# On the Self-Diffusion of Ions in a Polyelectrolyte Solution ⊘

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neighboring cells means essentially[7] that the conditional probability for the occupation of a cell, when a neighboring cell is occupied in a given manner, is only directly dependent on this neighboring cell (i.e., independent of a particular occupation of a third cell neighbor to the second). In a completely analogous way the conditional probability for the occupation of the position **s** neighboring a cell $v$ at a given configuration

($\mathbf{r}^\nu$) is in the present method only directly dependent on ($\mathbf{r}^\nu$), as is clearly seen from the form of $f(\mathbf{s} \mid \mathbf{r}^\nu)$.

Finally, the systematic use of the grand canonical ensemble is definitely superior to a hole theory in truly describing the density fluctuations in a cell. In addition, the present method enables one to get rid of any assumption of a lattice structure of the neighborhood of the cell.

# On the Self-Diffusion of Ions in a Polyelectrolyte Solution

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The self-diffusion of ions in a polyelectrolyte solution is investigated both with respect to the average time an ion is associated with a particular polyelectrolyte molecule and with respect to the effect of the electrostatic field of the macro-ions on the macroscopic self-diffusion constant. The results on the macroscopic self-diffusion constant are shown to be generally compatible with experiments on self-diffusion of counterions in polyelectrolyte solutions. On the other hand, the study of the time of association of a counterion with a particular macro-ion yields results which cannot be reconciled with the common interpretation of transference experiments on the same solutions.

## INTRODUCTION

IN 1950 Wall and his co-workers[1-3] observed a very interesting and puzzling phenomenon. Performing transference experiments with radioactive sodium counterions as tracers in a polyelectrolyte solution, they found that some counterions migrate toward the anode while others migrate to the cathode. They inferred from this behavior that part of the sodium ions are dragged along with a polymer macro-ion being bound to it for long time intervals of the order of at least several minutes before they escape from the macro-ion and become free to move in the opposite direction. To the best of our knowledge, since the discovery of this phenomenon, no explanation was offered for such a long time of association. It seems impossible to account for it by assuming formation of ion pairs between the fixed charges and counterions. The lifetime of association of small ion pairs can be obtained from Onsager's theory of the kinetic constants of ionic reactions[4] and is of the order of a small fraction

of a microsecond.[5] One is tempted, therefore, to attribute the phenomenon to properties of the polymer molecule as a whole. A possible mechanism by which an ion may be held by a charged polymer molecule is in the entrapment in the electrostatic field created around the charged macromolecule.[6]

In order to investigate this possibility we ask what is the average time of escape, i.e., the time it takes a specified counterion to escape from the electrostatic field of a polyelectrolyte molecule. This question as well as several other related questions can be answered using a method due to Pontrjagin et al.[7] This method provides a differential equation for the average time it

[1] Huizenga, P. F. Grieger, and F. T. Wall, J. Am. Chem. Soc. **72**, 2636 (1950).

[2] F. T. Wall and P. F. Grieger, J. Chem. Phys. **20**, 1200 (1952).

[3] F. T. Wall, P. F. Grieger, J. R. Huizenga, and R. H. Doremus, J. Chem. Phys. **20**, 1206 (1952).

[4] L. Onsager, J. Chem. Phys. **2**, 599 (1934).

[5] This can be estimated as follows: the kinetic constant of recombination of an ion pair such as, e.g., Na-acetate, is obtained from Eq. (26) of Onsager's paper. Expressed in moles per liter it is ~$5\times10^{10}$. The smallest value of the equilibrium *dissociation* constant that we could find in the literature for a Na-carboxylate ion-pair is that of Na-polymethacrylate, and is of the order of $10^{-2}$ [Table I in R. A. Harris and S. A. Rice, J. Phys. Chem. **58**, 725 (1954)]. This yields a kinetic dissociation constant $5\times10^{8}$. Its reciprocal is the desired lifetime of association.

[6] F. Osawa, N. Imai, and I. Kagawa, J. Polymer Sci. **13**, 93 (1954).

