Title: ION AND WATER TRANSPORT IN A NAFION MEMBRANE PORE: A STATISTICAL MECHANICAL MODEL WITH MOLECULAR STRUCTURE

Author(s): Stephen J. Paddison - MST-11
Reginald Paul - The University of Calgary
Thomas A. Zawodzinski Jr. - MST-11

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ION AND WATER TRANSPORT IN A NAFION® MEMBRANE PORE: A STATISTICAL MECHANICAL MODEL WITH MOLECULAR STRUCTURE


1Electronic and Electrochemical Materials and Devices Group
Los Alamos National Laboratory,
Los Alamos, NM 87545

2Department of Chemistry
The University of Calgary
Calgary, Alberta, Canada T2N 1N4

With the well established importance of the coupling of water and protons through electroosmotic drag in operating PEFCs we present here a derivation of a mathematical model that focuses on the computation of the mobility of an hydronium ion through an arbitrary cylindrical pore of a PEM with a non-uniform charge distribution on the walls of the pore. The total Hamiltonian is derived for the hydronium ion as it moves through the hydrated pore and is effected by the net potential due to interaction with the solvent molecules and the pendant side chains. The corresponding probability density is derived through solution of the Liouville equation. This probability density is then used to compute the friction tensor for the hydronium ion. We find two types of contributions: (a) due to the solvent-ion interactions for which we adopt the conventional continuum model; (b) due to the interaction between the pendant charges and the hydronium ion. The latter is a new result and displays the role of the non-uniform nature of the charge distribution on the pore wall.

INTRODUCTION

Nafion®, a perfluorosulfonic acid ionomer, continues to see application in fuel-cell systems because it exhibits good chemical stability, remarkable mechanical strength, good thermal stability, and high proton conductivity when sufficiently hydrated. Despite its use in polymer electrolyte fuel cells (PEFCs) and a hosts of other electrochemical devices, the mechanisms of ion and solvent transport in the membrane are incompletely understood. From the extensive experimental investigations (1-4) into proton and water transport within Nafion®, the following conclusions have been drawn: (a) the water self diffusion coefficient increases with increasing water content in the membrane; (b) the proton mobility (conductivity) increases with increasing hydration of the membrane; and (c) the electroosmotic drag coefficient (the number of water molecules associated with each proton) remains a constant value of 1 for membranes equilibrated with water vapor and jumps to values of between 2 and 3 for membranes immersed in liquid water. These observations strongly point to the importance of interactions of water and protons with the interfacial region of the membrane (specifically the pendant side chains terminating with sulfonic acid groups).

Based on characterization of structural and transport properties of these membranes, a number of models of the structure and molecular-level transport in hydrated polymer
electrolyte membranes (PEMs) have been proposed (5-11). Their success in predicting transport properties has been varied. However, an important aspect lacking in all these modeling efforts is the specific inclusion of molecular detail or description of the PEM. If one is to really understand the factors that affect transport of water and ions in PEMs to a level at which one can rationally propose new membranes with specific characteristics for particular processes or applications, then models of transport that contain microstructural and local molecular information must be developed and tested.

To this end, we have spent considerable effort to obtain molecular scale information on the structure of Nafion® through ab initio electronic structure calculations and dielectric continuum modeling (12-14). These calculations have characterized the hydrophilic sites and their interaction with water along with specific conformations of the pendant side chain. In addition, molecular dynamics simulations were performed (13,14) to obtain statistically significant structural parameters of the pendant side chains.

We present here our initial efforts in developing an ion and water transport model which incorporates molecular scale information for the displacement of an hydronium ion in an arbitrary pore of Nafion®.

**BASIC PORE MODEL**

As a model we consider a pore to be a cylinder of length $L$ and cross sectional radius $R$, filled with $N$ water molecules each possessing a dipole moment $\mu$. The walls of the pore will be assumed to consist of a periodic array of fixed anionic groups that exert a periodic potential within the contained volume. In our model we use both hydrodynamics and nonequilibrium statistical mechanics to describe the transport of hydronium ions through the pore. The geometry of our model is presented in the Figure 1. Here, $\alpha$ is an arbitrary hydronium ion that is being transported under the influence of an electric field $\vec{E}$ and subject to the action of intermolecular potentials due to the solvent water, of which only two representative molecules, $i$ and $j$, are shown, and a periodic potential due to the pendant groups on the wall of the pore.

The hydronium ion conductivity through the pore is derived in two steps: (1) the effective friction coefficient of the hydronium ion under the influence of the solvent and pendant groups is computed while the effect of the field, $\vec{E}$, is ignored; and (2) the electrical conductivity as a consequence of the field $\vec{E}$, with the friction coefficient from the previous step, is calculated assuming a linear ohmic response.

