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Modification of Bikerman model with specific ion sizes

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Abstract: Classical Poisson-Boltzman and Poisson-Nernst-Planck models can only work when ion concentrations are very dilute, which often mismatches experiments. Researchers have been working on the modification to include finite-size effect of ions, which is non-negelible when ion concentrations are not dilute. One of modified models with steric effect is Bikerman model, which is rather popular nowadays. It is based on the consideration of ion size by putting additional entropy term for solvent in free energy. However, ion size is non-specific in original Bikerman model, which did not consider speific ion sizes. Many researchers have worked on the extension of Bikerman model to have specific ion sizes. A direct extension of original Bikerman model by simply replacing the non-specific ion size to specific ones seems natural and has been acceptable to many researchers in this field. Here we prove this straight forward extension, in some limiting situations, fails to uphold the basic requirement that ion occupation sites must be identical. This requirement is necessary when computing entropy via particle distribution on occupation sites. We derived a new modified Bikerman model for using specific ion sizes by fixing this problem, and obtained its modified Poisson-Boltzmann and Poisson-Nernst-Planck equations.

1 Introduction

One of the major limitations of the Poisson-Boltzmann (PB) and Poisson-Nernst-Planck (PNP) models is the assumption of point-like ions without considering their sizes. These models based on mean field theories work well for dilute solutions, but breaks down when the electrolyte is concentrated and ions are crowded in it. High concentration would generally cause steric repulsions and additional correlations among ions. This problem becomes serious at certain situations. For example, the concentration of counter-ions can be unreasonably high near electrode surface, as predicted by PB, when electrode voltage is large. Another example occurs at selectivity filter in potassium channel, where potassium ion is strongly attracted into this extremely narrow filter by strong negative charges of oxygen from carbonyl groups of TVGYG amino acids forming the backbone of filter. Employing PB and PNP would over-estimate the population of potassium ion inside filter and give incorrect prediction of channel current. Therefore, many researchers have worked on the modification of PB and PNP models to include the steric effect of ions.

Among many modified PB and PNP models with steric effect based on local/non-local hard-sphere (HS) potential [6, 7], Bikerman model [1] has been a popular local HS model due to its easiness of application and qualitatively good agreement with experiments. It is also called Andelman model since Andelman's group independently rediscovered it in 1997 [2]. This model has been popular because it captures basic size effects of ions by using a rather simplified formulation. It modifies the free energy of an ionic system based on mean-field approximation by adding an ideal-gas-like solvent entropy term. This term also represents the excessive energy accounting for over-crowding of ions and solvent molecules [3].

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The free energy in Bikerman model treats all species of ions and solvent molecule with an identical size, and a modified PB/PNP model can then be derived through the minimization of this corrected free energy. A natural extension of original Bikerman model to account for specific ion sizes is simply replacing the identical ion size used in the original model by specific ion sizes and many researchers used that without rigorous derivation for justification. A thorough justification of this extension through serious derivation has been conducted only in a few literatures [4, 5]. However, the entropy part in the derivation of [4, 5] is based on traditional mean-field gas lattice model. It states the most probable state of particle distribution to reach maximum entropy is that each particle would occupy just one occupation site and each occupation site can at most be occupied by a single particle. To further calculate the entropy based on this idea by combinatorics and then simplify it by Stirling formula, we need to assume all occupation sites are identical in size (characterized by identical side length of cubical sites). Otherwise, combinatorics would not apply. When ion concentrations are extremely large in some limiting situations, the modified Bikerman model by simply replacing the identical ion size with specific ion sizes seems to fail to uphold this basic requirement of identical occupation sites as shown in latter section. The discussion and fixing of this problem will be the main theme of current study.

2 Review of Bikerman model

Suppose ion sepcies and the solvent molecules are treated as hard spheres and assumed to have the same diameter a. Taking binary electrolyte as an example, the free energy based on Bikerman model is given as follows,

$$F = U - TS \tag{1}$$

where U is internal energy, S is entropy, T is absolute temperature:

$$U = \int \left[-\frac{\epsilon}{2}|\nabla\phi|^2 + z_p e p\phi + z_n e n\phi\right] dV, \tag{2}$$

$$-TS = \int k_B T \left[p log\left(pa^3\right) + n log\left(na^3\right) + \frac{(1 - pa^3 - na^3)}{a^3} log\left(1 - pa^3 - na^3\right)\right] dV, \tag{3}$$

where ϕ is the electrostatic potential; p is the concentration of cation with the valence z_p; n is the concentration of anion with valence z_n; k_B is the Boltzmann constant.

