J. Chem. Soc., Faraday Trans. 2, 1987, **83**(12), 2271-2286

Ion Diffusion near Charged Surfaces

Exact Analytic Solutions

Derek Y. C. Chan

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

The problem of single-ion diffusion in the electric double layer near a planar surface has been studied within the Smoluchowski-Gouy-Chapman description. For the case of a symmetric electrolyte against a charged planar surface exact analytic solutions have been obtained. Explicit results for the cases of absorbing and reflecting boundary conditions at the charged surface are given. Solutions for other boundary conditions can be readily derived from the general solution.

1. Introduction

Much effort had been expended in obtaining a theoretical understanding of the equilibrium distribution of ions in the electrolyte in the vicinity of charged surfaces. As a consequence the utility and limitations of existing theories are sufficiently well known. For instance, with the 'primitive' model electrolyte (ions in a continuum solvent) machine simulations of such models have provided bench-mark results which can be tested against established and often-used theories.[1] As a consequence, it is possible in some cases to attribute any disagreement between theory and experiment to the theoretical model rather than to the approximate theoretical treatment of such models. However, it is only more recently that there has been a more systematic theoretical effort to examine the dynamical properties of ions in a non-uniform electroylyte.

A general model for describing the classical, as opposed to the quantum-mechanical, properties of an electrolyte at a charged interface would be to treat the ions as well as the solvent as distinct species with prescribed interaction potentials between the various species. We call this the 'civilized' model electrolyte. However, it will be very difficult to make much progress by analysing such a model because of its inherent complexities. In any case, many properties of interest, such as the equilibrium ionic density, are not very sensitive to the fine details embodied in the civilized model.[2-5]

The next level of abstraction is to account for the properties of the solvent by using a set of macroscopic parameters. For instance, the dielectric constant, ε, is used to account for the effects of the solvent on the coulombic interactions between the ions, and the diffusion constant, D, to account for the coupling between the relative motion between ions and the solvent molecules. The electrolyte is thus modelled as a collection of ions immersed in a dielectric and viscous continuum of prescribed properties; this constitutes the primitive model electrolyte. The formalism which furnishes the connections between the civilized and the primitive model electrolyte is well established.[6-10]

In treating the dynamical properties of a primitive model electrolyte near charged surfaces, one can begin with the many-body Fokker-Planck equation in an external field. This starting point requires that: (1) the relaxation of ionic and solvent momenta and of solvent configuration is fast compared to the time-scale for relevant changes in the ionic configuration, (2) the interaction potentials between the various ionic species are slowing varying over the ionic momentum correlation length $[D(m/kT)]^{1/2}$, and (3) the solvent-mediated dynamic coupling between the ions and with the surface may be neglected. As has been demonstrated in an earlier paper, we can then project out all but one of the particle coordinates to obtain a one-particle diffusion equation involving an effective external field that is time-dependent.[11] The time-dependence arises because of the possibility of correlation of ionic positions at different times. However, if we further assume that as the tagged ion moves, the remaining ions in the system can adjust their configurations instantly, then such time correlations can be ignored, and the result is a one-particle diffusion equation in which the ion moves in the one-particle equilibrium potential of mean force due to the presence of charged interface. This was called the 'instantaneous relaxation approximation.'[11]

If in the spirit of the Poisson–Boltzmann theory for treating the equilibrium properties of an electrical double layer, the exact one-particle equilibrium potential of mean force is approximated by the product of the ionic charge ($\nu_i e$), and the mean electrostatic potential $\psi(\boldsymbol{r})$, one obtains the Smoluchowski–Poisson–Boltzmann approximation for describing the diffusion of a single tagged ion near charged surfaces. The resulting diffusion equation for the one-particle propagator $f(\boldsymbol{r}, t)$, *i.e.* the probability density of finding the particle at $\boldsymbol{r}$ at time t, given an initial position $\boldsymbol{r}_0$ at $t=0$, is of the form

$$\partial f(\boldsymbol{r}, t)/\partial t = D\nabla\{[\nabla + \beta\nabla w(\boldsymbol{r})]f(\boldsymbol{r}, t)\} \tag{1.1}$$

where D is the single-ion diffusion constant in the solvent and $\beta \equiv 1/kT$. In the instantaneous relaxation approximation $w(\boldsymbol{r})$ is the exact one-particle equilibrium potential of mean force. In the Smoluchowski–Poisson–Boltzmann approximation $w(\boldsymbol{r})$ is approximated by $z_i e\psi(\boldsymbol{r})$, where the mean electrostatic potential $\psi(\boldsymbol{r})$ satisfies the Poisson–Boltzmann equation:

$$\nabla^2\psi(\boldsymbol{r}) = (4\pi e/\varepsilon)\sum_i n_i\nu_i \exp[-\beta\nu_i e\psi(\boldsymbol{r})]. \tag{1.2}$$

Here ε is the dielectric constant of the solvent and n_i is the number per unit volume of ions of species i in the bulk electrolyte.

The system of a set of counter-ions, but no co-ions, in between two identically and uniformly charged surfaces has been studied by stochastic dynamic simulation methods.[12] This simulation is equivalent to the solution of the many-body Fokker–Planck equation that describes the space–time evolution of the ionic system. Analytic solutions for the one-particle propagator in the Smoluchowski–Poisson–Boltzmann approximation have also been found.[13] For univalent ions, the Smoluchowski–Poisson–Boltzmann treatment appears to provide a sufficiently accurate description of the ion dynamics in the direction normal to the charged surfaces, subject to the limitation imposed by the Poisson–Boltzmann approximation of the potential of mean force. With the instantaneous relaxation approximation, *i.e.* when the Smoluchowski treatment of the diffusion process is coupled with the exact equilibrium potential of mean force, the results for the one-particle propagator are essentially identical to those obtained with stochastic dynamic simulations.[11]

In this paper we consider the problem of single-ion self-diffusion in a symmetric electrolyte near a single planar charged surface. This is a system commonly encountered in colloid and surface science and has applications in which one is required to know the diffusion processes of co-ions and counter-ions within the electrical double layer.

We consider the case in which the diffusing ion is a member of one of the species forming the symmetric electrolyte, which may be a counter-ion or co-ion. As discussed above, the diffusion process can be described by a one-particle Smoluchowski diffusion equation in an external field. The external field under which the diffusing ion moves is in fact generated by other ions and the charged surface as a result of mutual coulombic interactions as well as thermal motion of the ions. We shall use the Smoluchowski–Poisson–Boltzmann approximation, in which this external potential is approximated by the product of the charge of the diffusing ion and the mean equilibrium electrostatic potential in the diffuse layer, *i.e.* we use the same potential of mean force as in the

Gouy-Chapman theory for the equilibrium properties of the double layer.[14-16] To avoid confusion with earlier work we shall call this the Smoluchowski-Gouy-Chapman approximation.