**DERIVATION OF MODEL**

**Governing Equations**

The total Hamiltonian $H_T$ for step (1) may be written as:

$$H_T(\vec{p}_\alpha, \vec{r}_\alpha, \vec{p}, \vec{r}) = \frac{\vec{p}_\alpha^2}{2m_\alpha} + \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + V(\vec{r}_\alpha, \vec{r}) \cdot \vec{p}_\alpha$$

[1]

The quantities appearing in this equation have the following definitions: (a) $\vec{p}_\alpha$ is the momentum of the hydronium ion and $m_\alpha$ its mass; (b) unless explicitly stated to the
contrary, any variable without a subscript refers to a collection of \( N \) vectors corresponding to the solvent molecules. Accordingly, the momentum and coordinate vectors for the water molecules are given by:

\[
\vec{p} = \{\vec{p}_1, \vec{p}_2, \ldots, \vec{p}_N\} \quad \vec{r} = \{\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N\}
\]  

[2]

The mass of a water molecule is indicated by \( m \) and is treated as a structure-less particle (i.e., the atoms are not distinguished); (c) \( V(\vec{r}_a, \vec{r}) \) is the total potential energy of the system and is composed of the following contributions:

\[
V(\vec{r}_a, \vec{r}) = \sum_{i=1}^{N} V_{\alpha}(\vec{r}_a, \vec{r}_i) + \Psi(\vec{r}_a) + \sum_{i<j}^{N} V_{\alpha}(\vec{r}_i, \vec{r}_j) + \sum_{i=1}^{N} V_{\alpha}(\vec{r}_i)
\]  

[3]

Now the various potential energy terms in Eq. [3] have the following functional forms:

(i) \( V_{\alpha} \) is the interaction potential between the hydronium ion and a water molecule. This is assumed to be a typical ion-dipole interaction:

\[
V_{\alpha}(\vec{r}_a, \vec{r}_i) = \frac{\mu e \cos \gamma}{4\pi \varepsilon |\vec{r}_a - \vec{r}_i|^2}
\]  

[4]

where \( \gamma \) is the angle made by the vector pointing from \( \alpha \) to the center of the dipole axis of water with the dipolar axis itself. Since in most of the work that has so far been done in this field the solvent is assumed to be a continuum we will reduce the level of sophistication in our work by considering a thermal average over \( \gamma \) and thereby ignoring the rotational contribution to the friction coefficient:

\[
V_{\alpha}(\vec{r}_a, \vec{r}_i) = \frac{\mu e \cos \gamma}{4\pi \varepsilon |\vec{r}_a - \vec{r}_i|^2} e^{-\frac{\mu e \cos \gamma}{4\pi \varepsilon k T |\vec{r}_a - \vec{r}_i|^2}}
\]

Here, \( K \) is a normalization constant for the thermal distribution function. Expanding the exponential and retaining only linear terms we get:

\[
V_{\alpha}(\vec{r}_a, \vec{r}_i) = \frac{\pi}{0} \int \frac{\mu e \cos \gamma}{4\pi \varepsilon |\vec{r}_a - \vec{r}_i|^2} e^{-\frac{\mu e \cos \gamma}{4\pi \varepsilon k T |\vec{r}_a - \vec{r}_i|^2}}
\]

\[
\approx -\frac{\mu^2 e^2}{48\pi^2 \varepsilon^2 k T |\vec{r}_a - \vec{r}_i|^4}
\]  

[5]

\( \varepsilon \) is the permittivity of the medium, \( k \) is the Boltzmann constant, \( T \) is the temperature and \( e \) the charge of the hydronium ion.

(ii) \( \Psi(\vec{r}_a) \) is the periodic potential energy experienced by the hydronium ion due to the pendant groups on the pore wall. If we assume that these groups are located with a spacing of \( L/n \) where \( n \) is an integer then this potential energy term may be written:

\[
\Psi(\vec{r}_a) = \Psi(\vec{r}_a, \theta_a, z_a) = V_0 e \sin \left( \frac{2\pi n z_a}{L} \right)
\]  

[6]

where \( V_0 \) is the amplitude of the potential and \( L \) is the length of the pore.
(iii) $V_s(\vec{r}_i - \vec{r}_j)$ is the solvent-solvent interaction potential which is assumed to be a dipole-dipole interaction (thermally averaged over all rotational angles):

$$V_s(\vec{r}_i - \vec{r}_j) = \frac{2\mu^4}{3(4\pi\varepsilon_0)^2 kT} \frac{1}{|\vec{r}_i - \vec{r}_j|^6}$$

