

# Theoretically computed proton diffusion coefficients in hydrated PEEKK membranes

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A recently derived molecular structure–function model based on non-equilibrium statistical mechanics has been used to compute proton friction and diffusion coefficients in 65% sulfonated PEEKK membranes at various degrees of hydration. Morphological parameters, taken from recent SAXS measurements, including pore radius and average separation distance of the sulfonate fixed sites within the pore, along with results from electronic structure explicit water calculations for *para*-toluene sulfonic acid, were used as input parameters in the model. For membranes where the hydration levels ( $\lambda$ ) were 15, 23, and 30 H<sub>2</sub>O's/SO<sub>3</sub><sup>-</sup>, the model predicted proton diffusion coefficients of  $4.13 \times 10^{-10}$ ,  $1.23 \times 10^{-9}$ , and  $1.54 \times 10^{-9}$  m<sup>2</sup> s<sup>-1</sup>, respectively. These values were obtained without any attempt at fitting to the results obtained from pulsed-field gradient NMR experiments. These computed diffusion coefficients are all within approximately 15% of the measured values; demonstrating the substantial predictive capability of the model. Furthermore, this investigation has shown that at the lower water content ( $\lambda = 15$ ) the transport of the proton may be adequately described as vehicular in nature, while at the two higher water contents ( $\lambda = 23, 30$ ) there is a contribution *via* structural diffusion.

## Introduction

Low temperature polymer electrolyte fuel cells (PEMFCs) utilizing hydrogen or methanol as the fuel (specifically, direct methanol fuel cells (DMFCs)) provide promising candidates for transportation applications and for use in portable electronic devices. These prospective applications have stimulated considerable interest in the development of polymer-based proton conducting materials during the past two decades. Eventual commercial use of PEMFCs will depend on obtaining fundamental understanding and consequent optimization/improvement of the following: (i) electro-oxidation of the fuel at the anode; (ii) membrane conductivity; (iii) management of the water within the membrane, and for DMFCs (iv) minimization of methanol crossover within the cell.<sup>1</sup> This work focuses on elucidating membrane structure–function issues pertaining to the second and third factors.

A suitable membrane should be both thermally and mechanically stable and perform with high proton conductivity and essentially no solvent (*i.e.* water and methanol) transport (anode to cathode) at temperatures that provide good reaction kinetics at the electrodes. Due to the economic potential of DMFCs, a substantial number of trends and strategies in membrane design/development have emerged. These include the utilization of various materials including: the venerable poly(perfluoro) sulfonic acid polymers (*i.e.* Nafion<sup>®</sup>), polyetherketones (*i.e.* PEEKK, PEEK *etc.*),<sup>2</sup> polybenzimidazole,<sup>3</sup> polystyrene–divinylbenzene mixtures radiation-grafted to poly(tetrafluoroethylene-co-hexafluoropropylene),<sup>4</sup> Nafion<sup>®</sup> impregnated microporous PTFE (*i.e.* Gore-Select<sup>®</sup>),<sup>5</sup> sulfonated styrene–ethylene/butylene–styrene triblock polymer,<sup>6</sup> and polyphosphazenes.<sup>7</sup>

Although the efforts in development and experimental characterization of these materials have been considerable, many performance features are not well understood. Some of this deficiency is due to the complexity of the membranes when hydrated, which usually consist of a hydrophobic polymeric matrix micro-separated from water and ion containing domains.<sup>8</sup> In an effort to understand the function of these materials, a number of models have been developed utilizing various approaches.<sup>9–13</sup> Generally, the predictive capability of these models has been limited, due to their phenomenological nature and the use of ‘fitting’ parameters. For modeling to play a role in the development of new materials with improved performance, the molecular structure (specifically, the water/polymer interface) and polymer morphology must be integral components.

Thus, we have expended considerable effort in developing a fundamental understanding of proton conduction through modeling that specifically includes: (1) molecular information of water–polymer, water–ion, and water–water interactions; (2) hydration dependant polymer morphology; and (3) water cluster geometry. Previous work has focused on obtaining structural information of the polymeric components that form the polymer/water interface and a molecular description of the interactions of water with sulfonic acid groups (perfluorinated and aromatic) using *ab initio* techniques and dielectric continuum modeling with solvation theory.<sup>14–20</sup> Results of these theoretical studies along with experimentally determined pore parameters were implemented in a parallel effort: the derivation and development of a molecular structure proton and water transport model for hydrated PEMs.<sup>21–23</sup> This non-equilibrium statistical mechanical model, without resorting to any ‘adjustable’ parameters, predicted proton diffusion coefficients

in Nafion<sup>®</sup> membranes with water contents of 6 and 13 H<sub>2</sub>O's/SO<sub>3</sub><sup>-</sup>,<sup>22</sup> and more recently, fully hydrated Nafion<sup>®</sup>,<sup>24</sup> all in excellent agreement with experimental measurements.<sup>25</sup> In addition, the model has shown great sensitivity to membrane specific parameters; including anionic charge distribution and pore geometry.<sup>23</sup> With the sulfonated polyetherketones (PEEK, PEEKK, *etc.*) showing substantial promise as membranes for DMFCs,<sup>8</sup> and the fact that they exhibit different transport properties and swelling behavior, in this work we apply our transport model to these aromatic based ionomers. Some of the results in this investigation were presented earlier.<sup>26</sup>

## Transport model

Our model focuses on the computation of the velocity-independent friction coefficient for the coupled transport of a proton and a water molecule (*i.e.* a hydronium ion) in a hydrated pore/channel of a Nafion<sup>®</sup> membrane. The pore is assumed to possess a cylindrical geometry with length  $L$  and cross sectional radius  $R$ , filled with  $N$  water molecules each possessing a dipole moment  $\mu$ . The sulfonate functional groups in the pore are modeled as radially symmetric, axially periodic arrays, of fixed ions (*i.e.* point charges) each possessing a charge of  $-e$ . The pore consists of  $n$  equally distributed arrays ( $f_n$  SO<sub>3</sub><sup>-</sup> groups on each array) with a separation distance of  $L_z$ .

