

Image Effects and Ion Diffusion Times in Lamella Systems

Derek Y. C. Chan

Department of Mathematics, University of Melbourne, Parkville, Victoria, Australia 3052

Donald A. McQuarrie*

Department of Chemistry and Institute of Theoretical Dynamics, University of California, Davis, CA 95616, USA

Analytical and numerical results are given for the effects of ionic image interactions for ion diffusion in an electrolyte confined between dielectric boundaries in a lamella geometry. The calculation is based on the Smoluchowski model for single-ion diffusion in a mean field and the linear Debye–Hückel treatment of image interactions between the diffusing ions and the dielectric boundaries. Results for the mean first passage times are given for a range of surface separations and electrolyte concentrations.

In the Smoluchowski model for single-ion diffusion in a mean field the central quantity is the propagator $P(\mathbf{r}, |r_0)$, which is the probability density of finding an ion at position \mathbf{r} at time t , given that the ion was at r_0 at time $t = 0$. The propagator satisfies the diffusion equation¹

$$\partial P(\mathbf{r}, |r_0)/\partial t = D\nabla\{[\nabla + \beta\nabla w(\mathbf{r})]P(\mathbf{r}, |r_0)\} \quad (1)$$

where D is the single-ion diffusion constant in the solvent, $\beta = 1/kT$, and $w(\mathbf{r})$ is the one-particle equilibrium potential of mean force. Recent studies of the ion diffusion problem have focussed on diffusion between charged surfaces governed by the Gouy–Chapman potential of mean force,² diffusion in electrolytes with only counter ions confined between charged surfaces,³ as well as electrolyte systems confined in a semi-infinite domain.^{4,5}

In this paper, we consider the diffusion of a single ion belonging to a symmetric ($v:v$) electrolyte bounded by two uncharged planar surfaces in the lamella geometry. We assume that the relative permittivity of each planar surface is different from that of the solvent, and so ion diffusion is influenced by the ionic image interactions with the dielectric boundaries. In particular, we derive the first passage times for ions arriving at the dielectric surfaces. Calculations of mean first passage times involve evaluations of integrals of the potential of mean force only,^{3,6} explicit solutions of eqn. (1) are not required. In the next section we derive the result for the potential of mean force $w(z)$ on an ion due to image interactions with two dielectric boundaries based on the linear Debye–Hückel treatment. General expressions for the mean first passage time, to linear order in $w(z)$, for arrival of diffusing ions at the dielectric boundaries, and explicit analytic and numerical results are given below.

Potential of Mean Force due to Image Interactions

The geometry we use for the ion diffusion problem is shown in Fig. 1. The symmetric ($v:v$) electrolyte with n ions of each species per unit volume is characterized by the Debye screening parameter κ ($\kappa^2 \equiv 8\pi\beta n v^2 e^2/\epsilon$), where ϵ is the relative permittivity of the solvent and e is the protonic charge. The uncharged dielectric boundaries with relative permittivity ϵ_w , are located at a distance $2(a+b)$ apart, where a is the ionic radius, which measures the distance of closest approach between ionic centres and the dielectric boundary. Therefore, the ion diffusion domain is restricted to the region $-b < z < b$.

Image interactions between an ion (charge q may be positive or negative) located at r_0 and the dielectric boundaries can be obtained from a suitable Green's function. In the

linear Debye–Hückel theory, the Green's function can be found by solving

$$\begin{aligned} \nabla^2 G(\mathbf{r}, r_0) &= 0; & |z| > (a+b) \\ &= \kappa^2 G(\mathbf{r}, r_0) - (4\pi q/\epsilon)\delta(\mathbf{r} - r_0); & |z| < (a+b) \end{aligned} \quad (2)$$

subject to the usual continuity conditions of $G(\mathbf{r}, r_0)$ and $\epsilon\partial G(\mathbf{r}, r_0)/\partial z$ at the boundaries $z = \pm c \equiv \pm(a+b)$. Eqn. (2) may be solved by taking the Fourier transform with respect to the coordinates parallel to the boundary

$$\hat{G}(k, z, z_0) = \int d^2\rho \exp(-i\mathbf{k} \cdot \boldsymbol{\rho}) G(\boldsymbol{\rho}, z, z_0) \quad (3)$$

to give

$$\frac{d^2 \hat{G}}{dz^2} - k^2 \hat{G} = 0; \quad |z| \geq c \quad (4a)$$

$$\frac{d^2 \hat{G}}{dz^2} - (k^2 + \kappa^2) \hat{G} = -\frac{4\pi q}{\epsilon} \delta(z - z_0) \exp(-i\mathbf{k} \cdot \boldsymbol{\rho}_0); \quad |z| < c \quad (4b)$$