(iv) $V_p(\vec{r}_i)$ is the potential energy of a water molecule (taken as dipole) due to the periodic field, $\vec{E}_p$, produced by the pendant charges. Now from Eq. [6] the pendant field at the location of a solvent molecule $i$ is given by:

$$\vec{E}_p = -\vec{\nabla}_i \Psi(\vec{r}_i) = -\kbar \frac{2\pi \varepsilon_0 \mu n}{L} \cos \left( \frac{2\pi n z_i}{L} \right) \cos \delta$$

where $\kbar$ is a unit vector along the z-axis. The potential energy of the dipolar water molecule is:

$$V_p(\vec{r}_i) = -\vec{\mu} \cdot \vec{E}_p = \frac{2\pi \varepsilon_0 \mu n}{L} \cos \left( \frac{2\pi n z_i}{L} \right) \cos \delta$$

where $\delta$ is the angle that the dipole makes with the field $\vec{E}_p$. If we assume, as a first approximation, that the water dipoles are aligned with the field $\vec{E}_p$, then we may set $\cos \delta = 1$ which leads to the final form:

$$V_p(\vec{r}_i) = \frac{2\pi \varepsilon_0 \mu n}{L} \cos \left( \frac{2\pi n z_i}{L} \right)$$

With the description of the system presented above, we are essentially dealing with an $N+1$ body problem composed of the solvent molecules and a single hydronium ion. At this point we will assume that the hydronium ion concentration is low enough so that interactions between them can be ignored and it is sufficient to examine the dynamics of a single ion. The motion of the ensemble of hydronium ions leads to a current and this will be examined in the next step of the calculation. Furthermore, the pendant groups have been treated as fixed objects on the wall of the pore and thus possess no dynamics of their own and serve only to provide a field in which the hydronium ions are transported. It is our objective to compute the contribution made by this field to the ionic friction.

The time dependent distribution function $f_{N+1}(\vec{p}_\alpha, \vec{r}_\alpha, \vec{p}, \vec{r}, t)$ must satisfy the Liouville equation (15):

$$i \frac{\partial f_{N+1}}{\partial t} = L_T f_{N+1}$$

where $L_T$ is the Liouville operator for the system which is given by:
Substitution of $H_T$ from Eqs. [1] and [3] yields:

$$L_T = \sum_{k=1}^{N} \left( \frac{\partial H_T}{\partial \bar{p}_k} \cdot \frac{\partial}{\partial r_k} - \frac{\partial H_T}{\partial \bar{r}_k} \cdot \frac{\partial}{\partial \bar{p}_k} \right) + \sum_{k<l} \left( \frac{\partial H_T}{\partial \bar{p}_k} \cdot \frac{\partial}{\partial \bar{r}_k} - \frac{\partial H_T}{\partial \bar{r}_k} \cdot \frac{\partial}{\partial \bar{p}_k} \right)$$

[10]

Substitution of $H_T$ from Eqs. [1] and [3] yields:

$$L_T = -i \frac{\bar{p}_a}{m_a} \cdot \frac{\partial}{\partial \bar{r}_a} - i \sum_{k=1}^{N} \frac{\bar{p}_k}{m_k} \cdot \frac{\partial}{\partial \bar{r}_k} - i \sum_{k<l} \frac{\partial V_{al}(\bar{r}_a - \bar{r}_l)}{\partial \bar{r}_a} \cdot \frac{\partial}{\partial \bar{r}_k} + i \sum_{k<l} \frac{\partial V_{al}(\bar{r}_a - \bar{r}_l)}{\partial \bar{r}_k} \cdot \frac{\partial}{\partial \bar{p}_a}$$

$$+ i \sum_{k=1}^{N} \frac{\partial V_{al}(\bar{r}_a - \bar{r}_l)}{\partial \bar{p}_a} \cdot \frac{\partial}{\partial \bar{r}_k} + i \sum_{k<l} \frac{\partial V_{al}(\bar{r}_a - \bar{r}_l)}{\partial \bar{r}_k} \cdot \frac{\partial}{\partial \bar{p}_a}$$

[11]

The total force experienced by the hydronium ion within the pore can be calculated from the Liouville operator:

$$\bar{F}_a(\bar{r}_a) = \frac{\partial}{\partial \bar{r}_a}$$

[12]

The average force experienced by the hydronium ion is given by:

$$\langle \bar{F}_a(\bar{p}_a, \bar{r}_a, t) \rangle = \int d\bar{r} d\bar{p} \bar{F}_a(\bar{r}_a, \bar{r}) f_{N+1}(\bar{p}_a, \bar{r}_a, \bar{p}, \bar{r}, t)$$

[13]

where the $N+1$ body distribution function $f_{N+1}(\bar{p}_a, \bar{r}_a, \bar{p}, \bar{r}, t)$ is obtained by solving the full Liouville Eq. [9]. Such an exact calculation is impossible and therefore a more approximate route must be adopted.