The system Hamiltonian for the pore is taken to have the form:

$$H_T(\mathbf{p}_z, \mathbf{r}_z, \mathbf{p}, \mathbf{r}) = \frac{p_z^2}{2m_z} + \sum_{i=1}^N \frac{p_i^2}{2m} + V(\mathbf{r}_z, \mathbf{r}), \quad (1)$$

where  $\mathbf{p}_z$ ,  $\mathbf{r}_z$ , and  $m_z$  are, respectively, the momentum, position, and mass of the hydronium ion;  $\mathbf{p}$ , and  $\mathbf{r}$  the collection of momentum and position vectors of the  $N$  water molecules each with a mass  $m$ ; and  $V(\mathbf{r}_z, \mathbf{r})$  the total potential energy of the system. The latter is assumed to consist of the following four terms:

$$V(\mathbf{r}_z, \mathbf{r}) = \sum_{i=1}^N V_{zs}(|\mathbf{r}_z - \mathbf{r}_i|) + V_{zp}(\mathbf{r}_z) + \sum_{i < j}^N V_{ss}(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_{i=1}^N V_{sp}(\mathbf{r}_i). \quad (2)$$

The first term is the interaction potential energy between the hydronium ion and the  $i$ th water molecule and is assumed to be a typical ion-dipole interaction. If the rotational contributions are ignored one obtains the simplified expression:

$$V_{zs}(|\mathbf{r}_z - \mathbf{r}_i|) \approx -\frac{\mu^2 e^2}{48\pi^2 \epsilon^2 kT} \frac{1}{|\mathbf{r}_z - \mathbf{r}_i|^4}, \quad (3)$$

where  $\epsilon$  is the permittivity of the water in the pore,  $k$  the Boltzmann constant, and  $T$  the temperature.

The second term is the potential energy experienced by the hydronium ion due to the sulfonate groups. As indicated earlier, these sulfonate groups are distributed periodically in the pore and if the length of their intrusion within the pore is  $R - \tau$  (thus  $\tau$  is the radial separation distance of the hydronium ion from the fixed sites) and axial spacing  $L/n$ , and one assumes that the hydronium ion is transported along the axial center of the pore, then this potential energy term is assumed to have the form:

$$V_{zp}(\mathbf{r}_z) = \Psi_0 \cos\left(\frac{2\pi n z_z}{L}\right) = \frac{en \sum (-e)}{\pi \epsilon L} K_0 \left(\frac{2\pi n \tau}{L}\right) \cos\left(\frac{2\pi n z_z}{L}\right), \quad (4)$$

where the sum (in the explicit expression) is over all the fixed groups on each array, and  $z_z$  the axial coordinate of the hydronium ion (located at the center of the pore—as specified earlier). Eqn. (4) is a simplification of an exact result derived by Grønbech-Jensen *et al.*<sup>27</sup> using Lekner summations of coulombic interactions in three-dimensional systems having periodicity in one and two dimensions; the former being relevant for our chosen anionic charge distribution.

The third term in eqn. (2) is the potential energy due to water–water interactions, which are assumed to be dipole–dipole interactions according to:

$$V_{ss}(|\mathbf{r}_i - \mathbf{r}_j|) = \frac{2\mu^4}{3(4\pi\epsilon)^2 kT} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|^6}, \quad (5)$$

where, once again, a thermal average has been performed over all rotational angles. If it were possible to carry out a complete  $N$  body calculation then it would be possible to treat the solvent molecules on the same footing as the ions. This would imply that the permittivity  $\epsilon$  appearing in eqns. (3) and (5) would be replaced by the vacuum permittivity, *i.e.*  $\epsilon_0$ . Unfortunately, such an exhaustive treatment cannot be carried out and the solvent is therefore treated, to some extent, as a continuum. A very similar approach is adopted in the well-known Debye–Huckel theory of electrolytes, an account of which can be found in any elementary textbook of physical chemistry. It is seen that the permittivity  $\epsilon$  rather than  $\epsilon_0$  is used in the Coulombic potential energy of the ion and the resulting expression implemented in a Boltzmann distribution.

The final term describes the potential energy of the water molecules due to interaction with the fixed sulfonate groups. Under the assumption that the water dipoles are aligned with the field due to the fixed sites (an assumption that is really only valid for the water molecules occupying the first hydration shell around each sulfonate group), this term may be approximated with the expression:

$$V_{sp}(\mathbf{r}_i) \approx \frac{-2\pi\mu\Psi_0 n}{eL} \sin\left(\frac{2\pi n z_i}{L}\right). \quad (6)$$

It should be clear at this point that our system as described, is an  $N + 1$  body problem consisting of  $N$  water molecules and a single hydronium ion. In a real membrane pore there is one proton for every sulfonate group. Ignoring the presence of the ‘other’ protons will undoubtedly have certain ramifications. Perhaps the most significant is that the presence of the other protons will result in increased shielding of the interaction of the anionic groups with the hydronium ion and the water molecules. Thus, ignoring these protons will result in over estimating the potential energy (calculated in eqns. (4) and (6)) and the consequent friction experienced by the hydronium ion. However, without specific information concerning the distribution of the protons in the pore, the effects of the other protons will not be included in the model at this point. In addition, the effects of proton–proton interactions are not accounted for in our model. The contribution of these repulsive interactions to the friction coefficient, however, will be rather insignificant. Clearly, at the higher water contents, error(s) introduced by ignoring the other protons become less significant.