Without loss of generality, we may choose $\boldsymbol{\rho}_0 = 0$, so that a particular integral of eqn. (4b) is

$$\hat{G}_p(k, z, z_0) = \frac{2\pi q}{\epsilon p} \exp(-p|z - z_0|) \quad (5)$$

with $p = \sqrt{(k^2 + \kappa^2)}$.

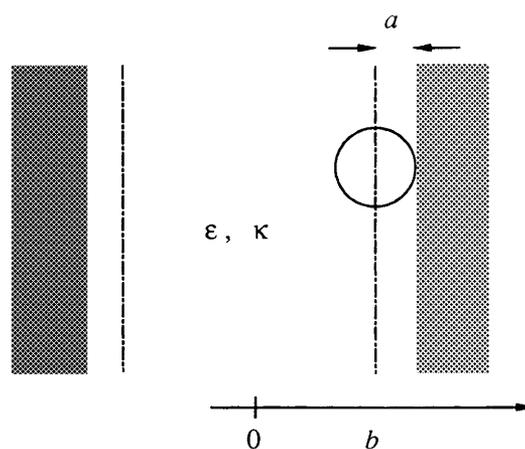


Fig. 1 Geometry of the ion diffusion domain

If we solve eqn. (4) and match both $\hat{G}(k, z, z_0)$ and $\varepsilon d\hat{G}(k, z, z_0)/dz$ at $z = \pm c$, then we obtain

$$\begin{aligned} \hat{G}(k, z, z_0) = & \frac{2\pi q\Delta}{\varepsilon p\mathcal{D}} \{ \Delta \exp[-p(z - z_0 + 4c)] \\ & + \exp[-p(2c - z - z_0)] \\ & + \Delta \exp[-p(4c + z + z_0)] \\ & + \exp[-p(z + z_0 + 2c)] \} \\ & + \frac{2\pi q}{\varepsilon p} \exp(-p|z - z_0|) \end{aligned} \quad (6)$$

where

$$\Delta = \frac{p\varepsilon - k\varepsilon_w}{p\varepsilon + k\varepsilon_w} \quad (7)$$

and

$$\mathcal{D} = 1 - \Delta^2 \exp(-4pc) \quad (8)$$

with $c = a + b$.

If we let $z \rightarrow z_0$ in $\hat{G}(k, z, z_0)$, then we obtain

$$\begin{aligned} \lim_{z \rightarrow z_0} \hat{G}(k, z, z_0) = & \hat{\phi}(k, z_0) \\ & + \{ \text{a constant term, independent of } z_0 \} \end{aligned}$$

with

$$\hat{\phi}(k, z_0) = \frac{2\pi q\Delta}{\varepsilon p\mathcal{D}} \{ \exp[-p(2c - 2z_0)] + \exp[-p(2c + 2z_0)] \} \quad (9)$$

The terms that are independent of z_0 are self-energy terms, which give rise to no forces on the ions and hence do not contribute to the diffusion process. In the linear theory (keeping only terms proportional to q^2), the potential of mean force $w(z)$ due to image interactions is given by

$$\begin{aligned} w(z) = & \frac{q}{2} \phi(z) \\ = & \frac{q}{2} \frac{1}{(2\pi)^2} \int d^2k \hat{\phi}(k, z) \\ = & \frac{q^2}{2\varepsilon} \int_k^\infty dp \sum_{n=0}^\infty \Delta^{2n+1} \{ \exp\{-2p[(2n+1)c - z]\} \\ & + \exp\{-2p[(2n+1)c + z]\} \} \end{aligned} \quad (10)$$