Owing to the simplications afforded by the Gouy-Chapman treatment of a symmetric electrolyte, the cases of a diffusing co-ion or counter-ion proceed along almost identical lines. The general problem of diffusion in a semi-infinite domain will be set up in the next section, and a general solution to the diffusion equation will be given in section 3. The specific solutions for the diffusion of co-ion and counter-ions with absorbing and reflecting boundary conditions are given in sections 4 and 5. Detailed numerical results are presented in section 6. Those readers who are not interested in the detailed derivations can proceed on to the results sections of sections 4 and 5 as well as to section 6 without loss of continuity.

2. General Formulation

Consider the generic problem of the diffusion of a single tagged particle in the semi-infinite half space $z>0$. The particle is subject to an external potential $w(z)$ which is only a function of the normal coordinate z. The Smoluchowski equation for the one-particle propagator $f(\boldsymbol{r}, t)$, reads

$$\partial f(\boldsymbol{r}, t)/\partial t = D\nabla\{[\nabla + \beta\, \mathrm{d}w(z)/\mathrm{d}z] f(\boldsymbol{r}, t)\}. \tag{2.1}$$

We define the Fourier transform of the propagator with respect to the coordinates $\boldsymbol{\rho} = (x, y)$ by

$$F(\boldsymbol{k}, z, t) = \int \mathrm{d}^2\boldsymbol{\rho}\, \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\rho}) f(\boldsymbol{r}, t). \tag{2.2}$$

In anticipation of the electrolyte problem which has the Debye length $(1/\kappa)$ as a natural length scale, we introduce the dimensionless quantities

$$\xi \equiv \kappa z \tag{2.3}$$

$$\tau \equiv \kappa^2 D t \tag{2.4}$$

$$q \equiv k/\kappa \tag{2.5}$$

$$u(\xi) \equiv \beta w(z) \tag{2.6}$$

as well as the non-dimensional propagator $\varphi(q, \xi, \tau)$

$$F(\boldsymbol{k}, z, t) \equiv \kappa\varphi(q, \xi, \tau). \tag{2.7}$$

The Smoluchowski equation for $\varphi(q, \xi, \tau)$ is then

$$\partial^2\varphi/\partial\xi^2 + (\mathrm{d}u/\mathrm{d}\xi)(\partial\varphi/\partial\xi) + (\mathrm{d}^2u/\mathrm{d}\xi^2 - q^2)\varphi = \partial\varphi/\partial\tau. \tag{2.8}$$

The particle is taken to be at the initial position $(\boldsymbol{\rho}_0, z_0)$ at $t=0$. In view of the cylindrical symmetry in the x- and y-directions we can, without loss of generality, choose the origin of our coordinate system so that $\boldsymbol{\rho}_0 = (0, 0)$. As a result, the initial condition for $\varphi(q, \xi, \tau)$ becomes

$$\varphi(q, \xi, \tau=0) = \delta(\xi - \xi_0). \tag{2.9}$$

Using the Laplace transform

$$\tilde{\varphi}(q, \xi, s) = \int_0^\infty \mathrm{d}\xi\, \exp(-s\tau)\varphi(q, \xi, \tau) \tag{2.10}$$

the partial differential equation (2.8) can be converted into an ordinary differential equation for $\tilde{\varphi}(q, \xi, s)$:

$$\tilde{\varphi}''+u'\tilde{\varphi}'-(s+q^2-u'')\tilde{\varphi}=-\delta(\xi-\xi_0) \tag{2.11}$$

where the prime denotes a derivative with respect to ξ. Eqn (2.11) can be cast into the normal form with the substitution

$$\tilde{\varphi}(q, \xi, s)\equiv v(q, \xi, s)\exp[-u(\xi)/2] \tag{2.12}$$

to give a generic differential equation for $v(q, \xi, s)$ which must be solved for the diffusion problem

$$v''-[s+q^2+(u')^2/4-u''/2]v=-\exp[u(\xi_0)/2]\delta(\xi-\xi_0). \tag{2.13}$$

The derivation of this equation only involved the assumption that the external potential $w(z)$ is a function of the normal coordinate z, but independent of x and y.

We also need to specify boundary conditions before the solution to eqn (2.13) can be completely determined. As $z\rightarrow\infty$ or $\xi\rightarrow\infty$ we expect $v(q, \xi, s)$ and all its derivatives to vanish. At $\xi=z=0$ we shall consider two types of boundary conditions for the propagator:

(i) the absorbing boundary condition requires

$$f(r, t)|_{z=0}=0 \quad \text{at } z=0 \tag{2.14a}$$

which translates to the condition

$$v(q, \xi, s)|_{\xi=0}=0 \tag{2.14b}$$

(ii) the reflecting boundary condition, which requires the flux to vanish:

$$J_z(z=0)\equiv[\partial f/\partial z+\beta(\mathrm{d}w/\mathrm{d}z)f]_{z=0}=0 \tag{2.15a}$$

implies

$$[v'(q, \xi, s)+[u'(\xi)/2]v(q, \xi, s)]_{\xi=0}=0. \tag{2.15b}$$

We observe that a time-independent solution of eqn (2.1) which satisfies the reflecting boundary condition (2.15a) is

$$f(\boldsymbol{r}, t)=g(\boldsymbol{\rho})\exp[-\beta w(z)]. \tag{2.16}$$

However, the requirement that $f(\boldsymbol{r}, t)$ is normalized, namely

$$\int \mathrm{d}^2\boldsymbol{\rho}\int_0^\infty \mathrm{d}z f(\boldsymbol{r}, t)\,\mathrm{d}^3\boldsymbol{r}=1 \tag{2.17}$$

mean that if the potential of mean force $w(z)\rightarrow 0$, as $z\rightarrow\infty$, then a solution of the form of eqn (2.16) is unacceptable, as it cannot meet the normalization condition over z in eqn (2.17).

We now consider the case of diffusion under a Gouy-Chapman potential of mean force.

3. The Smoluchowski–Gouy–Chapman Model

According to the Gouy-Chapman theory[14-16] the mean electrostatic potential $\psi(z)$ in a symmetric $\nu:\nu$ electrolyte occupying the half space $z>0$ adjacent to a planar charged surface at $z=0$ bearing a uniform surface charge is given by the Poisson-Boltzmann equation:

$$\mathrm{d}^2\psi(z)/\mathrm{d}z^2=(8\pi n\nu e/\varepsilon)\sinh[\beta\nu e\psi(z)]. \tag{3.1}$$