The variation of F with respect to ϕgives the Poisson equation,

$$-\nabla \cdot (\epsilon\nabla\phi) = z_p e p + z_n e n \tag{4}$$

By doing the variation of F with respect to p and n, we can obtain the chemical potentials for cation and anion, respectively.

$$\frac{\partial F}{\partial p} = \mu_p = z_p e\phi + k_B T\left[log\left(pa^3\right) - log\left(1 - pa^3 - na^3\right)\right] \tag{5}$$

$$\frac{\partial F}{\partial n} = \mu_n = z_n e\phi + k_B T\left[log\left(na^3\right) - log\left(1 - pa^3 - na^3\right)\right] \tag{6}$$

Subtracting Eq. (6) from Eq. (5), we get

$$p = n\, exp\left(\beta\left(\mu_p - \mu_n\right) - \beta(z_p - z_n) e\phi\right) \tag{7}$$

where $\beta = \frac{1}{k_B T}$. Note that when equilibrium, μ_p and μ_n would be uniform in space. Assuming electroneutrality in the region far away, i.e., $z_p p + z_n n = 0, \quad \phi \to 0$, as $x \to \infty$, we then obtain from Eq. (7),

$$e^{\beta(\mu_p - \mu_n)} = \frac{-z_n}{z_p} \tag{8}$$

and thus

$$p = -n\frac{z_n}{z_p} e^{-\beta(z_p - z_n)e\phi} \tag{9}$$

From Eq. (5), we get

$$\frac{pa^3}{1 - pa^3 - na^3} = e^{\beta(\mu_p - z_p e\phi)} \tag{10}$$

Substitute Eq. (9) into Eq. (6), we obtain

$$\frac{na^3}{1 + n\frac{z_n}{z_p}a^3 e^{-\beta(z_p - z_n)e\phi} - na^3} = e^{\beta(\mu_n - z_n e\phi)} \tag{11}$$

Hence,

$$n = \frac{1}{a^3}\frac{1}{1 + e^{-\beta(\mu_n - z_n e\phi)} - \frac{z_n}{z_p}e^{-\beta(z_p - z_n)e\phi}} \tag{12}$$

For bulk solution, $p \to p_b, \quad n \to n_b, \quad \phi \to 0$, and Eq. (12) gives

$$e^{\beta\mu_n} = \frac{n_b a^3}{1 - \left(1 - \frac{z_n}{z_p}\right) n_b a^3} \tag{13}$$

Substituting Eq. (13) into Eq. (12), we can obtain the concentration of anion.

$$n = \frac{n_b e^{-\beta z_n e\phi}}{1 - \nu + \nu\frac{\left(z_p e^{-\beta z_n e\phi} - z_n e^{-\beta z_p e\phi}\right)}{\left(z_p - z_n\right)}} \tag{14}$$

where $\nu = \left(1 - \frac{z_n}{z_p}\right) n_b a^3 = (p_b + n_b)a^3$ is the volume fraction of ions at bulk solution.

Substituting Eq. (14) into Eq. (9), we can further obtain the concentration of cation,

$$p = \frac{p_b e^{-\beta z_p e\phi}}{1 - \nu + \nu\frac{\left(z_p e^{-\beta z_n e\phi} - z_n e^{-\beta z_p e\phi}\right)}{\left(z_p - z_n\right)}} \tag{15}$$

Finally, substiuting Eqs. (14) and (15) into Eq. (4), we obtain the modified PB equation based on Bikerman model (or called Poisson-Fermi equation since p and n above follow Fermi-Dirac distribution instead of Boltzmann distribution),

$$-\nabla \cdot (\epsilon\nabla\phi) = \frac{z_p e p_b e^{-\beta z_p e\phi} + z_n e n_b e^{-\beta z_n e\phi}}{1 - \nu + \nu\frac{\left(z_p e^{-\beta z_n e\phi} - z_n e^{-\beta z_p e\phi}\right)}{\left(z_p + z_n\right)}} \tag{16}$$