For an aqueous system, we have $\varepsilon \gg \varepsilon_w$ so that to a good approximation we may replace $\Delta \rightarrow 1$ in eqn. (10). The expression for $w(z)$ then simplifies to

$$\begin{aligned} w(z) \approx & \frac{q^2}{4\varepsilon} \sum_{n=0}^\infty \left(\frac{\exp\{-2\kappa[(2n+1)c - z]\}}{(2n+1)c - z} \right. \\ & \left. + \frac{\exp\{-2\kappa[(2n+1)c + z]\}}{(2n+1)c + z} \right) \end{aligned} \quad (11)$$

This expression for $w(z)$ is similar to that derived by Bell and Levine⁷ and Levine.⁸

Mean First Passage Times

Mean first passage times of diffusing species in an external field $w(z)$ can be calculated from the normalized equilibrium

probability $f(z)$ defined by

$$f(z) = \frac{\exp[-\beta w(z)]}{\int_{-b}^b dx \exp[-\beta w(x)]} \quad (12)$$

In the theory that is linear in $w(z)$, this reduces to

$$f(z) \approx \frac{1}{2b} \left[1 - \beta w(z) + \frac{\beta}{2b} \int_{-b}^b dx w(x) \right] \quad (13)$$

where terms proportional to $(\beta w)^2$ or higher have been omitted. Similarly, we have

$$\frac{1}{f(z)} \approx 2b \left[1 + \beta w(z) - \frac{\beta}{2b} \int_{-b}^b dx w(x) \right] \quad (14)$$

The mean first passage time for a diffusing ion located initially at z to reach either dielectric boundary is given by³

$$\tau(z) = J_1(-b, z) - \frac{J_1}{J_0} J_0(-b, z) \quad (15)$$

where

$$\begin{aligned} J_1(-b, z) = & \int_{-b}^z \frac{dx}{Df(x)} \int_x^b dy f(y) \\ \approx & \frac{1}{D} \left[b(z+b) + (b^2 - z^2)/2 - 2\beta \right. \\ & \left. \times \int_{-b}^z dx x w(x) - \beta(z+b) \int_z^b dx w(x) \right] \end{aligned} \quad (16)$$

$$\begin{aligned} J_0(-b, z) = & \int_{-b}^z \frac{dx}{Df(x)} \\ \approx & \frac{2b}{D} \left[(z+b) + \beta \int_{-b}^z dx w(x) \right. \\ & \left. - \frac{\beta(z+b)}{2b} \int_{-b}^b dx w(x) \right] \end{aligned} \quad (17)$$

and

$$J_0 \equiv J_0(-b, b) \approx \frac{4b^2}{D} \quad (18)$$

$$J_1 \equiv J_1(-b, b) \approx \frac{2b^2}{D} \quad (19)$$

To arrive at eqn. (16) we have interchanged orders of integration in several terms. Therefore, to linear order in $w(z)$ we have

$$D\tau(z)/b^2 = \frac{1}{2} [1 - (z/b)^2] + T(z) \quad (20)$$

where $T(z)$ represents the dimensionless excess mean first passage time due to image interactions while the first term in eqn. (20) is the dimensionless free diffusion result. The explicit form for $T(z)$ to linear order in the potential of mean force $w(z)$ is

$$T(z) = \frac{2\beta}{b^2} \int_{|z|}^b dx x w(x) + \frac{\beta|z|}{b^2} \int_0^{|z|} dx w(x) - \frac{\beta}{b} \int_0^b dx w(x) \quad (21)$$

where we have used the fact that $w(x)$ is an even function of x .

We also calculate the position-averaged mean first time for a diffusing ion located to reach either dielectric boundary. The average is over all initial positions of the diffusing ion weighted with the equilibrium distribution of initial positions.

Formally, this position-averaged mean first passage time in reduced units is defined by

$$D\langle\tau(z)\rangle/b^2 = \frac{D}{b^2} \int_{-b}^b \tau(z)f(z) dz \quad (22)$$

$$\equiv \frac{1}{3} + \langle T(z) \rangle$$

where to linear order in the potential of mean force $w(z)$

$$\langle T(z) \rangle = \frac{2\beta}{b^3} \int_0^b dx x^2 w(x) - \frac{2\beta}{3b} \int_0^b dx w(x) \quad (23)$$

where once again we have utilized the parity of $w(x)$ and have interchanged orders of integration in several terms.