[7] L. Pontrjagin, A. Andronow, and A. Witt, Soviet Phys.—JETP **3**, 172 (1933). A description of this method is also contained in M. Leontowitch, *Statistical Mechanics* (State Publishing House of Technical-Theoretical Literature, Moscow, 1944). Essentially the same results are obtained by a somewhat different method by G. Klein, Proc. Roy. Soc. (London) **A211**, 431 (1952).

takes a particle moving under the combined effect of thermal agitation and a stationary field of force to reach a specified boundary. We shall present, in Sec. 2, a somewhat detailed account of this interesting work. In Sec. 3, the average time of escape of a counterion is derived in the form of a double integral whose value depends on the nature of the electrostatic potential. By estimating the value of this integral for several models of potential distribution, one finds that the average time of escape is by several orders of magnitude shorter than the time of migration of an ion from one compartment to the other in Wall's transference experiments. In Wall's terminology this would mean an *infinite* rate of exchange between the *bound* and *free* states of the counterions. Thus, if one assumes that the binding of a counterion to a macro-ion is due to entrapment in the electrostatic potential of the latter (plus, possibly, ion-pair formation between counterions and fixed charges) one should expect a uniform average *mobility* of counterions, contrary to Wall's observation. We are therefore forced into the conclusion that the entrapment assumption is unable to account for Wall's transference experiments.

Yet, there can be no doubt but that the electrostatic field of the macro-ion slows down the motion of the counterions, on a macroscopic scale. Such a motion is considered in Sec. 4 as a diffusion in a stationary periodic field with a periodicity of macromolecular dimensions. It is to be expected that, if the polyelectrolyte solution is macroscopically homogeneous, the average time for an ion to reach a macroscopic boundary from an interior point should follow the same pattern as in the case of free diffusion, with an effective diffusion constant replacing the hydrodynamic one. The ratio of these two constants, which we call the diffusion ratio, may then be obtained in terms of certain averages over the local macro-ion potential. It will be shown that this is indeed the case for a one-dimensional model and that the macro-ionic potentials calculated from experimental values of the diffusion ratio are in agreement with those obtained by other methods.

## 2. METHOD OF PONTRJAGIN, ANDRONOW, AND WITT

Let us consider a closed region $V$, bound by a surface $S$. A conservative field of force $\mathbf{F}(\mathbf{r}) = -e\nabla\psi(\mathbf{r})$ is defined in the region and is required to be finite everywhere in the region. A particle, which in our case will be an ion, moves in the region under the combined influence of thermal agitation and the force $F$. We define a probability function $W(r, t)$ as the probability that a particle which is located at the point $\mathbf{r}$ at time $t=0$ will have reached the bounding surface $S$ *during* the time interval $(0, t)$. Evidently, for a point $\mathbf{s}$ on the surface $W(\mathbf{s}, t) = 1$ for all $t$. For an interior point we have $W(\mathbf{r}, \infty) = 1$, while $W(\mathbf{r}, 0) = 0$; moreover, one may assert the stronger condition

$$\lim_{\tau \to 0}[W(r, \tau)/\tau] = 0. \qquad (1)$$

We wish now to relate the probability $W$ at time $\tau$ to its value at a later time $t+\tau$. For this purpose we define a function $v(\mathbf{r}, t, \varrho)$ such that $v(\mathbf{r}, t, \varrho)d\varrho$ is the transition probability of a particle, from a point $\mathbf{r}$ at time $t=0$, a volume element $d\varrho$ about the point $\varrho$ at time $t$, *without* having touched the surface $S$ during the time interval $(0, t)$. The function $v(\mathbf{r}, t, \varrho)$ is normalized in the sense that

$$\int_V v(\mathbf{r}, t, \varrho)d\varrho = 1 - W(\mathbf{r}, t). \qquad (2)$$

When $t$ tends to zero, $W(r, t)$ tends to zero, and $v$ approaches the ordinary transition probability for all interior points.

It is clear that the following integral equation holds:

$$W(\mathbf{r}, t+\tau) = W(\mathbf{r}, \tau) + \int_V v(\mathbf{r}, \tau, \varrho)W(\varrho, t)d\varrho. \qquad (3)$$

The meaning of the above equation is as follows: If the particle has reached the surface during the interval $(0, t+\tau)$ then either it reached the surface during the time interval $(0, \tau)$ or else it got to a point $\varrho$ at time $\tau$ without having touched the surface and then reached the surface from the point $\rho$ in the time interval $(\tau, \tau+t)$.