The time dependant distribution of the position and momentum of all the particles of the system,  $f_{N+1}(\mathbf{P}_z, \mathbf{r}_z, \mathbf{p}, \mathbf{r}; t)$ , satisfies the Liouville equation:

$$i \frac{\partial f_{N+1}}{\partial t} = L_T f_{N+1}, \quad (7)$$

where  $L_T$  is the Hermitian Liouville operator given by the Poisson bracket:

$$L_T = i\{H_T, \}. \quad (8)$$

The total force on the hydronium ion,  $\mathbf{F}_z(\mathbf{r}_z, \mathbf{r})$ , may be calculated with the relation:

$$\mathbf{F}_z(\mathbf{r}_z, \mathbf{r}) = iL_T \mathbf{p}_z = - \sum_{k=1}^N \frac{\partial V_{zs}(|\mathbf{r}_z - \mathbf{r}_k|)}{\partial \mathbf{r}_z} - \frac{\partial V_{zp}(\mathbf{r}_z)}{\partial \mathbf{r}_z} \equiv \mathbf{F}_{zs}(\mathbf{r}_z, \mathbf{r}) + \mathbf{F}_{zp}(\mathbf{r}_z), \quad (9)$$

and the corresponding average force,  $\langle \mathbf{F}_z \rangle$ , according to:

$$\langle \mathbf{F}_z \rangle(\mathbf{p}_z, \mathbf{r}_z; t) = \int d\mathbf{r} d\mathbf{p} \mathbf{F}_z(\mathbf{r}_z, \mathbf{r}) f_{N+1}(\mathbf{p}_z, \mathbf{r}_z, \mathbf{p}, \mathbf{r}; t). \quad (10)$$

where the  $N+1$  body distribution function  $f_{N+1}(\mathbf{p}_z, \mathbf{r}_z, \mathbf{p}, \mathbf{r}; t)$  is obtained through solution of eqn. (7). Such an exact solution is not possible, and therefore a more approximate route is devised for evaluation of the average force needed in the calculation of the friction coefficient of the hydronium ion.

As a first simplification we assume that *at least* two time scales can be identified in the problem: (a) a slow hydrodynamic time scale  $\tau_H$  associated with the motion of the hydronium ion and (b) a much more rapid time scale  $\tau_M$  associated with the relaxation of all the other degrees of freedom. As a consequence of this approximation,  $\tau_M \gg \tau_H$ , the ionic velocity  $\mathbf{v}_z$  will appear almost as a constant compared to the rates of relaxation of the other degrees of freedom. Such an approximation is made in deriving the well-known Stokes law and in the so-called Brownian approximations and, indeed, all the criticisms that are leveled against the employment of these theories for the transport of small molecular species can also be made in our case as well. Despite these criticisms Stokes law still remains as a cornerstone in practically all theories of electrolyte transport. It is in common with the spirit of these, commonly used and indeed very successful theories, that we employ exactly the same approximation in our work. A Galilean coordinate transformation from the laboratory reference frame to a new reference frame moving with velocity  $\mathbf{v}_z$  (*i.e.* with the hydronium ion) results in a system Hamiltonian

$$H_0(\mathbf{r}_z, \mathbf{p}, \mathbf{r}) = \sum_{i=1}^N \frac{m(\mathbf{v}_i + \mathbf{v}_z)^2}{2} + V(\mathbf{r}_z, \mathbf{r}). \quad (11)$$

With use of eqns. (8) and (11) the explicit form of the Liouville operator corresponding to this new reference frame,  $L_0$ , is:

$$L_0 = -i \sum_{k=1}^N \frac{\mathbf{p}_k}{m} \cdot \frac{\partial}{\partial \mathbf{r}_k} - i \sum_{k=1}^N \frac{\partial V_{zs}(|\mathbf{r}_z - \mathbf{r}_k|)}{\partial \mathbf{r}_z} \cdot \frac{\partial}{\partial \mathbf{p}_k} + i \sum_{k < j}^N \frac{\partial V_{ss}(|\mathbf{r}_k - \mathbf{r}_j|)}{\partial \mathbf{r}_k} \cdot \left( \frac{\partial}{\partial \mathbf{p}_k} - \frac{\partial}{\partial \mathbf{p}_j} \right) + i \sum_{k=1}^N \frac{\partial V_{sp}(\mathbf{r}_k)}{\partial \mathbf{r}_k} \cdot \frac{\partial}{\partial \mathbf{p}_k} \quad (12)$$

It is also assumed that the water molecules at large distances from the hydronium ion are at equilibrium with a distribution given by:

$$\rho_{\text{eq}}(\mathbf{r}_z, \mathbf{p}, \mathbf{r}) = \frac{1}{Q} \exp \left[ -\beta \left( \sum_{i=1}^N \frac{m(\mathbf{v}_i + \mathbf{v}_z)^2}{2} + V_s(\mathbf{r}_z, \mathbf{r}) \right) \right], \quad (13)$$

where  $Q$  is the canonical ensemble partition function, *i.e.*  $Q = \left( \frac{2\pi m}{\beta} \right)^{3N/2} \int d\mathbf{r} e^{-\beta V_s(\mathbf{r}_z, \mathbf{r})}$ ,  $\beta = 1/kT$ , and  $V_s(\mathbf{r}_z, \mathbf{r}) \equiv V(\mathbf{r}_z, \mathbf{r}) - \Psi(\mathbf{r}_z)$ . The velocity of the hydronium ion is assumed to be small and so truncation of a Taylor expansion of the equilibrium distribution function about  $\mathbf{v}_z$  gives:

$$\rho_{\text{eq}}(\mathbf{r}_z, \mathbf{p}, \mathbf{r}) \approx \left( 1 - \beta \sum_{j=1}^N \mathbf{p}_j \cdot \mathbf{v}_z \right) \rho^f(\mathbf{r}_z, \mathbf{p}, \mathbf{r}), \quad (14)$$

where  $\rho^f$  is an  $N$  body distribution function defined by:

$$\rho^f(\mathbf{r}_z, \mathbf{p}, \mathbf{r}) \equiv \frac{1}{Q} \exp \left\{ -\beta \left[ \sum_{i=1}^N \frac{p_i^2}{2m} + V_s(\mathbf{r}_z, \mathbf{r}) \right] \right\}. \quad (15)$$