The Debye screening parameter κ is given by

$$\kappa^2 = 8\pi n\beta\nu^2 e^2/\varepsilon. \tag{3.2}$$

Introducing the dimensionless potential

$$Y(\xi) \equiv \beta\nu e\psi(z) \tag{3.3}$$

where $\xi = \kappa z$, the Poisson-Boltzmann equation becomes

$$Y''(\xi) = \sinh Y(\xi). \tag{3.4}$$

In the Gouy-Chapman model the one-particle potential of mean force experienced by an ion of valence $(\eta\nu)$ is

$$w(z) = \eta\nu e\psi(z). \tag{3.5}$$

Since we confine ourselves to the case in which the tagged ion belongs one of the species of the $\nu:\nu$ symmetric electrolyte, we know that $\eta = \pm 1$. As a result the non-dimensional potential of mean force $u(\xi) \equiv \beta w(z) = \beta\eta\nu e\psi(z)$ also obeys the differential equation

$$u''(\xi) = \sinh u(\xi). \tag{3.6}$$

The boundary conditions on $u(\xi)$ are $u(\xi) \to 0$, as $\xi \to \infty$ and

$$u(0) = -|Y_0| \equiv -|\beta\nu e\psi(0)|, \quad \text{for counter-ions} \tag{3.7a}$$

$$= |Y_0| \equiv |\beta\nu e\psi(0)|, \quad \text{for co-ions.} \tag{3.7b}$$

Using the boundary conditions, the first integral of eqn (3.6) is

$$u'(\xi) = -2\sinh[u(\xi)/2] \tag{3.8}$$

and the explicit form of $u(\xi)$ is

$$u(\xi) = 2\ln\{[1+\gamma\exp(-\xi)]/[1-\gamma\exp(-\xi)]\} \tag{3.9}$$

with

$$\gamma \equiv \tanh[u(0)/4]. \tag{3.10}$$

Using eqn (3.6) and (3.8) in eqn (2.13), the differential equation for the function $v/(q, \xi, s)$ becomes

$$v''(q,\xi,s) - [p^2 - \{1-\exp[-u(\xi)]\}/2]v(q,\xi,s) = -\exp[u(\xi_0)/2]\delta(\xi-\xi_0) \tag{3.11}$$

where

$$p^2 \equiv s + q^2 \equiv s + k^2/\kappa^2. \tag{3.12}$$

The two independent solutions of the homogeneous equation [right-hand side of eqn (3.11) equals zero] are

$$v_<(q,\xi,s) = \exp(p\xi)[2p - E(\xi)] \tag{3.13}$$

$$v_>(q,\xi,s) = \exp(-p\xi)[2p + E(\xi)] \tag{3.14}$$

where

$$E(\xi) \equiv \exp[-u(\xi)]. \tag{3.15}$$

That eqn (3.13) and (3.14) are indeed solutions of the homogeneous equation can be verified by direct substitution and using eqn (3.8) to simplify the results.

The particular integral of eqn (3.11) is

$$v_{PI}(q,\xi,s) = -v_<(q,\xi_{\min},s)v_>(q,\xi_{\max},s)/[WE(\xi_0)] \tag{3.16}$$

where

$$\xi_{\min} \equiv \min(\xi, \xi_0) \tag{3.17a}$$

$$\xi_{\max} \equiv \max(\xi, \xi_0) \tag{3.17b}$$

and W is the Wronskian

$$W \equiv v_< v'_> - v'_< v_> = -2p(4p^2-1). \tag{3.18}$$

The general solution of eqn (3.11) which vanishes in the limit $\xi \to \infty$ is

$$v(q, \xi, s) = \exp(-p|\xi-\xi_0|)[2p - E(\xi_{\min})][2p + E(\xi_{\max})]/[2p(4p^2-1)E(\xi_0)] + A\exp(-p\xi)[2p+E(\xi)] \tag{3.19}$$

where A is a constant to be determined by applying the boundary condition at $\xi = 0$. The cases of absorbing and reflecting boundaries will be considered in detail in the next two sections.

4. Absorbing Boundary Condition

With the absorbing boundary condition at $\xi = 0$, we have $v(q, \xi = 0, s) = 0$, so that the constant A in eqn (3.19) is

$$A = -\exp(-p\xi_0)\{[2p - E(0)][2p + E(\xi_0)]\}/\{2p(4p^2-1)E(\xi_0)[2p + E(0)]\}. \tag{4.1}$$

The solution to eqn (3.11) becomes

$$v(q, \xi, s) \equiv G(\xi, p)/[2p(4p^2-1)E(\xi_0)] \tag{4.2}$$

with

$$G(\xi, p) = \exp(-p|\xi-\xi_0|)[2p - E(\xi_{\min})][2p + E(\xi_{\max})] - \exp[-p(\xi+\xi_0)][2p - E(0)][2p + E(\xi_0)][2p + E(\xi)]/[2p + E(0)] \tag{4.3}$$

$\xi_{\min} = \min(\xi, \xi_0)$, $\xi_{\max} = \max(\xi, \xi_0)$, $E(\xi) \equiv \exp[-u(\xi)/2]$ and $p^2 \equiv s + q^2$.

Using eqn (2.12), namely $\tilde{\varphi} = v\exp(-u/2)$, the non-dimensional propagator $\varphi(q, \xi, \tau)$ can now be found by an inverse Laplace transform

$$\varphi(q, \xi, \tau) = (2\pi \mathrm{i})^{-1}[E(\xi)/E(\xi_0)] \int_{\mathrm{I}} \mathrm{d}s \exp(s\tau) G(\xi, p)/[2p(4p^2-1)] \tag{4.4}$$

where the path of the integration (I) lies to the right of all singularities of the integrand on the complex s-plane and runs from $-\mathrm{i}\infty$ to $+\mathrm{i}\infty$ (see fig. 1). The points $p = \pm 2$ are not poles of the integrand in eqn (4.4), since the term $G(\xi, p)$ also vanishes at $p = \pm 2$. The only singularity of the integrand is a branch cut along the negative real s axis, extending between the branch point $s = -q^2$ (q real) and $s = -\infty$.

Using the Cauchy integral theorem, the contour (I) in eqn (4.4) may be translated to go around the branch cut along contours (II) and (III) as indicated in fig. 1, so that eqn (4.4) for the non-dimensional propagator becomes, after some algebra

$$\varphi(q, \xi, \tau) = (4\pi \mathrm{i})^{-1}[E(\xi)/E(\xi_0)] \times \left\{\int_{\mathrm{II}} + \int_{\mathrm{III}}\right\} \mathrm{d}s \exp(s\tau) G(\xi, p)/[p(4p^2-1)] \tag{4.5}$$

$$= -(4\pi)^{-1}[E(\xi)/E(\xi_0)] \exp(-q^2\tau) \times \int_0^\infty \mathrm{d}\zeta \exp(-\zeta\tau)[G(\xi, \mathrm{i}\sqrt{\zeta}) + G(\xi, -\mathrm{i}\sqrt{\zeta})]/[\sqrt{\zeta}(4\zeta+1)] \tag{4.6}$$

$$= (4\pi)^{-1}[E(\xi)/E(\xi_0)] \exp(-q^2\tau) \times \int_0^\infty \mathrm{d}\zeta \exp(-\zeta\tau)\Phi_A(\xi, \zeta)/[\sqrt{\zeta}(4\zeta+1]. \tag{4.7}$$

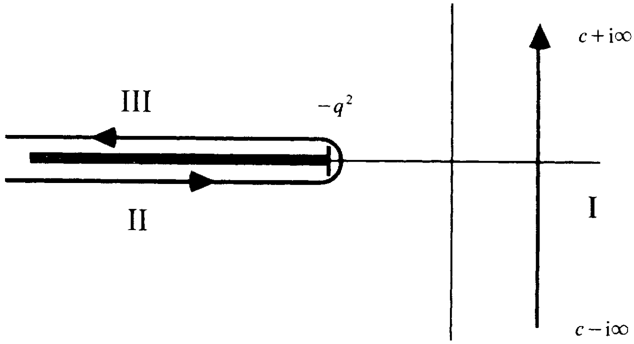

Fig. 1. Contours for the inverse Laplace transform in the complex s-plane and the location of the branch cut.