For a symmetric z:z electrolyte, i.e., $z_p = -z_n = z$, and letting $p_b = n_b = c_0$, Eqs. (14) and (15) can be reduced to

$$n = \frac{c_0 e^{\beta z e\phi}}{1 + 2\nu sinh^2\left(\frac{\beta z e\phi}{2}\right)}, \qquad p = \frac{c_0 e^{-\beta z e\phi}}{1 + 2\nu sinh^2\left(\frac{\beta z e\phi}{2}\right)} \tag{17}$$

and then Eq. (16) can be written as

$$\nabla \cdot (\epsilon\nabla\phi) = \frac{2zec_0 sinh\left(\beta z e\phi\right)}{1 + 2\nu sinh^2\left(\frac{\beta z e\phi}{2}\right)} \tag{18}$$

Here $\nu = 2c_0 a^3$. When ion concentrations are dilute, i.e., $\nu \ll 1$, Eq. (18) is further reduced to classical PB equation for z:z electrolyte:

$$\nabla \cdot (\epsilon\nabla\phi) = 2zec_0 sinh\left(\beta z e\phi\right) \tag{19}$$

3 Extension of Bikerman model to account for specific ion size

The derivation above is based on the assumption that cation and anion have the same diameter a. Bikerman model has been often modified for cation and anion to accommodate specific ion diameters by a direct extension of chemical potentials in Eqs. (5) and (6) to

$$\mu_p = z_p e\phi + k_B T log\left(\frac{pa_p^3}{1 - pa_p^3 - na_n^3}\right) \tag{20}$$

$$\mu_n = z_n e\phi + k_B T log\left(\frac{na_n^3}{1 - pa_p^3 - na_n^3}\right) \tag{21}$$

where a_p and a_n are diameters for cation and anion respectively. [4, 5] gives a rigorous derivation of Eqs. (20) and (21) from mean-field lattice gas model. For equilibrium, from Eqs. (20) and (21), we can obtain the following equations from uniform distribution of chemcal potentials and equating the chemical potential anywhere to that of bulk solution, where electro-neutrality is assumed:

$$k_B T log\left(\frac{p_b a_p^3}{1 - p_b a_p^3 - n_b a_n^3}\right) = z_p e\phi + k_B T log\left(\frac{pa_p^3}{1 - pa_p^3 - na_n^3}\right) \tag{22}$$

$$k_B T log\left(\frac{n_b a_n^3}{1 - p_b a_p^3 - n_b a_n^3}\right) = z_n e\phi + k_B T log\left(\frac{na_n^3}{1 - pa_p^3 - na_n^3}\right), \tag{23}$$

and we can further derive

$$p = \frac{p_b exp\left(-\beta z_p e\phi\right)}{1 + p_b a_p^3 \left(exp\left(-\beta z_p e\phi\right) - 1\right) + n_b a_n^3 \left(exp\left(-\beta z_n e\phi\right) - 1\right)} \tag{24}$$

$$n = \frac{n_b exp\left(-\beta z_n e\phi\right)}{1 + p_b a_p^3 \left(exp\left(-\beta z_p e\phi\right) - 1\right) + n_b a_n^3 \left(exp\left(-\beta z_n e\phi\right) - 1\right)}. \tag{25}$$

We can further obtain the modifed PB equation based on this version of Bikerman model considering specific ion size:

$$-\nabla \cdot (\epsilon \nabla \phi) = \frac{z_p e p_b exp\left(-\beta z_p e\phi\right) + z_n e n_b exp\left(-\beta z_n e\phi\right)}{1 + p_b a_p^3 \left(exp\left(-\beta z_p e\phi\right) - 1\right) + n_b a_n^3 \left(exp\left(-\beta z_n e\phi\right) - 1\right)} \tag{26}$$

With $a_p^3 = a_n^3 = a^3$, Eq. (26) can be reduced to Eq. (16).