In the new reference frame the time evolution of the hydronium ion through the pore is governed by the equation of motion:

$$i \frac{\partial \rho(\mathbf{r}_z, \mathbf{p}, \mathbf{r}, t)}{\partial t} = L_0 \rho(\mathbf{r}_z, \mathbf{p}, \mathbf{r}, t) \quad (16)$$

where  $\rho(\mathbf{r}_z, \mathbf{p}, \mathbf{r}, t)$  is the time-dependent distribution function. A formal solution of eqn. (16) is

$$\rho(\mathbf{r}_z, \mathbf{p}, \mathbf{r}, t) = e^{-iL_0 t} \rho(\mathbf{r}_z, \mathbf{p}, \mathbf{r}, 0) = e^{-iL_0 t} \rho_{\text{eq}}(\mathbf{r}_z, \mathbf{p}, \mathbf{r}). \quad (17)$$

With substitution of eqn. (14) into eqn. (17) and use of a standard identity, the expression for the distribution of the fluid around the hydronium ion becomes:

$$\rho(\mathbf{r}_z, \mathbf{p}, \mathbf{r}, t) = \rho^f - \beta \left( \sum_{j=1}^N \mathbf{p}_j \right) \rho^f \cdot \mathbf{v}_z - \frac{\beta}{i} \int_0^t dt' e^{-iL_0 t'} L_0 \left( \sum_{j=1}^N \mathbf{p}_j \right) \rho^f \cdot \mathbf{v}_z \quad (18)$$

The moving hydronium ion introduces perturbations in the surrounding medium; some of these are of a transient nature and will rapidly vanish, while others will result in a nonequilibrium stationary state (moving with the ion) denoted by the distribution function  $\rho(\mathbf{r}_z, \mathbf{p}, \mathbf{r})$ . Mathematically the latter are realized in the limit of  $t \rightarrow \infty$  in eqn. (18). Clearly, the average force on the hydronium ion is then

$$\langle \mathbf{F}_z \rangle(\mathbf{r}_z) = \int d\mathbf{r} d\mathbf{p} \mathbf{F}_z(\mathbf{r}_z, \mathbf{r}) \rho(\mathbf{r}_z, \mathbf{p}, \mathbf{r}). \quad (19)$$

Upon insertion of  $\rho(\mathbf{r}_z, \mathbf{p}, \mathbf{r})$  into eqn. (19) only the third term (of eqn. (18)) makes a non-vanishing contribution to the average force and thus one is left with

$$\langle \mathbf{F}_z \rangle(\mathbf{r}_z) = -\frac{\beta}{i} \int_0^\infty dt' \int d\mathbf{r} d\mathbf{p} \mathbf{F}_z(\mathbf{r}_z, \mathbf{r}) e^{-iL_0 t'} L_0 \left( \sum_{j=1}^N \mathbf{p}_j \right) \rho^f \cdot \mathbf{v}_z. \quad (20)$$

Evaluation of this average force on the hydronium ion requires application of the Liouville operator on the sum of the momenta of all the water molecules, *i.e.*

$$iL_0 \sum_{j=1}^N \mathbf{p}_j = \sum_{k=1}^N \frac{\partial V_{zs}(|\mathbf{r}_z - \mathbf{r}_k|)}{\partial \mathbf{r}_z} + \sum_{k=1}^N \frac{\partial V_{ps}(\mathbf{r}_k)}{\partial \mathbf{r}_k} \equiv -\mathbf{F}_{zs}(\mathbf{r}_z, \mathbf{r}) - \mathbf{F}_{ps}(\mathbf{r}). \quad (21)$$

Thus, with substitution of this result and the total force (eqn. (9)) into eqn. (19) we obtain for the average force on the hydronium ion:

$$\langle \mathbf{F}_z \rangle(\mathbf{r}_z) = -\beta \int_0^\infty dt \int d\mathbf{r} d\mathbf{p} (\mathbf{F}_{zs}(\mathbf{r}_z, \mathbf{r}) + \mathbf{F}_{zp}(\mathbf{r}_z, \mathbf{r})) e^{-iL_0 t} \times (\mathbf{F}_{zs}(\mathbf{r}_z, \mathbf{r}) + \mathbf{F}_{ps}(\mathbf{r}, \mathbf{r})) \rho^f \cdot \mathbf{v}_z. \quad (22)$$

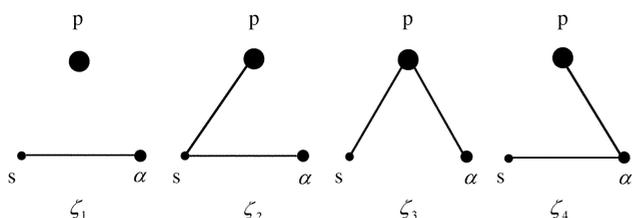
The average force on the hydronium ion is proportional to its velocity according to:

$$\langle \mathbf{F}_z \rangle = -\zeta \cdot \mathbf{v}_z$$

and thus the scalar friction coefficient for the ion may be calculated from the relation:

$$\zeta_z = \frac{\beta}{3} \int_0^\infty dt \text{Tr} \left( \langle \mathbf{F}_{zs} e^{-iL_0 t} \mathbf{F}_{zs} \rangle_0 + \langle \mathbf{F}_{zs} e^{-iL_0 t} \mathbf{F}_{ps} \rangle_0 + \langle \mathbf{F}_{zp} e^{-iL_0 t} \mathbf{F}_{ps} \rangle_0 + \langle \mathbf{F}_{zp} e^{-iL_0 t} \mathbf{F}_{zs} \rangle_0 \right) \quad (23)$$