The term $\Phi_A(\xi, \zeta)$, which is independent of the Fourier variable q, is given by

$$\begin{aligned}\Phi_A(\xi,\zeta) = 2[4\zeta + E^2(0)]^{-1}(&\cos\sqrt{\zeta}(\xi+\xi_0)\{4\zeta[E(0)-E(\xi_0)][E(0)-E(\xi)]\\&-[4\zeta+E(0)E(\xi_0)][4\zeta+E(0)E(\xi)]\}\\&+2\sqrt{\zeta}\sin\sqrt{\zeta}(\xi+\xi_0)\{[4\zeta+E(0)E(\xi)][E(\xi_0)-E(0)]\\&+[4\zeta+E(0)E(\xi_0)][E(\xi)-E(0)]\})\\&+2\cos\sqrt{\zeta}(\xi-\xi_0)[4\zeta+E(\xi_0)E(\xi)]\\&-4\sqrt{\zeta}\sin\sqrt{\zeta}(\xi-\xi_0)[E(\xi)-E(\xi_0)].\end{aligned} \tag{4.8}$$

Using eqn (2.2) and (2.7) the inverse Fourier transform over the variable $k = \kappa q$ can now be carried out to recover the propagator in terms of $\boldsymbol{r}$ and t

$$\begin{aligned}f(\boldsymbol{r}, t) &= (2\pi)^{-2}\int d^2\boldsymbol{k}\exp(-i\boldsymbol{k}\cdot\boldsymbol{\rho})F(\boldsymbol{k}, z, t)\\&= (2\pi)^{-2}\int d^2\boldsymbol{k}\exp(-i\boldsymbol{k}\cdot\boldsymbol{\rho})\kappa\varphi(q,\xi,\tau)\\&= (4\pi Dt)^{-1}\exp(-\rho^2/4Dt)\kappa\varphi(0,\xi,\tau).\end{aligned} \tag{4.9}$$

Eqn (4.7) and (4.9) constitute the final expression for the ion diffusion propagator with an absorbing boundary condition at the charged surface. The remaining integral over ζ in eqn (4.7) cannot be evaluated in closed form, but has to be carried out numerically. We pursue this point in more detail in section 6. The two cases of a diffusing co-ion or counter-ion rests on the choice of the Boltzmann factor $E(\xi) = \exp[-u(\xi)]$ according to the specifications given in eqn (3.6)-(3.10).

We also introduced the xy-averaged propagator $\bar{f}(z, t)$:

$$\bar{f}(z, t) \equiv \int d^2\boldsymbol{\rho} f(\boldsymbol{r}, t). \tag{4.10}$$

Since diffusion in the x- and y-directions is not subjected to an external field, the xy-averaged propagator $\bar{f}(z, t)$ is very simply related to the full propagator $f(\boldsymbol{r}, t)$:

$$\begin{aligned}f(\boldsymbol{r}, t) &= (4\pi Dt)^{-1}\exp(-\boldsymbol{\rho}^2/4Dt)\bar{f}(z, t)\\&= (4\pi Dt)^{-1}\exp(-\boldsymbol{\rho}^2/4Dt)\kappa\varphi(0,\xi,\tau).\end{aligned} \tag{4.11}$$

From eqn (4.6) we see that the large time limit, $t \to \infty$, behaviour of the non-dimensional propagator $\varphi(q, \xi, \tau)$ is governed by the analytic properties of the factor $\Phi_A(\xi, \zeta)/[\sqrt{\zeta}(4\zeta+1)]$ around $\zeta \approx 0$. With a little algebra, it can be shown that as $\zeta \to 0$

$$\Phi_A(\xi, \zeta)/[\sqrt{\zeta}(4\zeta+1)] \propto \sqrt{\zeta} + \mathcal{O}(^3\sqrt{\zeta}) \tag{4.12}$$

so that in the limit $\tau \to \infty$, for some fixed value of ξ, we have the asymptotic result

$$\varphi(0, \xi, \tau) \approx (4\sqrt{\pi})^{-1}[E(\xi)/E(\xi_0)]a(\xi)\tau^{-3/2} \tag{4.13}$$

with

$$a(\xi) = 4(\xi+\xi_0)E(\xi_0)E(\xi)/E(0) + 8\{1-[E(\xi_0)/E(0)]\}\{1-[E(\xi)/E(0)]\}$$
$$-\xi E(\xi)[4-\xi_0 E(\xi_0)] - \xi_0 E(\xi_0)[4-\xi E(\xi)]. \tag{4.14}$$

Thus we see that the large time limiting form of the xy-averaged propagator $\bar{f}(z, t)$ varies as $t^{-3/2}$ and the full propagator $f(\boldsymbol{r}, t)$ varies as $t^{-5/2}$. This asymptotic limit can also be obtained from a direct analysis of eqn (4.4) in the limit $\tau \to \infty$.

In the free diffusion limit, $u(\xi) = 0$, *i.e.* $E(\xi) = 1$, the xy-averaged propagator $\bar{f}(z, t)$ reduces to

$$\bar{f}(z, t) = [2(\pi D t)^{1/2}]^{-1}\{\exp[-(z-z_0)^2/4Dt] - \exp[-(z+z_0)^2/4Dt]\} \tag{4.15}$$

and the full propagator becomes

$$f(\boldsymbol{r}, t) = [2(\pi D t)^{1/2}]^{-3}\{\exp[-(z-z_0)^2/4Dt] - \exp[-(z-z_0)^2/4Dt]\}. \tag{4.16}$$

5. Reflecting Boundary Condition

When we impose a reflecting boundary condition at the charged surface, we can apply the zero-flux condition (2.15) to determine the unknown coefficient A in the general solution of the one-particle diffusion equation (3.19) in a Gouy-Chapman double layer. Combining eqn (2.15*b*) and (3.19) we find

$$A = \exp(-p\xi_0)\frac{[2p - E(0) + u'(0)][2p + E(\xi_0)]}{\{2p(4p^2-1)E(\xi_0)[2p + E(0) - u'(0)]\}}. \tag{5.1}$$

The solution to eqn (3.11) can then be written in the form

$$v(q, \xi, s) \equiv H(\xi, p)/[2p(4p^2-1)E(\xi_0)] \tag{5.2}$$

with

$$H(\xi, p) = \exp(-p|\xi-\xi_0|)[2p - E(\xi_{\min})][2p + E(\xi_{\max})]$$
$$+ \exp[-p(\xi+\xi_0)][2p - E(0) + u'(0)][2p + E(\xi_0)]$$
$$\times [2p + E(\xi)]/[2p + E(0) - u'(0)]. \tag{5.3}$$

Using eqn (2.12), namely $\tilde{\varphi} = v\exp(-u/2)$, the non-dimensional propagator $\varphi(q, \xi, \tau)$ can now be found by an inverse Laplace transform

$$\varphi(q, \xi, \tau) = (2\pi i)^{-1}[E(\xi)/E(\xi_0)]\int_I ds \exp(s\tau)H(\xi, p)/[2p(4p^2-1)] \tag{5.4}$$

where the path of the integration (I) lies to the right of all singularities of the integrand on the complex s-plane and runs from $-i\infty$ to $+i\infty$ (see fig. 1). Again the points $p = \pm 2$ are not poles of the integrand in eqn (5.4), since the term $H(\xi, p)$ also vanishes at $p = \pm 2$. The only singularity of the integrand is a branch cut along the negative real s axis, extending between the branch point $s = -q^2$ (q real) and $s = -\infty$.