However, here we think Eqs. (20) and (21), though can be reduced to chemical potential for original PB when ionic concentrations are dilute, still might have some minor problem when concentration of cation or anion is extremely large in some situations as mentioned above. This minor problem, an inconsistency with some criterion underlying the traditional calculation of entropy via combinatorics, can be comprehended by taking the limit $\phi \to -\infty$ for Eq. (24), and we obtain $p \to \frac{1}{a_p^3}$. Similarly, letting $\phi \to \infty$ for Eq. (25), we obtain $n \to \frac{1}{a_n^3}$. It means as the magnitude of electric potential approaches infinity, the concentration of counter-ion will increases as well. Size of occupation site will decrease accordingly due to crowdness, but will limit to $max\left\{a_p, a_n\right\}$, since each cation and anion particle are requested to occupy identical site, which provides the necessary combinatorial basis when computing entropy based on mean-field lattice gas model. Ion concentrations p and n should both approach $\frac{1}{a^3}$ with $a = max\left\{a_p, a_n\right\}$ due to single-ion site occupation at this limiting situation instead of $\frac{1}{a_p^3}$ and $\frac{1}{a_n^3}$ respectively. This is illustrated in Fig. 1(a). The limitation that each identical site can only be occupied by a single particle at most would cause quite an uneconomic use of space when ions are extremely crowded (under high concentrations) and size of a certain species of ion is much larger than the others. However, if ions can be packed like Fig. 1(b) instead of Fig. 1(a) at extreme high concentrations. The use of space would be more economic. If multiple ions of the same species can occupy a site like Fig. 1(b) when ion concentrations are extremely large, it would justify the limits $n \to \frac{1}{a_n^3}$ and $p \to \frac{1}{a_p^3}$ as $\phi \to \pm\infty$ without compromise to the limit $p, n \to \frac{1}{a^3}$ with $a = max\left\{a_p, a_n\right\}$, since occupation sites can still maintain to be identical. The entropy computation under this extreme packing case requires a new derivation, which will lead to a newly modified Bikerman model as shown in next section. One might argue that Coulomb force will be very large if ions are packed like Fig. 1(b), and will hinder this kind of arrangement especially when Coulomb force between ions are repulsive. Actually Coulomb forces between ions are delicate when there exists solvent molecule, and packing of ions like Fig. 1(b) can be possible. Also, we can treat all species of particles here carrying no chrage, since we are deriving their entropy only.

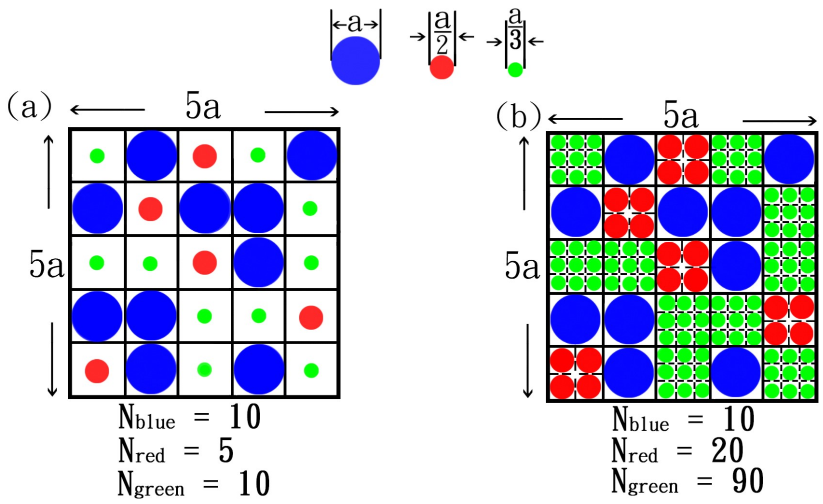

Figure 1: (a) The most probable distribution of blue, red and green particles to compute the entropy by mean-field lattice gas model in the case of crowdness. Note that the occupation site needs to be identical to justify the combinatorics used in entropy computation. (b) Modification of (a) to allow extra number of particles of the same kind to reside in each identical occupation site in the case of extreme crowdness. Here $r_{blue} = 1$, $r_{red} = 4$, $r_{green} = 9$.