where  $\langle \rangle_0$  denotes an average over the  $N$  body distribution function  $\rho^f(\mathbf{r}_z, \mathbf{p}, \mathbf{r})$ , defined in eqn. (15). The friction coefficient consists of four force–force correlation terms (denoted  $\zeta_1$ ,  $\zeta_2$ ,  $\zeta_3$ , and  $\zeta_4$ ) that may be given the following pictorial representations:



where  $p$  = pendant (*i.e.* sulfonate group),  $s$  = solvent, and  $\alpha$  = the hydronium ion. The term  $\zeta_1$  corresponds to an average force experienced by the hydronium ion due to only the solvent (*i.e.* water) molecules, and  $\zeta_2$  is the average force on the hydronium ion due to the pendant groups *via* the solvent medium. Similar physical meanings can be given to the other representations.

Examination of the first force–force correlation function,  $\zeta_1$ , indicates it involves only the force the water exerts on the hydronium ion ( $\mathbf{F}_{zs}$ ) and so is taken to be either the friction coefficient of a hydronium ion in bulk water calculated with the Stokes relation (*i.e.*  $\zeta_1 = 6\pi\eta\alpha$ ), or the friction coefficient of a proton in bulk water derived from experimental diffusion measurements (*i.e.*  $\zeta_1 = kT/D_{\text{exp}}$ ,  $D_{\text{exp}} = 9.311 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ <sup>28</sup>). The choice of the numerical value of  $\zeta_1$  is dependent on the nature of the water (in the pore) through which the proton moves and is discussed below. Thus, we explicitly evaluate only the latter three terms in eqn. (23) taking their sum to be a correction,  $\zeta^{(c)}$ :

$$\zeta^{(c)} = \zeta_2 + \zeta_3 + \zeta_4 \quad (24)$$

In order to calculate these contributions to the friction coefficient, the following steps are carried out:

(1) The forces  $\mathbf{F}_{zs}$ ,  $\mathbf{F}_{ps}$  and  $\mathbf{F}_{zp}$  are inserted from eqns. (9) and (21), to yield:

$$\begin{aligned} \zeta_2 &= \frac{-e\mu^3 n^2 \Psi_0}{9\epsilon^2 L^2 (kT)^2} \int_0^\infty dt \left\langle \sum_{k=1}^N \sum_{l=1}^N \frac{(z_x - z_l)}{|\mathbf{r}_x - \mathbf{r}_l|^6} e^{-iL_0 t} \cos\left(\frac{2\pi n z_k}{L}\right) \right\rangle_0 \\ \zeta_3 &= \frac{8\mu n^3 \pi^3 \Psi_0^2}{3L^3 \epsilon kT} \sin\left(\frac{2\pi n z_x}{L}\right) \int_0^\infty dt \left\langle e^{-iL_0 t} \sum_{k=1}^N \cos\left(\frac{2\pi n z_k}{L}\right) \right\rangle_0 \\ \zeta_4 &= \frac{-e^2 \mu^2 n \Psi_0}{18\pi \epsilon^2 L (kT)^2} \sin\left(\frac{2\pi n z_x}{L}\right) \int_0^\infty dt \left\langle e^{-iL_0 t} \sum_{k=1}^N \frac{(z_x - z_k)}{|\mathbf{r}_x - \mathbf{r}_k|^6} \right\rangle_0 \end{aligned} \quad (25)$$

These three equations may be written in a generic and compact form as:

$$\zeta_j \equiv \Omega \int_0^\infty dt \langle \Re_1 e^{-iL_0 t} \Re_2 \rangle_0; \quad j = 2, 3, 4 \quad (26)$$

(2) The ensemble average  $\langle \rangle_0$  is computed by integration over the coordinates  $\mathbf{r}$  and momenta  $\mathbf{p}$  with the equilibrium distribution function  $\rho^f(\mathbf{r}_z, \mathbf{p}, \mathbf{r})$  defined in eqn. (15). It is evident

that, apart from the hydronium ion  $\alpha$ , the function  $\rho^f(\mathbf{r}_z, \mathbf{p}, \mathbf{r})$  is defined in the phase space of the  $N$  water molecules, however, a brief examination of the potentials involved in the problem shows that only one- and two- body potentials enter the calculation and therefore only one- and two-body reduced distribution functions appear in the averages in eqn. (25). Furthermore, since  $\rho^f(\mathbf{r}_z, \mathbf{p}, \mathbf{r})$  can be expressed as a product of two functions:

$$\rho^f(\mathbf{r}_z, \mathbf{p}, \mathbf{r}) = \Phi_N(\mathbf{p}) P_N(\mathbf{r}_z, \mathbf{r}),$$

the integration over the momentum variables can be carried out in a trivial manner. The bulk of the computation, therefore, involves just the two functions  $P_1(\mathbf{r}_1)$  and  $P_2(\mathbf{r}_1, \mathbf{r}_2)$  defined in the following manner:

$$\begin{aligned} P_1(\mathbf{r}_1) &= \int d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N P_N(\mathbf{r}) \text{ and } P_2(\mathbf{r}_1, \mathbf{r}_2) \\ &= \int d\mathbf{r}_3 d\mathbf{r}_4 \dots d\mathbf{r}_N P_N(\mathbf{r}) \end{aligned} \quad (27)$$