The results given in eqn. (21) for the excess mean first passage time $T(z)$ and in eqn. (23) for the position-averaged mean first passage time $\langle T(z) \rangle$ are correct to linear order in the potential for mean force $w(z)$. To obtain expressions for the first passage times under image interactions between the diffusing ion and the dielectric boundaries, we combine eqn. (11) for the potential of mean force for image interactions with eqn. (21) and (23). The final expressions for the mean first passage times are:

$$T(z) = \frac{\beta q^2}{4\epsilon b} \left\{ 2c \sum_{n=0}^{\infty} (2n+1) [S_n(b) - S_n(z)] \right. \\ + \sum_{n=0}^{\infty} [bD_n(b) - |z|D_n(z)] \\ \left. + \frac{2}{\kappa} \left(\frac{\exp(-2\kappa c)}{1 - \exp(-4\kappa c)} \right) [\cosh(\kappa z) - \cosh(\kappa b)] \right\} \quad (24)$$

and

$$\langle T(z) \rangle = \frac{\beta q^2}{4\epsilon b} \sum_{n=0}^{\infty} \left[\frac{2}{3} [1 - 3(2n+1)^2(c/b)^2] D_n(b) \right. \\ + \frac{1}{2(\kappa b)^2} \left(\{1 - 2\kappa[(2n+1)c + b]\} \right. \\ \times \exp\{-2\kappa(2n+1)c - b\} \\ - \{1 - 2\kappa[(2n+1)c - b]\} \\ \left. \times \exp\{-2\kappa[(2n+1)c + b]\} \right) \left. \right] \quad (25)$$

where

$$D_n(z) \equiv E_1\{2\kappa[(2n+1)c + |z|]\} - E_1\{2\kappa[(2n+1)c - |z|]\} \quad (26)$$

$$S_n(z) \equiv E_1\{2\kappa[(2n+1)c + |z|]\} - E_1\{2\kappa[(2n+1)c - |z|]\} \quad (27)$$

and

$$E_1(z) \equiv \int_z^{\infty} dt [\exp(-t)/t] \quad (28)$$

is the exponential integral.

Results

We now give numerical results for the effects of image interactions on the mean first passage times of arrival at either of the dielectric boundaries. The ionic cutoff parameter or ionic radius a is taken to be 2 Å throughout and ionic concentrations are specified in terms of the Debye screening parameter

κ appropriate to a 1 : 1 aqueous electrolyte at 298 K. In Fig. 2 we show the behaviour of the dimensionless excess mean first passage time $T(z)$ [eqn. (24)] for various values of the separation b between the dielectric boundaries at low and