For Brownian motion in a viscous medium in the presence of a field of force, the particle has an average velocity at a point, proportional to the force, i.e., the following limit exists:

$$\lim_{\tau \to 0} \frac{\langle \rho_i - r_i \rangle}{\tau} = \frac{F_i}{f}, \qquad (4)$$

where $f$ is the hydrodynamic friction coefficient. Furthermore, the diffusion coefficient $D = kT/f$ is related to the second moment of the displacement according to

$$\lim_{\tau \to 0} \frac{\langle (\rho_i - r_i)(\rho_i - r_j) \rangle}{\tau} = 2D\delta_{ij}. \qquad (5)$$

For all higher moments it is assumed that

$$\lim_{\tau \to 0}\tau^{-1}(\rho_i - r_i)^l(\rho_i - r_j)^m(\rho_k - r_k)^n = 0, \quad l+m+n > 2. \qquad (6)$$

In view of the fact that the function $v(\mathbf{r}, \tau, \varrho)$ approaches the ordinary transition probability as $\tau$ approaches zero, the moments of $v(\mathbf{r}, \tau, \varrho)$ approach the moments of the ordinary transition probability for $\tau \to 0$, and we have from Eqs. (4), (5), and (6)

$$F_i/f = \lim_{\tau \to 0}\tau^{-1}\int_V (\rho_i - r_i)v(\mathbf{r}, \tau, \rho)d\varrho, \qquad (7a)$$

$$2D\delta_{ij} = \lim_{\tau \to 0}\tau^{-1}\int_V (\rho_i - r_i)(\rho_j - r_j)v(\mathbf{r}, \tau, \varrho)d\varrho, \qquad (7b)$$

$$0 = \lim_{\tau \to 0}\tau^{-1}\int_V (\rho_i - r_i)^l(\rho_j - r_j)^m(\rho_k - r_k)^n v(\mathbf{r}, \tau, \varrho)d\varrho$$

$$(l+m+n) > 2. \qquad (7c)$$

We now use the integral equation for $W(\mathbf{r}, t)$ [Eq. (3)], to derive a partial differential equation. Expanding $W(\varrho, t)$ about the point $\mathbf{r}$ we have

$$\frac{\partial W(\mathbf{r}, t)}{\partial t} = \lim_{\tau \to 0} \tau^{-1}[W(\mathbf{r}, t+\tau) - W(\mathbf{r}, t)]$$

$$= \lim_{\tau \to 0} \tau^{-1}\left\{ -W(\mathbf{r}, t) + W(\mathbf{r}, \tau) \right.$$

$$+ \int d\varrho v(\mathbf{r}, \tau, \rho)\left[ W(\mathbf{r}, t) + \sum_i (\rho_i - r_i)\frac{\partial W}{\partial r_i} \right.$$

$$+ \frac{1}{2!}\sum_{i,j}(\rho_i - r_i)(\rho_j - r_j)\frac{\partial^2 W}{\partial r_i \partial r_j} + \frac{1}{3!}\sum_{i,j,k}(\rho_i - r_i)(\rho_j - r_j)$$

$$\left.\left. \times (\rho_k - r_k)\frac{\partial^3 W}{\partial r_i \partial r_j \partial r_k} + \cdots \right]\right\}. \quad (8)$$

Making use of the various limiting properties of $v$ and $W$ presented in the previous equations we obtain in the limit

$$\partial W/\partial t = f^{-1}\mathbf{F}\cdot\nabla W + D\nabla^2 W. \quad (9)$$

The probability that a particle located at $r$ at time $t=0$ will arrive at the surface in the interval $(t, t+dt)$ is $(\partial W/\partial t)(r, t)dt$. Therefore, the average time for a particle to arrive at the surface is

$$\bar{t}(\mathbf{r}) = \int_0^\infty t\frac{\partial W(\mathbf{r}\cdot t)}{\partial t}dt. \quad (10)$$

If we successfully differentiate Eq. (9) with respect to $t$, multiply it by $t$, and then integrate with respect to $t$, we obtain for the left-hand side

$$\int_0^\infty t\frac{\partial^2 W}{\partial t^2}dt = t\frac{\partial W}{\partial t}\Big|_0^\infty - \int_0^\infty \frac{\partial W}{\partial t}dt = -1, \quad (11)$$

and the equation for $\bar{t}$ becomes

$$(1/f)\mathbf{F}\cdot\nabla\bar{t} + D\nabla^2\bar{t} = -1, \quad (12)$$

with the boundary condition that $\bar{t}$ is zero on $S$.

If $F = -e\nabla\psi$ is the electrostatic force acting on an ion of charge $e$, it is convenient to introduce a reduced electrostatic potential

$$\varphi = -e\psi/kT. \quad (13)$$

Equation (12) may then be written as follows:

$$\nabla^2\bar{t} + \nabla\varphi\cdot\nabla\bar{t} = -1/D \quad (14)$$

or, using $e^\varphi$ as an integrating factor, we have

$$\nabla\cdot(e^\varphi\nabla\bar{t}) = -e^\varphi/D. \quad (15)$$

This equation will be the basis of the discussion in the following sections.