Using the Cauchy integral theorem, the contour (I) in eqn (5.4) may be translated to go around the branch cut along contours (II) and (III) as indicated in fig. 1, so that eqn (5.4) for the non-dimensional propagator becomes, after some algebra,

$$\varphi(q,\xi,\tau)=(4\pi\mathrm{i})^{-1}[E(\xi)/E(\xi_0)]$$
$$\times\left\{\int_{II}+\int_{III}\right\}\mathrm{d}s\,\exp(s\tau)H(\xi,p)/[p(4p^2-1)] \tag{5.5}$$
$$=-(4\pi)^{-1}[E(\xi)/E(\xi_0)]\exp(-q^2\tau)$$
$$\times\int_0^\infty \mathrm{d}\zeta\,\exp(-\zeta\tau)\{H(\xi,\mathrm{i}\sqrt{\zeta})+H(\xi,-\mathrm{i}\sqrt{\zeta})\}/[\sqrt{\zeta}(4\zeta+1)] \tag{5.6}$$
$$=(4\pi)^{-1}[E(\xi)/E(\xi_0)]\exp(-q^2\tau)$$
$$\times\int_0^\infty \mathrm{d}\zeta\,\exp(-\zeta\tau)\Phi_R(\xi,\zeta)/[\sqrt{\zeta}(4\zeta+1)]. \tag{5.7}$$

The term $\Phi_R(\xi,\zeta)$, which is independent of the Fourier variable q, is given by

$$\Phi_R(\xi,\zeta)=2[4\zeta E^2(0)+1]^{-1}(\cos\sqrt{\zeta}(\xi+\xi_0)\{4\zeta[1-E(0)E(\xi_0)][1-E(0)E(\xi)]$$
$$-[4\zeta E(0)+E(\xi_0)][4\zeta E(0)+E(\xi)]\}$$
$$+2\sqrt{\zeta}\sin\sqrt{\zeta}(\xi+\xi_0)\{[4\zeta E(0)+E(\xi)][E(0)E(\xi_0)-1]$$
$$+[4\zeta E(0)+E(\xi_0)][E(0)E(\xi)-1]\})$$
$$-2\cos\sqrt{\zeta}(\xi-\xi_0)[4\zeta+E(\xi_0)E(\xi)]$$
$$+4\sqrt{\zeta}\sin\sqrt{\zeta}(\xi-\xi_0)[E(\xi)-E(\xi_0)]. \tag{5.8}$$

As with the case of the absorbing boundary, the full propagator $f(\boldsymbol{r},t)$ can be found from eqn (2.2), (2.7), (5.7) and (5.8):

$$f(\boldsymbol{r},t)=(4\pi Dt)^{-1}\exp(-\rho^2/4Dt)\kappa\varphi(0,\xi,\tau) \tag{5.9}$$

and is related to the xy-averaged propagator

$$\bar{f}(z,t)\equiv\int \mathrm{d}^2\boldsymbol{\rho}\,f(\boldsymbol{r},t). \tag{5.10}$$

by

$$f(\boldsymbol{r},t)=(4\pi Dt)^{-1}\exp(-\boldsymbol{\rho}^2/4Dt)\bar{f}(z,t)$$
$$=(4\pi Dt)^{-1}\exp(-\boldsymbol{\rho}^2/4Dt)\kappa\varphi(0,\xi,\tau). \tag{5.11}$$

The large time limit, $t\to\infty$, behaviour of the non-dimensional propagator $\varphi(q,\xi,\tau)$ is governed by the analytic properties of the factor $\Phi_R(\xi,\zeta)/[\sqrt{\zeta}(4\zeta+1)]$ around $\zeta\approx 0$. It can be shown that as $\zeta\to 0$

$$\Phi_R(\xi,\zeta)/[\sqrt{\zeta}(4\zeta+1)]\propto\zeta^{-1/2}+\mathcal{O}(\zeta^{1/2}) \tag{5.12}$$

so that in the limit $\tau\to\infty$, for some fixed value of ξ, we have the asymptotic result

$$\varphi(0,\xi,\tau)\approx[(\pi\tau)^{1/2}]^{-1}\exp[-u(\xi)]$$
$$\approx[(\pi\kappa^2Dt)^{1/2}]^{-1}\exp[-\eta\beta\nu e\psi(z)]. \tag{5.13}$$

This asymptotic limit can also be obtained from a direct analysis of eqn (5.4) in the limit $\tau\to\infty$. We see from eqn (5.10), (5.11) and (5.13) that the large-time limiting form of the xy-averaged propagator $\bar{f}(z,t)$ varies as $t^{-1/2}$ and the full propagator $f(\boldsymbol{r},t)$ varies as $t^{-3/2}$. The time decay is, as expected, slower than the absorbing case, for which $\bar{f}(z, t)$ and $f(\boldsymbol{r}, t)$ vanishes as $t^{-3/2}$ and $t^{-5/2}$, respectively. Moreover, we can see from eqn (5.13) that the spatial distribution of the propagator is simply the equilibrium Boltzmann distribution; however, the magnitude of this distribution decays as $t^{-1/2}$ as the probability density 'leaks away into the bulk'.

In the free-diffusion limit, $u(\xi)=0$, *i.e.* $E(\xi)=1$, the *xy*-averaged propagator $\bar{f}(z, t)$ reduces to

$$\bar{f}(z, t)=[2(\pi Dt)^{1/2}]^{-1}\{\exp[-(z-z_0)^2/4Dt]+\exp[-(z+z_0)^2/4Dt]\} \qquad (5.15)$$

and the full propagator becomes

$$f(\boldsymbol{r}, t)=[2(\pi Dt)^{1/2}]^{-3}\{\exp[-(z-z_0)^2/4Dt]+\exp[-(z+z_0)^2/4Dt]\}. \qquad (5.16)$$