Owing to the fact that the ion/dipole and field/dipole interactions are much stronger than the dipole/dipole interaction it is possible to write:  $P_2(\mathbf{r}_1, \mathbf{r}_2) \approx P_1(\mathbf{r}_1)P_1(\mathbf{r}_2)$  and we have:

$$\begin{aligned} P_1(\mathbf{r}_1) &= \frac{N}{g^2} z(\mathbf{r}_1), P_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{N^2}{g^2} z(\mathbf{r}_1)z(\mathbf{r}_2) \\ g &\equiv \int d\mathbf{r} z(\mathbf{r}) \end{aligned} \quad (28)$$

where

$$\begin{aligned} z(\mathbf{r}_i) &= \exp \left[ -\beta \left\{ \frac{a_1}{|\mathbf{r}_x - \mathbf{r}_i|^4} + a_3 \sin\left(\frac{2\pi n z_i}{L}\right) \right\} \right] \\ a_1 &= -\frac{\mu^2 e^2}{48\pi^2 \epsilon^2 kT}, \quad a_3 = -\frac{2\pi \mu \Psi_0 n}{eL} \end{aligned}$$

It is imperative to bear in mind the fact that the integrands in eqn. (26) will diverge when  $|\mathbf{r}_x - \mathbf{r}_i| = 0$ . Such a divergence is physically unreasonable and is eliminated in our calculations by *assuming the existence of hard-core repulsive interactions for short intermolecular distances.*

(3) The time displacement operator is expanded as a power series according to:

$$e^{iL_0 t} = \sum_{p=0}^{\infty} \frac{(-iL_0 t)^p}{p!} \quad (29)$$

Substitution of this expansion in eqn. (26) produces a power series in which only the even powers of the operator  $L_0$  produce a non-vanishing result and thus the correction to the friction coefficient is expressed as:

$$\zeta_j = K \int_0^\infty dt \left( c_{0j} - \frac{1}{2} c_{2j} t^2 + \dots \right) \quad (30)$$

In principle one would need to compute an infinite number of coefficients  $c_{pj}$ , however Paul<sup>29</sup> has shown by comparison with several molecular simulation results that the infinite series in eqn. (30) can be approximated by a [0,2] Padé approximant so that:

$$\zeta_j = K \left( \frac{c_{0j}^{\frac{3}{2}} \pi}{\sqrt{2c_{2j}}} \right) \quad (31)$$

Thus the correction to the friction coefficient can be calculated from only the first two coefficients in eqn. (30). The final spatial integrations that lead to numerical values for  $c_{0j}$  and have to be carried out numerically.

**Table 1** Input parameters for hydrated 65% sulfonated PEEKK membrane pores

Water content, $\lambda$	$R/\text{\AA}$	$d_{\text{SO}_3^-}/\text{\AA}$	$\tau/\text{\AA}$	$L/\text{\AA}$	$n$	$N$	$f_s$	$-\Psi_0/\text{J}$
15	7	9	6.4	40	5	375	25	$3.63 \times 10^{-22}$
23	9.5	9	9	48	6	828	36	$3.69 \times 10^{-23}$
30	12	9	11	56	7	1470	49	$7.48 \times 10^{-24}$

## Results and discussion

Friction and diffusion coefficients were computed for 65% sulfonated PEEKK membranes at ambient temperature (298.15 K) and three distinct water contents:  $\lambda$  (the number of  $\text{H}_2\text{O}'\text{s}/\text{SO}_3^-$ ) = 15, 23, and 30. The input parameters needed in the transport model were taken from electronic structure calculations of water clusters of *para*-toluene sulfonic acid<sup>20</sup> and SAXS measurements.<sup>30</sup> This information is collected together in Table 1 and includes specifically: the radius of the pore ( $R$ ), the average separation distance of the sulfonate groups ( $d_{\text{SO}_3^-}$ ), the average radial distance the hydronium ion is from the sulfonate groups ( $\tau$ ), the length of the pore ( $L$ ), the number of axially positioned radially symmetric arrays of sulfonate groups ( $n$ ), the total number of water molecules in the pore ( $N$ ), the total number of fixed sites in the pore ( $f_s$ ), and the amplitude of the periodic potential ( $\Psi_0$ ). In the calculation of the last quantity (a parameter specific to the transport model—see refs. 22 and 23), it has been assumed that the hydronium ion moves along the center of the pore.

Examination of the parameters in Table 1, indicates that with increasing membrane hydration, the size of the water domains (*i.e.* pores) increases beyond that due solely to the increase in water content. This trend is clearly tracked by observing the increase in the value of the total number of fixed sites ( $f_s$ ) and the total number of water molecules ( $N$ ). This phenomenon is consistent with what has been seen in Nafion<sup>®</sup> membrane pores.<sup>31</sup> Now despite the observed increase in volume of the pore with hydration, the average separation distance of the sulfonate groups remains constant (9 Å); this coming directly from the experimental measurements.<sup>8,30</sup> Finally, it is worth noting that the amplitude (and thus strength) of the electrostatic field due to the presence of the anionic groups along the walls of the pore ranges over nearly two orders of magnitude. Clearly, the increase in the radius of the pore has a substantial impact on the electrostatic field experienced by a hydronium ion moving along the center of the pore.

Computed friction and diffusion coefficients along with experimentally measured diffusion coefficients at the three water contents are presented in Table 2. The friction coefficient correction terms ( $\zeta_2$ ,  $\zeta_3$ , and  $\zeta_4$ ) are the result of taking a simple arithmetic average of the value of the term computed for points equally distributed along the axis of the pore, separated by a distance of 1 Å. Examination of the numerical value of these terms shows that the friction on the hydronium ion is largely due to the interaction of the sulfonate groups with the proton *via* the water molecules ( $\zeta_2$ ); as opposed to direct electrostatic interactions of the fixed sites with the hydronium ion ( $\zeta_3$  and  $\zeta_4$ ). This is consistent with previous observations with Nafion<sup>®</sup> membrane pores,<sup>20</sup> and suggests that transport of the proton in the pore will be hindered through interaction with

water that is ‘bound’ (at least to a degree) due to the electrostatic field of the fixed sites. We also note the dramatic decrease in  $\zeta_3$  as the water content is increased. As this correction term accounts for the friction on the hydronium ion due to direct interaction with the fixed sites, this trend clearly shows the influence of increasing the diameter of the pore on the diffusion of the proton.