It is instructive to note that when the field $F$ is zero, one may directly write the solutions for a line, cylinder, and sphere. One has

One-dimensional case: length of line $2L$,

$$\bar{t}(x) = (L^2 - x^2)/2D; \quad (16a)$$

Two-dimensional case: radius of cylinder $\rho_0$,

$$\bar{t}(\rho) = (\rho_0^2 - \rho^2)/4D; \quad (16b)$$

Three-dimensional case: radius of sphere $R$,

$$\bar{t}(\mathbf{r}) = (R^2 - r^2)/6D. \quad (16c)$$

## 3. TIME OF ESCAPE FROM THE FIELD OF A POLYELECTROLYTE MOLECULE

Consider a polyelectrolyte solution, either with or without added salt. Each macromolecule in the solution occupies, on the average, a volume $V$; namely, $V$ is the total volume of the solution divided by the number of macromolecules. We assume as an approximation, that the volume is a sphere of radius $R$, and that the fixed ions of the polyelectrolyte molecule are distributed in a spherically symmetric fashion. The electrostatic potential within this sphere, as well as the distribution of the free ions, is assumed to be determined by the Poisson–Boltzmann equation.

We now fix our attention on a specified free ion, located at a point $r$, within the volume $V$ and ask what is the average time that it will take the ion to escape from the specified volume, i.e., to get to the surface of the sphere, where the electrostatic field is zero. The answer to this question is obtained from the spherically symmetric form of Eq. (15). In this case we have

$$(1/r^2)(d/dr)[r^2 e^\phi(d\bar{t}/dr)] = -(e^\phi/D), \quad (17)$$

with the boundary conditions that $\bar{t}$ vanishes on a surface of radius $R$, and is finite throughout the region. The solution is then given by

$$\bar{t}(r) = D^{-1}\int_r^R dr' r'^{-2}\exp[-\phi(r')]\int_0^{r'} dr'' r''^2 \exp[\phi(r'')]$$

$$\text{(spherical model)}. \quad (18)$$

If we assume cylindrical symmetry, i.e., if a polyelectrolyte molecule is considered to be rodlike, then the equation for $\bar{t}(\rho)$ is easily seen to be

$$\bar{t}(\rho) = D^{-1}\int_\rho^{\rho_0} d\rho' \rho'^{-1}\exp[-\phi(\rho')]\int_0^{\rho'} d\rho'' \rho'' \exp[\phi(\rho'')]$$

$$\text{(cylindrical model)}. \quad (19)$$

The one-dimensional analog of the same problem is also of interest. One considers here the model of parallel charged sheets a distance $2L$ apart, and asks for the average time for a labeled ion to escape from the region assigned to a particular sheet. The answer is

$$\bar{t}(x) = D^{-1}\int_x^L dx' \exp[-\phi(x')]\int_0^{x'} dx'' \exp[\phi(x'')]$$

$$\text{(parallel sheets model)}. \quad (20)$$

As we indicated already in the introduction, our interest in the problem of the escape time of counterions originated from the puzzling phenomenon of the long time of association observed by Wall *et al.* Assuming that association is essentially due to entrapment in the electrostatic field, we are now in a position to calculate these times provided the potential $\phi(r)$ is known. It is of interest, however, at the outset to check whether any reasonable potential may provide values of $\bar{t}(x)$ which are comparable in order of magnitude with those obtained from the above mentioned experiments. We shall therefore try first a rough estimate for the upper bound of $\bar{t}(0)$, the time to escape from the center of the field, where $\phi$ has its maximum value, this time being of course longer than the time of escape from any other point. Replacing $\exp[\phi(r'')]$ and $\exp[-\phi(r')]$ in Eq. (17) by their maximum values $\exp[\phi(0)]$ and $\exp[-\phi(R)]$, respectively, we get

$$t(0) < D^{-1} \exp(\Delta\phi) \int_0^R dr' x' - 2 \int_0^{r'} dr'' r''^2$$

$$= \exp(\Delta\phi)(R^2/6D) = \exp(\Delta\phi) t_0(0), \quad (21)$$

where $\Delta\phi$ is the maximum potential difference within the macromolecular region and $t_0$ is the field-free diffusion time.