6. Numerical Results

We present results of numerical evaluations of the propagator for a selection of parameters. The propagators are calculated by performing the integral in eqn (4.7) for the absorbing case or the integral in eqn (5.7) for the reflecting case. Our results will be given in terms of the non-dimensional *xy*-averaged propagator defined by

$$\varphi(\xi, \tau)\equiv\varphi(q=0, \xi, \tau) \qquad (6.1)$$

where the function $\varphi(q, \xi, \tau)$ is given by eqn (4.7) and (4.8) for the absorbing case or eqn (5.7) and (5.8) for the reflecting case. Here $\xi\equiv\kappa z$ is the dimensionless distance from the surface and $\tau\equiv\kappa^2 Dt$ is the dimensionless time. The function $\varphi(\xi, \tau)$ is related to the full propagator $f(\boldsymbol{r}, t)$ as well as the *xy*-averaged propagator $\bar{f}(z, t)\equiv\int d^2\boldsymbol{\rho} f(\boldsymbol{r}, t)$ by eqn (4.11) or (5.11). Explicitly, $\varphi(\xi, \tau)$ is given by

$$\varphi(\xi, \tau)=(4\pi)^{-1}[E(\xi)/E(\xi_0)]\int_0^\infty d\zeta\,\exp(-\zeta\tau)\Phi(\xi, \zeta)/[\sqrt{\zeta}(4\zeta+1)] \qquad (6.2)$$

where the function $\Phi(\xi, \zeta)$ is $\Phi_A(\xi, \zeta)$ for the absorbing case [eqn (4.8)] or $\Phi_R(\xi, \zeta)$ for the reflecting case [eqn (5.8)]. The quantity $E(\xi)$ is the Boltzmann factor of the diffusing ion involving the mean electrostatic potential given by the Gouy-Chapman theory. It is defined by eqn (3.6)-(3.10) for co-ion and counter-ions.

To evaluate eqn (6.2) numerically, we first remove the $\sqrt{\zeta}$ dependence in the integrand by changing to the new variable

$$X=(\zeta\tau)^{1/2} \qquad (6.3)$$

so that eqn (6.2) becomes

$$\varphi(\xi, \tau)=(\sqrt{\tau}/2\pi)[E(\xi)/E(\xi_0)]\int_0^\infty dX\,\exp(-X^2)\Phi(\xi, X^2/\tau)/(4X^2+\tau). \qquad (6.4)$$

It is now in the form that we can use a Gauss-Hermite quadrature to evaluate the integral.[17] A ten-point rule in the range of the integral $(0, \infty)$ will afford a very rapid evaluation of this integral for various combinations of ξ, ξ_0 and τ. Provided the parameter values are not too extreme, this method readily gives seven digits' accuracy or better. A Fortran program to calculate $\varphi(\xi, \tau)$ is available on request.

Some sample plots of the non-dimensional *xy*-averaged propagator $\varphi(\xi, \tau)$ are given in fig. 2-6. Free-diffusion results are shown in fig. 2 for both absorbing and reflecting boundaries.

The propagators for counter-ion diffusion with reflecting and absorbing boundary conditions are given in fig. 3 and 4. From the results in fig. 3, we see that the propagators for counter-ion diffusion with reflecting boundary conditions rapidly attains a monotonic profile which is reminiscent of the equilibrium profile for counter-ions. As the magnitude

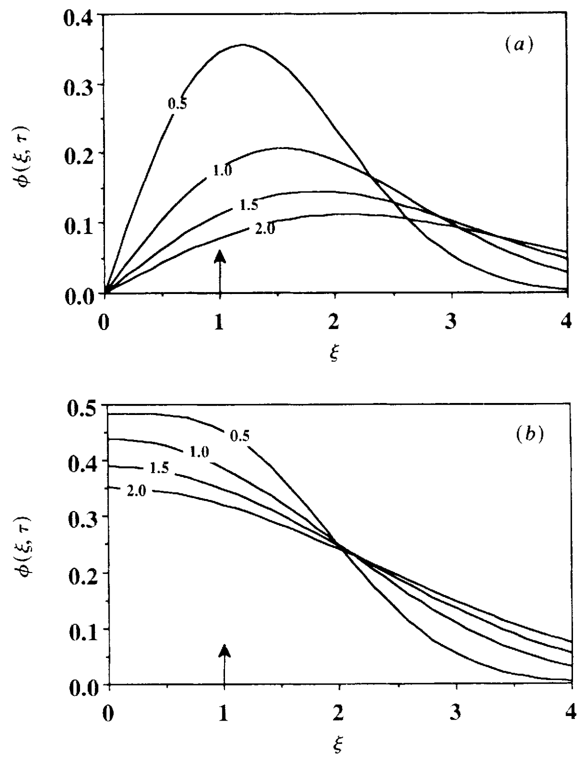

Fig. 2. Non-dimensional xy-averaged free diffusion propagators, $\varphi(\xi, \tau)$ as a function of position $\xi \equiv \kappa z$ for (a) absorbing and (b) reflecting boundary conditions. Various values of the dimensionless time $\tau \equiv \kappa^2 Dt$ are indicated. The $\uparrow$ indicates the initial position at $\xi_0 = 1$.

of the surface potential Y_0 increases, the faster the propagator attains the monotonic profile, with a larger value $\varphi(\xi = 0, \tau)$ at the surface. As expected, this profile will eventually become smeared out over the diffusion spatial domain $0 < \xi < \infty$ as time progresses.

The results for counter-ions with an absorbing boundary, fig. 4, indicate that the dominant mechanism for the decay of the propagator amplitude is through absorption at the surface. Decay by diffusion out to 'infinity' is a slower process. We can see this phenomenon in the variations of the results as the magnitude of the surface potential increases. At higher surface potentials the counter-ions are pulled towards the surface more rapidly, which facilitates the loss through absorption at the surface. Consequently, the propagator amplitude at the same space-time coordinate near the surface decreases as the magnitude of the surface potential increases.

The propagators for co-ion diffusion with reflecting and absorbing boundary conditions are given in fig. 5 and 6. For the reflecting boundary (fig. 5) the decay of the propagator amplitude is only *via* diffusion towards infinity. The lower surface values of $\varphi(\xi = 0, \tau)$ at higher surface potentials are consequences of the larger electrostatic repulsion experienced by the co-ions near the surface. However, because the decay of the propagator amplitude by diffusion towards infinity is a relatively slow process, the co-ions establish a quasi-equilibrium state in which the magnitudes of the propagator maxima at equal times are higher for higher (*i.e.* more repulsive) surface potentials.