4 Modification of Bikerman model to include specific ion sizes

When computing entropy, in the approach of traditional mean-field discrete lattice gas model, charge carriers are distributed over a three dimensional cubic lattice where the volume of a single site is a^3. Thus, by dividing space into discrete cells (lattice sites) and limiting the occupation of each cell to a single ion would give us the most probable distribution used to calculate the entropy. Cell site length $a$can be as small as the maximum diameter of ions at most no matter how crowded ions are. This explains why diameter of cation and anion are set to be the same (maximum diameter among them) in original Bikerman model. However, it seems plausible that the presence of ions with large difference in size could lead to a new distribution in the situation of high ion concentrations as shown in Fig. 1(b). For this case of highly packed and crowded ions, we assume each cell can allow the occupation of multiple ions of the same kind, when that ion is not the biggest one among all. Based on this, the entropy will turn out somewhat different from before, and will be illustrated as below.

Consider the free energy for an aqueous electrolyte system,

$$F = U - TS = \sum_{j=1}^{K} \tilde{N}_j q_j \phi - k_B T \log W \tag{27}$$

where $q_j = z_j e$, $\tilde{N}_j$ is the total number of j-species ions and N_j is number of identical cells occupied by j-species particles with $\tilde{N}_j \geq N$. If an identical site can allow r_j j-species ions to occupy as illustrated in Fig. 1(b), we can then relate $\tilde{N}_j$ and N_j by $\tilde{N}_j = N_j r_j$. The entropy based on the most probable distribution of all ions and solvent molecules over a total of N available identical sites in a system is

$$W = \prod_{j=1}^{K} W_j = \frac{N!}{N_1!\,(N-N_1)!}\,\frac{(N-N_1)!}{N_2!\,(N-N_1-N_2)!}\cdots\frac{\left(N-\sum_{j=1}^{K-1} N_j\right)!}{N_K!\left(N-\sum_{j=1}^{K} N_j\right)!}\,\frac{\left(N-\sum_{j=1}^{K} N_j\right)!}{N_{K+1}!} = \frac{N!}{\left(\prod_{j=1}^{K} N_j!\right) N_{K+1}!}. \tag{28}$$

Note that, after all the ions are distributed, there are $N - \sum_{j=1}^{K} N_j = N_{K+1}$ sites that will be filled by solvent molecules. Also, the underlying criterion for the above combinatorics to hold is that all particle occupation sites must be identical in size, and this criterion is uphold here, even at limiting situations, with the reasoning of an identical site able to be occupied by multiple particles.

So the free energy becomes

$$F=\sum_{j=1}^{K}\tilde{N}_j q_j\phi-k_BT\,log\frac{N!}{\left(\prod_{j=1}^{K}N_j!\right)N_{K+1}!} \tag{29}$$

Using the Stirling formula $logM!\approx MlogM-M$ with $M\gg 1$, we can rewrite the free energy as

$$\begin{aligned}F&=\sum_{j=1}^{K}\tilde{N}_j q_j\phi-k_BT\,[NlogN-N-\sum_{j=1}^{K}N_jlogN_j+\sum_{j=1}^{K}N_j-\left(N-\sum_{j=1}^{K}N_j\right)log\left(N-\sum_{j=1}^{K}N_j\right)+\left(N-\sum_{j=1}^{K}N_j\right)]\\&=\sum_{j=1}^{K}\tilde{N}_j q_j\phi-k_BT\left[Nlog\frac{N}{N-\sum_{j=1}^{K}N_j}-\sum_{j=1}^{K}N_jlog\frac{N_j}{N-\sum_{j=1}^{K}N_j}\right]\end{aligned} \tag{30}$$