The radius of macromolecular region is of the order of several hundred angstroms; the corresponding value of $t_0(0)$ is of the order of $10^{-6}$ sec. The observations of Wall *et al.* indicate $t(0) > 10^2$ sec which implies $\exp(\Delta\phi) \times 10^8$ or $\Delta\phi > 18$. It should be noted, however, that since the above estimate is a rough one, the actual times of escape for even such high values of the potential might be of the order of milliseconds. To show this without too much computational work we give in the Appendix an exact evaluation of $t(0)$ for a simple one-dimensional model. There it is found that, for large $\Delta\phi$,

$$t(0)/t_0(0) \sim 2/\pi \exp(\tfrac{1}{2}\Delta\phi). \quad (22)$$

In spite of the obvious differences between the one-dimensional model and the real three-dimensional distribution of the potential, Eq. (22) may be safely considered as a better estimate than Eq. (21) for $t/t_0$. Neither theoretical nor experimental evaluations of $\Delta\phi$ give values nearly as high as those indicated by the above considerations. We must conclude therefore, that electrostatic forces cannot provide a rationale for the observed migration of counterions towards both the anode and the cathode in Wall's transference experiments.

## IV. LIMITING BEHAVIOR ON A MACROSCOPIC SCALE

For the situation described at the beginning of the preceding section, let us now consider the self-diffusion of labeled ions over macroscopic distances. Since on the macroscopic scale the system is homogeneous, we should expect on *a priori* grounds that this motion

should be characterized by a single effective diffusion constant $D'$ which is determined by the hydrodynamic diffusion constant $D$ and the local electrostatic field of the polyelectrolyte molecules. It is therefore to be expected that if we solve Eq. (15) over a macroscopic region, the limiting form of the average time to reach the surface from a point sufficiently far from the surface, will be given by one of the Eqs. (16), according to the shape of the region we choose, and with $D$ replaced by the effective $D'$.

We shall now show that this is indeed the case for the one-dimensional model. Consider a region bounded by the planes $x = -2nL$ and $x = 2nL = X$, where, again, $2L$ is the distance between adjacent charged planes and $n$ is a large integer. According to Eq. (12), the average time for an ion to reach a boundary plane from $x = 0$ is

$$\bar{t}(0) = D^{-1} \int_{x'=0}^{X} dx' \exp[-\phi(x')] \int_0^{x'} dx'' \exp[\phi(x'')].$$

$$\quad (23)$$

If we introduce the notation

$$x = 2Lm + \xi, \quad (0 \le m \le n-1),$$

$$(0 \le \xi \le 2L),$$

$$\langle e^{\pm\varphi} \rangle = \frac{1}{2L} \int_0^{2L} \exp[\pm\phi(\xi)] d\xi, \quad (24)$$

then Eq. (23) may be written

$$\bar{t}(0) = D^{-1} \sum_{m=0}^{n-1} \int_{\xi'-2mL}^{2(m+1)L} d\xi' \exp[-\phi(\xi')]$$

$$\times \left\{ 2mL \langle e^{\varphi} \rangle + \int_{\xi''=0}^{\xi'} \exp[\phi(\xi'')] d\xi'' \right\}$$

$$= D^{-1} \tfrac{1}{2} n(n-1)(2L)^2 \langle e^{\varphi} \rangle \langle e^{-\varphi} \rangle$$

$$+ n \int_{\xi'=0}^{2L} d\xi' \exp[-\phi(\xi')] \int_{\xi''=0}^{\xi'} d\xi'' \exp[\phi(\xi'')]. \quad (25)$$

As both $e^{\phi(x)}$ and $e^{-\phi(x)}$ are symmetric about $x = L$, the last double integral may be shown to be one-half of $(2L)^2 \langle e^{\varphi} \rangle \langle e^{-\varphi} \rangle$. The final results is then

$$\bar{t}(0) = \langle e^{\phi} \rangle \langle e^{-\phi} \rangle (X^2/2D). \quad (26)$$

The effective diffusion constant is therefore

$$D' = D/\langle e^{\varphi} \rangle \langle e^{-\varphi} \rangle. \quad (27)$$

Although in the derivation of Eq. (26) the plane $x = 0$ and the bounding planes $\pm X$ were chosen to coincide with charged planes, the result is independent of this choice. Had we not done this, the expression for $\bar{t}(0)$ would contain a linear term in $X$. This, however, would be macroscopically indistinguishable, to the extent that $(X+2L)^2$ is indistinguishable from $X^2$.