The results for co-ions with absorbing boundaries (fig. 6), tell a similar story. The decay in the propagator amplitude is now mainly *via* absorption at the surface. Thus

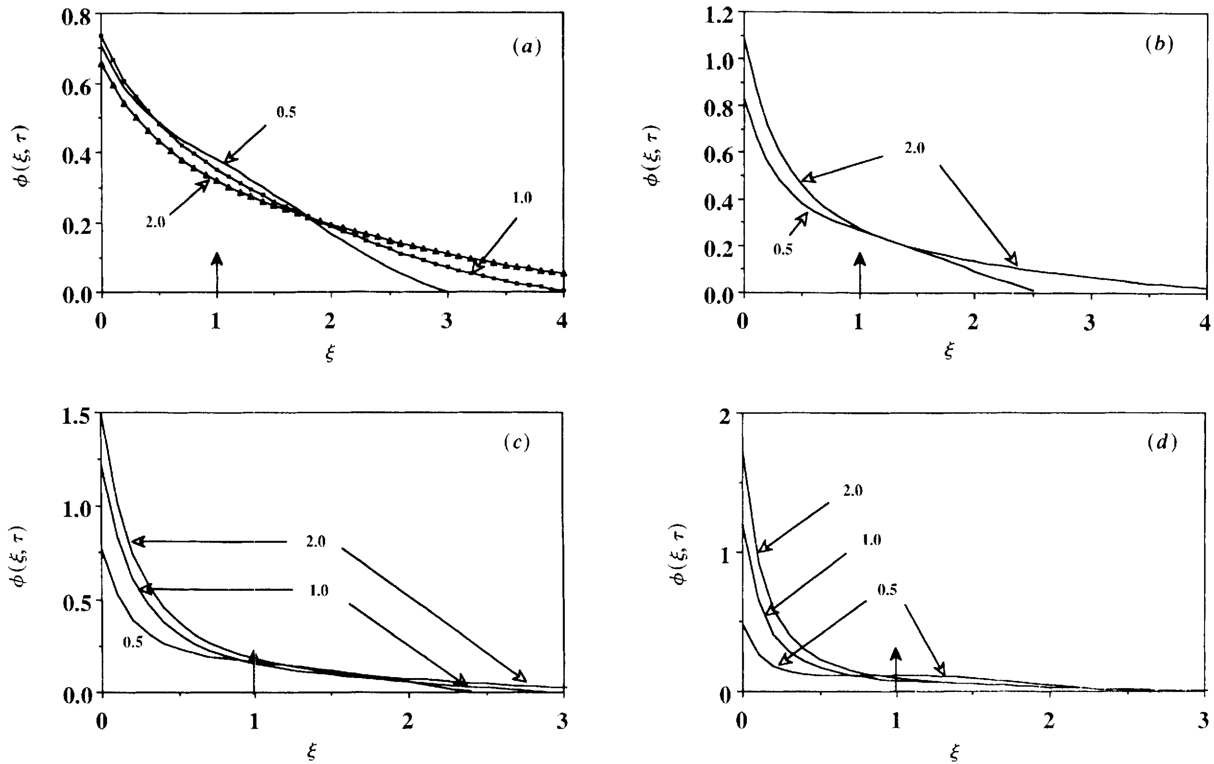

Fig. 3. Non-dimensional xy-averaged diffusion propagators, $\varphi(\xi, \tau)$ for counter-ions as a function of position $\xi \equiv \kappa z$ for reflecting boundary conditions. Various values of the dimensionless time $\tau \equiv \kappa^2 Dt$ are indicated and the reduced surface potential $Y_0 \equiv \beta e\psi(0)$ are as follows: (a) 1.0, (b) 2.0, (c) 3.0 and (d) 4.0. The ↑ denotes the initial position at $\xi_0 = 1$.

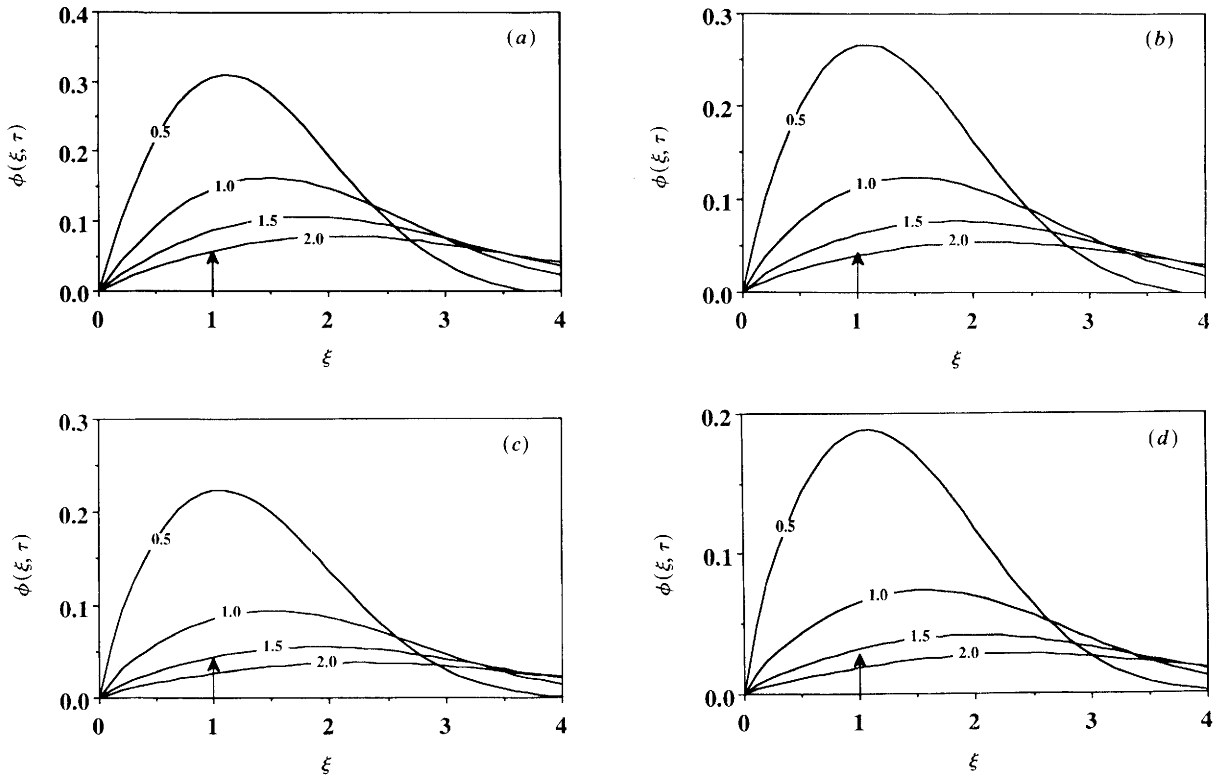

Fig. 4. Non-dimensional xy-averaged diffusion propagators, $\varphi(\xi, \tau)$ for counter-ions as a function of position $\xi \equiv \kappa z$ for absorbing boundary conditions. Various values of the dimensionless time $\tau \equiv \kappa^2 Dt$ indicated and the reduced surface potential $Y_0 \equiv \beta e\psi(0)$ are as in fig. 3. The $\uparrow$ denotes the initial position at $\xi_0 = 1$.