Using the follwing relation,

$$V=Na^3,\quad or\quad \frac{N}{V}=\frac{1}{a^3} \tag{31}$$

$$\frac{N_j}{N}=\frac{N_ja^3}{Na^3}=\frac{\frac{\tilde{N}_j}{r_j}r_ja_j^3}{V}=c_ja_j^3, \tag{32}$$

$$\frac{N_j}{V}=\frac{N_j}{N}\frac{N}{V}=c_j\frac{a_j^3}{a^3}=\frac{c_j}{r_j}. \tag{33}$$

where c_j is the concentration of j species; V is the volume of system; $a=max\{a_p,a_n\}$. The free energy per unit volume can be expressed as

$$f=\frac{F}{V}=\sum_{j=1}^{K}c_jq_j\phi-k_BT\left[\frac{1}{a^3}log\frac{1}{1-\sum_{j=1}^{K}c_ja_j^3}-\sum_{j=1}^{K}\frac{c_j}{r_j}log\frac{c_ja_j^3}{1-\sum_{j=1}^{K}c_ja_j^3}\right]. \tag{34}$$

For binary electrolyte,

$$f=pq_p\phi+nq_n\phi-k_BT\left[\frac{1}{a^3}log\frac{1}{1-pa_p^3-na_n^3}-\frac{p}{r_p}log\frac{pa_p^3}{1-pa_p^3-na_n^3}-\frac{n}{r_n}log\frac{na_n^3}{1-pa_p^3-na_n^3}\right],$$

and

$$\mu_p=\frac{\delta f}{\delta p}=q_p\phi+\frac{k_BT}{r_p}\,log\frac{pa_p^3}{1-pa_p^3-na_n^3} \tag{35}$$

$$\mu_n=\frac{\delta f}{\delta n}=q_n\phi+\frac{k_BT}{r_n}\,log\frac{na_n^3}{1-pa_p^3-na_n^3}. \tag{36}$$

Notes that if $r_p=r_n=1$, Eqs. (35) and (36) will reduce to Eqs. (20) and (21), and the derivation above is equivalent to the derivation in [4, 5]. Again for equilibrium and then chemical potentials being uniform in space,

$$\frac{k_BT}{r_p}\,log\frac{p_ba_p^3}{1-p_ba_p^3-n_ba_n^3}=q_p\phi+\frac{k_BT}{r_p}\,log\frac{pa_p^3}{1-pa_p^3-na_n^3} \tag{37}$$

$$\frac{k_BT}{r_n}\,log\frac{n_ba_n^3}{1-p_ba_p^3-n_ba_n^3}=q_n\phi+\frac{k_BT}{r_n}\,log\frac{na_n^3}{1-pa_p^3-na_n^3}. \tag{38}$$

Eqs. (37) and (38) are solved to obtain

$$p=\frac{p_bexp\left(-\beta z_pr_pe\phi\right)}{1+p_ba_p^3\left(exp\left(-\beta z_pr_pe\phi\right)-1\right)+n_ba_n^3\left(exp\left(-\beta z_nr_ne\phi\right)-1\right)} \tag{39}$$

$$n=\frac{n_bexp\left(-\beta z_nr_ne\phi\right)}{1+p_ba_p^3\left(exp\left(-\beta z_pr_pe\phi\right)-1\right)+n_ba_n^3\left(exp\left(-\beta z_nr_ne\phi\right)-1\right)}. \tag{40}$$

Again when $r_p = r_n = 1$, Eqs. (39) and (40) reduce to Eqs. (24) and (25). By taking the limit $\phi \to -\infty$ for Eq. (39), we obtain $p \to \frac{1}{a_p^3}$. Similarly, letting $\phi \to \infty$ for Eq. (40), we obtain $n \to \frac{1}{a_n^3}$. These justify the extremely crowded situation like Fig. 1(b). Note that, though same limits are reached as by Eqs. (24) and (25), now there is no contraint like $p, n \to \frac{1}{a^3}$ with $a = max\{a_p, a_n\}$ needed to be comprimised with. Substitue Eqs. (39) and (40) into Eq. (4), we obtain modified PB equation based on this corrected version of model,

$$-\nabla \cdot (\epsilon \nabla \phi) = \frac{z_p e p_b exp\left(-\beta z_p r_p e\phi\right) + z_n e n_b exp\left(-\beta z_n r_n e\phi\right)}{1 + p_b a_p^3 \left(exp\left(-\beta z_p r_p e\phi\right) - 1\right) + n_b a_n^3 \left(exp\left(-\beta z_n r_n e\phi\right) - 1\right)} \tag{41}$$