At the two higher water contents, the net friction coefficient ( $\zeta_z$ ) is the result of adding the sum of the correction terms to the friction coefficient of a proton in bulk water ( $4.42 \times 10^{-13} \text{ kg s}^{-1}$ ) derived from experiment.<sup>29</sup> This is in contrast with the lower water content where the correction terms were added to the Stokes friction coefficient for a hydronium ion in bulk water ( $2.69 \times 10^{-12} \text{ kg s}^{-1}$ ). The choice of the numerical value of  $\zeta_1$  is made clear when one considers that the diffusion coefficient of a hydronium ion in bulk water derived from the Stokes–Einstein relation ( $D_z = kT/6\pi\eta a$ ) is  $1.53 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , a value which is lower than the experimental proton diffusion coefficient for  $\lambda = 30$  and essentially equal to that at  $\lambda = 23$ . Clearly, the corresponding friction coefficient ( $2.69 \times 10^{-12} \text{ kg s}^{-1}$ ) when corrected (*i.e.* with the addition of  $\zeta^{(c)}$ ) will result in a computed net friction coefficient much too high. One expects the transport of the proton *via* a Grotthuss mechanism to be more significant at  $\lambda = 23$  and 30 because the water at the center of the pore is closer in character to bulk water than that at the lower water content.<sup>8</sup> Therefore, it is reasonable to include the transport of the proton *via* this intermolecular transfer mechanism through the value of  $\zeta_1$ . The question of which of the two values to select for  $\zeta_1$  is further indicated from the results of a recent investigation into the permittivity of the water within the pores of PEEKK membranes at these three water contents.<sup>32</sup> Theoretical results from this study indicated that the relative permittivity of the water in the center of a pore at the lowest water content (*i.e.*  $\lambda = 15$ ) is about 67; approximately 16% less than that of bulk water; while at the two higher water contents, the permittivity of the water is 80 even for distances of up to 1.5 Å from the center of the pore.

Comparing the computed diffusion coefficients ( $D_z$ ) with those derived from pulsed-field gradient NMR measurements ( $D_{\text{exp}}$ )<sup>8,30</sup> indicates that in all cases the calculated values are slightly lower (specifically, from 8% to 15% lower) than the experimental values. The agreement with the experiments is nevertheless quite good; probably within the error of the measurements. This was also observed for Nafion<sup>®</sup> pores at  $\lambda = 6$  and 13 where the computed diffusion coefficients were also as much as 15% lower than those derived from experimental measurements. We had previously suggested that this may in part be due to the treatment of the transport of the proton in a classical manner (*i.e.* *via* the vehicular mechanism) and the consequent failure to account for transport *via* structural diffusion,

**Table 2** Friction ( $\text{kg s}^{-1}$ ) and diffusion ( $\text{m}^2 \text{ s}^{-1}$ ) coefficients for hydrated 65% sulfonated PEEKK membranes

Water content, $\lambda$	$\zeta_2$	$\zeta_3$	$\zeta_4$	$\zeta_1$	$\zeta_z$	$D_z$	$D_{\text{exp}}$
15	$6.81 \times 10^{-12}$	$4.58 \times 10^{-13}$	$8.23 \times 10^{-15}$	$2.69 \times 10^{-12}$	$9.97 \times 10^{-12}$	$4.13 \times 10^{-10}$	$4.5 \times 10^{-10}$
23	$2.89 \times 10^{-12}$	$1.38 \times 10^{-14}$	$1.69 \times 10^{-15}$	$4.42 \times 10^{-13}$	$3.35 \times 10^{-12}$	$1.23 \times 10^{-9}$	$1.5 \times 10^{-9}$
30	$2.24 \times 10^{-12}$	$8.87 \times 10^{-15}$	$4.29 \times 10^{-16}$	$4.42 \times 10^{-13}$	$2.68 \times 10^{-12}$	$1.54 \times 10^{-9}$	$1.7 \times 10^{-9}$

*i.e.* the ‘‘Grotthuss’’ mechanism.<sup>22</sup> While no contribution from intermolecular (water–water) proton transfer was included in the calculation of proton diffusion coefficients for the Nafion<sup>®</sup> membrane pores (at  $\lambda = 6$  and 13), we did include this for the PEEKK membrane pores at the two higher water contents through our choice of  $\zeta_1$ . Despite this, the computed values of  $D_z$  are still lower than suggested by experiment.

This suggests that the model over estimates the effect of the  $-\text{SO}_3^-$  groups in retarding the mobility of the proton. The electrostatic field generated by the anionic fixed sites is probably too high (in the model) due to the neglect of the presence of the additional protons. Clearly, these protons will increase the shielding, over that due only from the water molecules, of the hydronium ion from interaction with  $-\text{SO}_3^-$  groups and reduce the effects of the latter on the water molecules in the pore. Thus inclusion of additional protons in our model will result in a decrease in the magnitudes of the computed friction coefficient correction terms and a consequent increase in the calculated proton diffusion coefficient. The main reason we did not include the presence of additional protons in the original formulation of the transport model was due to the fact that the distribution of these protons is not known to any degree of certainty. While others have assumed a Boltzmann distribution for the protons within the pore<sup>12,13</sup> this neglects proton dissociation effects due to differences in conjugate anionic bases as suggested by first principles molecular orbital calculations.<sup>17,19,20</sup> Furthermore, it has been recently argued that such a continuum distribution overestimates shielding effects in pores with radii of less than two Debye lengths.<sup>33</sup> Nevertheless, the inclusion of additional protons in the model is an important aspect that needs to be addressed in future work.

