $\exp(-Q_{max}(V)/k_B T)$
does NOT Saturate

Fermi Distribution Saturates

* Boltzmann. Berkeley 'Lectures on Gas Theory', 1904 (!)

Proof: System Must Contain Voids

Consider a system without voids,

i.e., with $V_{K+2} = 0$

Let's try to fill the volume

(1) with ions 1, 2, 3 ... K at concentrations $C_i(\mathbf{r})$

and

(2) with the single water species $K+1$

and then use a Fermi Distribution.

We will find a contradiction.

We can use a Fermi Distribution only if we include voids.

Proof: System Must Contain Voids

**Consider a system without voids,
i.e., with $V_{K+2} = 0$**

We will find a contradiction.

Fermi Distribution for Spheres Requires Voids

Consider a system without voids,

i.e., with $V_{K+2} = v_{K+2} = 0$

If the system is filled with spheres, with zero voids,
then the volume fraction of voids is zero: $\Gamma(\mathbf{voids}; \mathbf{r}) = 0$

$$\Gamma(\mathbf{voids}; \mathbf{r}) = 0 = \mathbf{1} - \underbrace{\sum_1^{K+1} v_i C_i(\mathbf{r})}_{\text{Ions + Water}} \quad (22)$$

$$\mathbf{1} = \underbrace{\sum_1^{K+1} v_i C_i(\mathbf{r})}_{\text{Ions + Water}} \quad (23)$$

Consider a system without voids,

i.e., with $V_{K+2} = v_{K+2} = 0$

If the system is filled with spheres, with zero voids,
then the volume fraction of voids $\Gamma(\mathbf{voids}; \mathbf{r}) = 1 - \sum_1^{K+1} v_i c_i(\mathbf{r}) = 0$

$$\text{Steric Potential} = S^{trc}(\text{filled with spheres}; \mathbf{r}) = \ln(\Gamma(\mathbf{voids}; \mathbf{r})/\Gamma^B) = \ln(0/\Gamma^B)$$

Ions + Water

$$\text{Steric Potential} = S^{trc}(\text{filled with spheres}; \mathbf{r}) = -\infty \quad (24)$$

Consider a system without voids,

i.e., with $V_{K+2} = v_{K+2} = 0$

If the system is filled with spheres, without voids,
then the volume fraction of voids $\Gamma(\mathbf{voids}) = \Gamma(\mathbf{voids}; \mathbf{r}) = 0$ is zero

$$\text{Steric Potential} = S^{trc}(\textit{filled with spheres}; \mathbf{r}) \stackrel{?}{=} -\infty \quad (25)$$

$$C_i(\mathbf{r}) = C_i^B \exp\left(-\frac{q_i}{k_B T} \phi(\mathbf{r}) + \overbrace{\frac{v_i}{v_0} S^{trc}(\mathbf{r})}^{-\infty}\right) \Rightarrow C_i(\mathbf{r}) \stackrel{?}{=} 0 \quad (26)$$

$C_i(\mathbf{r}) \stackrel{?}{=} 0$ contradicts our original assumption of general $C_i(\mathbf{r})$

Proof

Consider a system without voids,

i.e., with $V_{K+2} = v_{K+2} = 0$

Conclusion:

We must have voids if we use a Fermi Distribution

But we only need the

Total Void Volume,

or Volume Fraction

No other details are needed about the voids

Any Questions ?