However, when ion concentrations are dilute, i.e., $p_b a_p^3 \ll 1$, and $n_b a_n^3 \ll 1$, Eqs. (39) and (40) reduce to

$$p = p_b exp\left(-\beta z_p r_p e\phi\right), \qquad n = n_b exp\left(-\beta z_n r_n e\phi\right) \tag{42}$$

which violates the Boltzmann distribution that p and n should behave in dilute electrolyte:

$$p = p_b exp\left(-\beta z_p e\phi\right), \qquad n = n_b exp\left(-\beta z_n e\phi\right) \tag{43}$$

This problem is also observed in modified Nernst-Planck equations. For non-equilibrium system, we obtain flux by

$$J_p = -\frac{D_p}{k_B T} p \frac{\partial \mu_p}{\partial x}, \tag{44}$$

$$J_n = -\frac{D_n}{k_B T} n \frac{\partial \mu_n}{\partial x}. \tag{45}$$

Substitute Eqs. (35) and (36) into Eqs. (44) and (45), we obtain

$$J_p = -\frac{D_p}{k_B T} z_p e p \frac{\partial \phi}{\partial x} - \frac{D_p}{r_p}\left(\frac{\partial p}{\partial x} + \frac{p a_p^3}{1 - p a_p^3 - n a_n^3}\frac{\partial p}{\partial x} + \frac{p a_n^3}{1 - p a_p^3 - n a_n^3}\frac{\partial n}{\partial x}\right), \tag{46}$$

$$J_n = -\frac{D_n}{k_B T} z_n e n \frac{\partial \phi}{\partial x} - \frac{D_n}{r_n}\left(\frac{\partial n}{\partial x} + \frac{n a_p^3}{1 - p a_p^3 - n a_n^3}\frac{\partial p}{\partial x} + \frac{n a_n^3}{1 - p a_p^3 - n a_n^3}\frac{\partial n}{\partial x}\right). \tag{47}$$

When the ionic concentrations are very dilute meaning $p a_p^3 \ll 1$ and $n a_n^3 \ll 1$, Eqs. (46) and (47) are reduced to

$$J_p = -\frac{D_p}{k_B T} z_p e p \frac{\partial \phi}{\partial x} - \frac{D_p}{r_p}\frac{\partial p}{\partial x}, \tag{48}$$

$$J_n = -\frac{D_n}{k_B T} z_n e n \frac{\partial \phi}{\partial x} - \frac{D_n}{r_n}\frac{\partial n}{\partial x}, \tag{49}$$

which are not exact classical Nernst-Planck equations with diffusion coefficents decreased to $\frac{D_p}{r_p}$ and $\frac{D_n}{r_n}$ respectively in the diffusion terms above for p and n. Compared with original Bikerman model with an identical ion diameter which can be reduced to classical PB and PNP equations when ionic concentrations are dilute, the current model attempted to modify original Bikerman to include specific ion sizes unfortunately fails to reduce so.

5 Conclusions

The straight forward extension of Bikerman model to include specific ion sizes, though used by many researchers, actually does not uphold the ion occupation site to be identical, a fundamental requirement of mean-field lattice gas model, at extreme high ion conecntrations. The rigorous modification of Bikerman model to include specific ion sizes is derived in the current study. It fixes the occupation site problem, but unfortunately fails to reduce to classical PB and PNP as ion concentrations become dilute. Maybe models of steric effect to account for specific ion sizes are better not derived through modification of entropy but through the introduction of excessive chemical potential [6, 7].

Also in the version of straight forward extension of Bikerman model, the limits $n \to \frac{1}{a_n^3}$ and $p \to \frac{1}{a_p^3}$ as $\phi \to \pm\infty$, though do not uphold identical occupation site requirement globally, still uphold it locally. For example in the case of of electrolyte in contact with a charged wall with extremely high voltage, unlike the situation in Fig. 1(a) usually only one species of counter-ion will dominate the occupancy near wall surface, even the electrolyte consists of multiple species of counter-ions. It is usually because other energy barrier like solvation energy will end up only one species of counter-ion would be distributed near wall. Similar situation occurs at the selectivity filter of potassium channel, and that is how selectivity works.

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