## Conclusions

Our recently derived water–proton transport model has been used to compute proton friction and diffusion coefficients in 65% sulfonated PEEKK membranes at different degrees of hydration. With input from recent SAXS measurements of membranes at water contents of 15, 23, and 30  $\text{H}_2\text{O}/\text{SO}_3^-$  the model predicted proton diffusion coefficients of  $4.13 \times 10^{-10}$ ,  $1.23 \times 10^{-9}$ , and  $1.54 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ , respectively. These results agree quite well with pulsed-field-gradient NMR experiments; being between 8% and 15% lower than the experimental values. In addition, this investigation of proton diffusion for PEEKK membranes over a range of hydration levels, has confirmed the observation that the conduction mechanism is predominantly vehicular in nature, but at the higher water contents there is a contribution due to intermolecular proton transfer events (*i.e.* the Grotthuss mechanism). Thus this modeling effort has demonstrated the predictive capability of the model, as no appeal was made to any ‘adjustable’ or ‘fitting’ parameters.

Our calculations have attempted to elucidate the important role of the negatively charged  $-\text{SO}_3^-$  groups in the proton transport process. In many other models the effects of the fields generated by these groups have to some extent been either neglected or ascribed minor roles. While we have invoked some approximations in writing the analytic form for the potentials due to the  $-\text{SO}_3^-$  groups, care has been taken to maintain the integrity of the negatively charged moieties. This theoretical investigation has shown that the dominant means in which the fixed sites affect the diffusion of protons through the membrane pore, is through altering the structure of the water in the neighborhood of the protons in a manner that increases the water–proton interactions. Direct electrostatic interaction of the  $-\text{SO}_3^-$  groups with the proton is much less important in retarding the mobility of the proton. Finally, these computations have also suggested that the presence of the additional protons in the pore (a proton for each fixed site)

needs to be included in the model so that the friction on the proton due to the fixed sites is not over estimated. This extension to our transport model will be addressed in future work.

## List of symbols

$a$	radius of particle moving in a medium (Stokes relation)
$d_{\text{SO}_3^-}$	average separation distance of fixed sites
$D_z$	computed proton diffusion coefficient, $\text{m}^2 \text{ s}^{-1}$
$D_{\text{exp}}$	experimentally determined diffusion coefficient, $\text{cm}^2 \text{ s}^{-1}$ or $\text{m}^2 \text{ s}^{-1}$
$e$	fundamental charge ( $1.602 \times 10^{-19} \text{ C}$ )
$f_s$	total number of fixed sites in the pore
$\mathbf{F}_z$	total force experienced by hydronium ion/N
$\mathbf{F}_{\text{zp}}$	net force exerted on hydronium ion due to imposed electric field of fixed sites, $-\text{SO}_3^-$
$\mathbf{F}_{\text{zs}}$	net force exerted on hydronium ion due to water molecules
$\mathbf{F}_{\text{ps}}$	net force on water molecules due to imposed electric field of the fixed sites, $-\text{SO}_3^-$
$H_0$	Hamiltonian for system with reference frame at rest relative to hydronium ion/J
$i$	complex number, <i>i.e.</i> $\sqrt{-1}$
$k$	Boltzmann constant ( $1.381 \times 10^{-23} \text{ J K}^{-1}$ )
$L$	length of water cluster or pore in PEM, $\text{\AA}$
$L_0$	Liouville operator for system with reference frame at rest relative to hydronium ion
$m$	mass of a water molecule, kg
$n$	number of arrays of fixed sites distributed along the length of the pore
$N$	number of solvent (water) molecules with in the pore
$\mathbf{p}$	generalized momentum vector for all $N$ water molecules/kg $\text{m s}^{-1}$
$\mathbf{p}_z$	momentum (vector) of hydronium ion, kg $\text{m s}^{-1}$
$\mathbf{r}$	generalized position vector for all $N$ water molecules with in the pore, $\text{\AA}$
$\mathbf{r}_z$	position (vector) of hydronium ion, $\text{\AA}$
$R$	radius of water cluster or pore in PEM, $\text{\AA}$
$t$	time, s
$T$	temperature, K
$\mathbf{v}_z$	velocity of hydronium ion, $\text{m s}^{-1}$
$V$	total potential energy of all species in the pore, J
$z_z$	axial coordinate of hydronium ion, $\text{\AA}$
$z_i$	axial coordinate of an arbitrary solvent molecule, $\text{\AA}$
Greek	
$\alpha$	designation of arbitrary hydronium ion, usually a subscript
$\beta$	$1/kT$ , J
$\epsilon$	permittivity of the solvent, $7.119 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
$\underline{\zeta}$	finite friction tensor
$\zeta_1$	‘base’ or bulk water contribution to friction coefficient, $\text{kg s}^{-1}$
$\zeta_n$	$n = 2-4$ , friction coefficient correction terms, $\text{kg s}^{-1}$
$\zeta^{(c)}$	correction to friction coefficient (defined in eqn. (24)), $\text{kg s}^{-1}$
$\eta$	viscosity of medium, $\text{kg m}^{-1} \text{ s}^{-1}$
$\lambda$	number of water molecules per sulfonate group
$\mu$	dipole moment of water ( $6.17 \times 10^{-30} \text{ C m}$ )
$\rho_{\text{eq}}$	phase-space distribution function for system at equilibrium
$\tau$	the radial separation distance of the hydronium ion from the fixed sites, $\text{\AA}$
$\Psi_0$	amplitude of the potential energy due to the interaction of the hydronium ion with the pendant side chains, J
Subscripts	
$i, j$	arbitrary water molecule
$k$	arbitrary water molecule, used to designate the counting of pendant fixed group, <i>i.e.</i> $-\text{SO}_3^-$
$p$	pendant fixed group, <i>i.e.</i> $-\text{SO}_3^-$
$s$	solvent, <i>i.e.</i> water
Superscripts	
$c$	correction

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