The factor $\langle e^{\varphi} \rangle \langle e^{-\varphi} \rangle$ is always larger than unity, by Schwarz's inequality. We therefore see that the effect

TABLE I. The one-dimensional potential $\Delta\phi$ necessary to produce the measured values of $1/f$ in $0.0151N$ Na-polyacrylate.[8]

| % Neutralization | $1/f = D/D'$ | $\Delta\phi$ |
|---|---|---|
| 9.6 | 1.11 | 1.5 |
| 24.0 | 1.30 | 2.0 |
| 41.3 | 1.72 | 2.6 |
| 61.7 | 2.22 | 3.2 |
| 81.6 | 2.63 | 3.7 |

of any one-dimensional periodic field is to produce a macroscopic diffusion constant which is always smaller than the hydrodynamic diffusion constant. Using the solution of the one-dimensional Poisson-Boltzmann equation, cited in Eq. (I) of the Appendix, the "diffusion ratio" $(D/D')$ is

$$D/D' = (\tan\lambda/2\lambda)(1+\sin(2\lambda)/2\lambda). \quad (28)$$

A better evaluation of the diffusion ratio $D/D'$ should be obtained by integrating Eq. (15) over a macroscopic region for the three-dimensional case, i.e., with the macromolecular potential $\phi$ following the actual three-dimensional distribution of the polymer molecules in solution. This integration is, however, difficult and will not be attempted here. Instead, we wish to show that even Eq. (28) which is derived from the one-dimensional model agrees reasonably well with the experimental data obtained by Huizenga et al[8] on the self-diffusion of sodium ions in aqueous solutions of Na-polyacrylate. The diffusion ratio $D/D'$ is given in their notation by $1/f$. We have calculated, with the help of Eq. (28) and the equations of the Appendix, the potential differences which correspond to the measured values of the diffusion ratio. The results are given in Table I.

These values fall well within the range of potentials obtained by various experimental methods, as well as from theoretical models.[9] A more detailed quantitative comparison between the $\Delta\phi$'s obtained above and the potentials obtained by other methods does not seem justified, due to the approximate nature of the one-dimensional model. However, one should feel safe to

[8] Huizenga, P. F. Grieger, and F. T. Wall, J. Am. Chem. Soc. 72, 4228 (1950).
[9] See the recent monograph on *Polyelectrolyte Solutions*, by S. A. Rice and M. Nagasawa (Academic Press Inc., New York, 1961).

conclude from the above considerations that the retardations of the diffusive motion of counterions in polyelectrolyte solutions is caused by their entrapment in the electrostatic potential fields of the macro-ions, with the migration of these ions towards both the anode and the cathode in the transference experiments, cannot be explained by the same effect.

## ACKNOWLEDGMENT

## APPENDIX

The average time of escape for the one-dimensional model of parallel sheets is calculated as follows. We assume that the sheets are planes of homogeneous charge density, that the system has no added salt, and that it is electroneutral, namely that the surface charge is equal and opposite to the volume charge of the counterions.

If we take the charged planes to be located at $x = \cdots$, $-2L, 0, 2L, \cdots$, then the solution of the corresponding Poisson-Boltzmann equation is periodic, and in the interval $(-L, L)$ the reduced potential, $\phi = -e\psi/kT$, has the form

$$\phi = -2\ln\cos[\lambda(1-|x|/L)] \quad (-L \leq x \leq L), \quad (I)$$

where we have taken the potential at the midpoint between the charged planes to be zero. The constant $\lambda$ is then related to the potential at the plane $x=0$ by

$$\lambda = \arccos\exp(-\tfrac{1}{2}\phi_0). \quad (II)$$

Inserting this potential into Eq. (20), the result for the average time of escape from the region $(-L, L)$ associated with a charged plane is

$$\bar{t}(x) = (L^2/2D\lambda^2)\{\lambda(1-|x|/L)\tan\lambda$$

$$+\tfrac{1}{2}\sin a\lambda(1-|x|/L)[\tan\lambda-\tan\lambda(1-|x|/L)]\}, \quad (III)$$

and, in particular, the average time of escape starting from the charged surface is

$$\bar{t}(0) = L^2/2D(\tan\lambda/\lambda). \quad (IV)$$

When $\phi_0$ is very large, $\lambda$ approaches $\tfrac{1}{2}\pi$, and $\tan\lambda/\lambda$ approaches $(2/\pi)\exp(\tfrac{1}{2}\phi_0)$. In this model $\phi(\pm L)=0$, $\phi_0 = \Delta\phi$, and Eq. (22) holds therefore for large $\Delta\phi$.