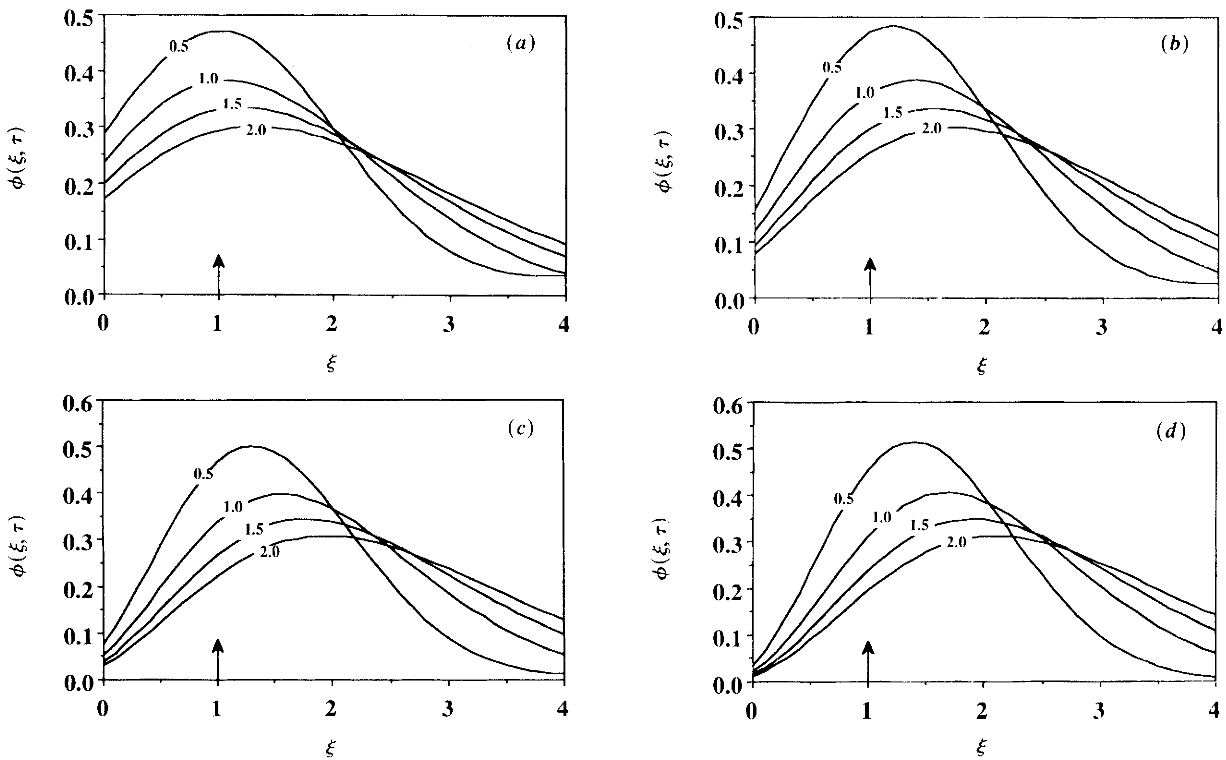

Fig. 5. Non-dimensional xy-averaged diffusion propagators, $\varphi(\xi, \tau)$ for co-ions as a function of position $\xi \equiv \kappa z$ for reflecting boundary conditions. Various values of the dimensionless time $\tau \equiv \kappa^2 Dt$ are indicated and the reduced surface potential $Y_0 \equiv \beta e\psi(0)$ are as in fig. 3. The ↑ denotes the initial position at $\xi_0 = 1$.

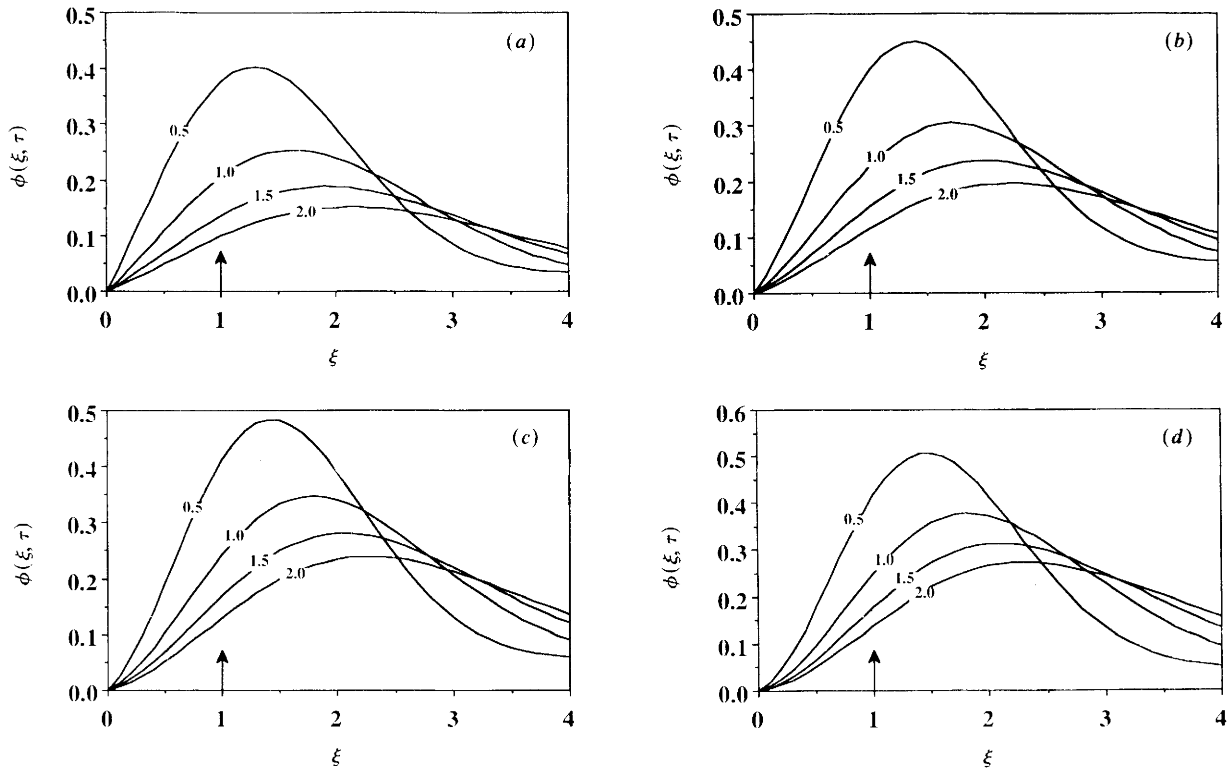

Fig. 6. Non-dimensional *xy*-averaged diffusion propagators, $\varphi(\xi, \tau)$ for co-ions as a function of position $\xi \equiv \kappa z$ for absorbing boundary conditions. Various values of the dimensionless time $\tau \equiv \kappa^2 Dt$ are indicated and the reduced surface potential $Y_0 \equiv \beta e\psi(0)$ are as in fig. 3. The ↑ denotes the initial position at $\xi_0 = 1$.

as the surface potential increases, the co-ions are repelled more strongly from the surface. As a consequence, the propagator maxima at equal times are again higher for higher surface potentials.

This calculation has contributed some exact analytical results for the ion diffusion problem in the Smoluchowski-Gouy-Chapman model. The favourable comparison between stochastic simulations and the Smoluchowski-Poisson-Boltzmann treatment of the model consisting of only univalent counter-ions between planar charged surfaces[11] would suggest that the present treatment is likely to be fairly good, at least for univalent electrolytes.

I thank Bertil Halle for arousing my interest in this subject, and also Barry Hughes and Lee White for providing constant stimulations. This work receives partial support from a Melbourne University Special Research Grant.

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Paper 7/570; *Received* 31*st March*, 1987