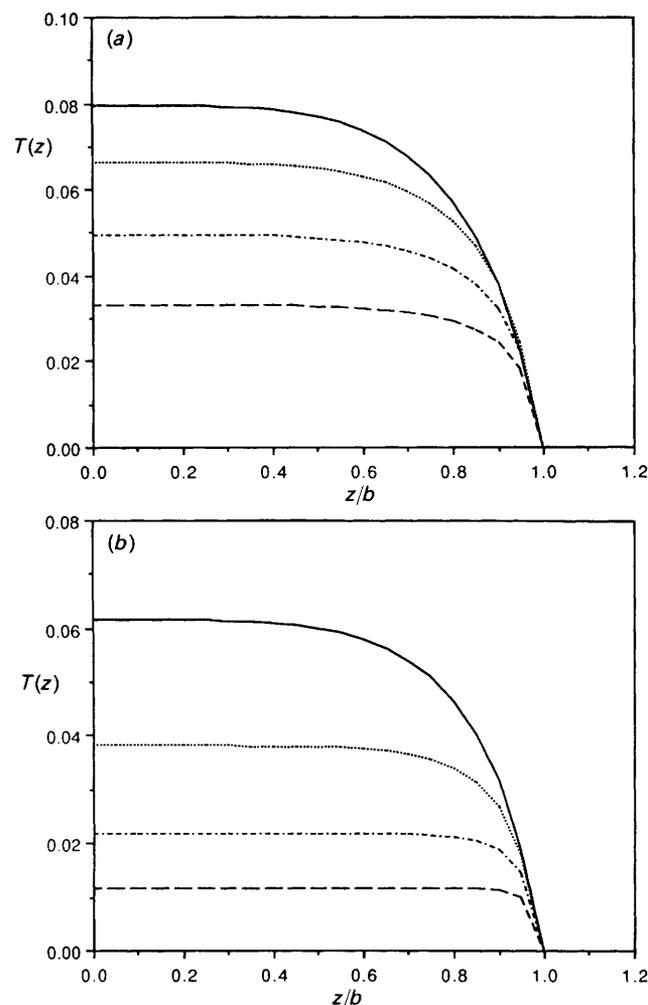


Fig. 2 Dimensionless excess mean first passage time $T(z)$ as a function of the initial position z of the diffusing ion; $\kappa a = 0.02$ (a), 0.2 (b); $b/\text{\AA} = 10$ (—), 25 (·····), 50 (-·-·-·), 100 (----)

high electrolyte concentrations. In Fig. 3 we show the variation of $T(z)$ with concentration for different relative initial positions of the diffusing ion with $b = 25$ Å. The mean first

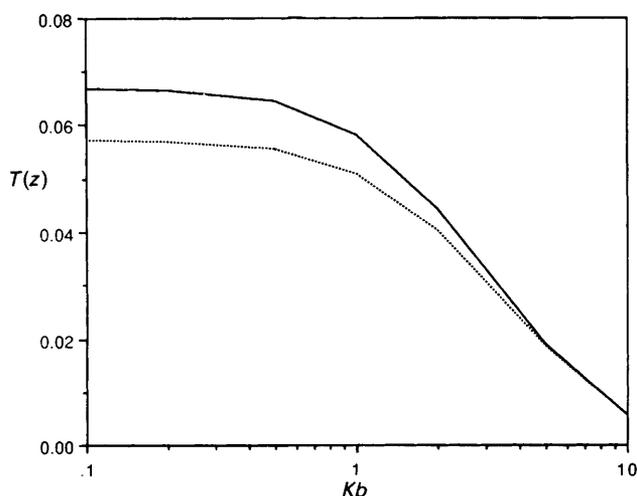


Fig. 3 Dimensionless excess mean first passage time $T(z)$ at different relative positions in the electrolyte; $b = 25$ Å; $z/b = 0.00$ (—), 0.75 (·····)

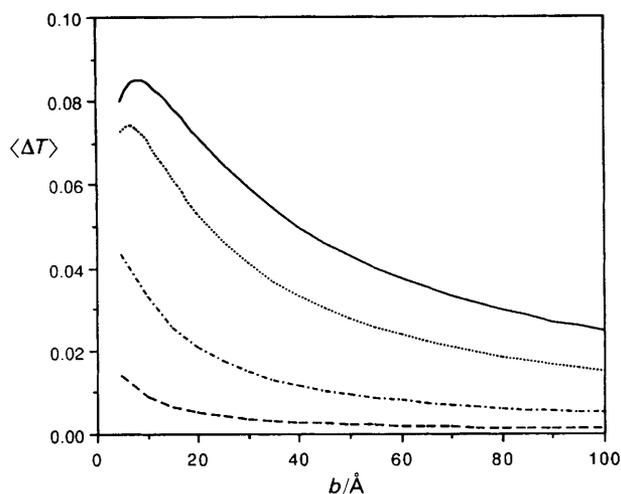


Fig. 4 Position-averaged dimensionless mean first passage time; $\kappa a = 0.1$ (—), 0.2 (·····), 0.5 (-·-·-·), 1.0 (----)

passage time averaged over initial positions $\langle T(z) \rangle$ [eqn. (25)] is shown in Fig. 4 for different electrolyte concentrations.

Compared with the effects of electrostatic interactions

between ions and a charged dielectric surface,² the effects of image interactions are relatively small in the linear regime and the results presented herein can be added as a perturbation correction. Whether these effects are small in the non-linear regime is not clear and is the subject of further investigation.

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