In order to simplify the problem we proceed in a manner similar to that adopted in the calculation of the Stokes' friction coefficient in hydrodynamics (16). In this type of calculation the hydronium ion is assumed to move with a fixed velocity $\bar{v}_a$ and the space fixed coordinate system shown in Fig. 1 is replaced by a moving frame of velocity $\bar{v}_a$. These two conditions enable us to eliminate the kinetic energy term of the hydronium ion in the Hamiltonian (Eq. [1]) since this ion may be treated as a fixed object. The solvent molecules in this new coordinate frame, however, now possess an average velocity - $\bar{v}_a$ and thus the $i$th solvent molecule must have a velocity $\bar{v}_i + \bar{v}_a$ leading to a new Hamiltonian:

$$H_0(\bar{r}_a, \bar{v}_a, \bar{r}) = \sum_{i=1}^{N} \frac{m(\bar{v}_i + \bar{v}_a)^2}{2} + V(\bar{r}_a, \bar{r})$$

[14]

where, as pointed out earlier, $\bar{v}_a$ is a constant and is now a parameter which will no longer appear as an argument in the various functions to be considered.

The Liouville operator $L_0$ corresponding to this Hamiltonian is obtained from Eq. [11] after eliminating all those operators that depend upon the momentum, $\bar{p}_a$, of the hydronium ion:
At large distances from the hydronium ion the solvent molecules are assumed to be in an equilibrium state \( \rho_{eq} \); the mathematical form for which may be written down immediately from the form of the Hamiltonian in Eq. [14]:

\[
\rho_{eq}(\vec{r}_a, \vec{v}_a, \vec{r}) = \frac{1}{Q} \exp \left[ -\beta \left( \sum_{j=1}^{N} \frac{m(\vec{v}_j + \vec{v}_a)^2}{2} + V(\vec{r}_a, \vec{r}) \right) \right]
\]  

[16]

here, \( Q \) is the partition function for this canonical distribution function, and \( \beta = 1/kT \). Assuming that the velocity of the hydronium ion is very small Eq. [16] may expanded as a Taylor series in \( \vec{v}_a \) retaining only the zero order and linear terms of this expansion:

\[
\rho_{eq}(\vec{r}_a, \vec{v}_a, \vec{r}) \approx \left( 1 - \beta \sum_{j=1}^{N} \vec{p}_j \cdot \vec{v}_a \right) \frac{1}{Q} \exp \left[ -\beta \left( \sum_{j=1}^{N} \frac{p_j^2}{2m} + V(\vec{r}_a, \vec{r}) \right) \right]
\]

[17]

where the definition of \( \rho' \), an \( N \)-body distribution function, is clear from Eq. [17]. The partition function can be obtained by integrating over all the momentum and space variables:

\[
Q = \left( \frac{2\pi m}{\beta} \right)^{3N/2} Z; \quad Z \equiv \int d\vec{r} e^{-\beta V(\vec{v}_a, \vec{r})}
\]

[18]

where \( Z \) is the so called configuration integral. \( \rho' \) may now be written in the more explicit form:

\[
\rho'(\vec{p}, \vec{r}) = \left( \frac{\beta}{2\pi m} \right)^{3N/2} \exp \left[ -\beta \sum_{j=1}^{N} \frac{p_j^2}{2m} \right] P_N(\vec{r})
\]

[19]

where \( P_N(\vec{r}) \equiv \frac{1}{Z} \exp[-\beta V(\vec{r}_a, \vec{r})] \)

[20]

As the hydronium ion progresses through the solvent it perturbs its equilibrium state into a time dependent state \( \rho(\vec{r}_a, \vec{p}, \vec{r}, t) \) which must satisfy a Liouville equation similar to Eq. [9] but with the reduced Liouville operator \( L_0 \):
In order to obtain \( \rho(\vec{r}_a, \vec{p}, \vec{r}, t) \) Eq. [21] must be solved given the initial condition of Eq. [17]. Such a solution can be obtained using standard methods to yield:

\[
\rho(\vec{r}_a, \vec{p}, \vec{r}, t) = e^{-iL_0t} \rho_{eq}(\vec{r}_a, \vec{p}, \vec{r}) = e^{-iL_0t} \left( 1 - \beta \sum_{j=1}^{N} \vec{p}_j \cdot \vec{v}_a \right) \rho^f(\vec{r}_a, \vec{p}, \vec{r})
\]  

[22]

Using a standard mathematical identity this equation can be rewritten in the following manner:

\[
\rho(\vec{r}_a, \vec{p}, \vec{r}, t) = \rho^f - \beta \left( \sum_{j=1}^{N} \vec{p}_j \right) \rho^f \cdot \vec{v}_a - \frac{\beta}{i} \int_0^t dt' e^{-iL_0t'} \left( \sum_{j=1}^{N} \vec{p}_j \right) \rho^f \cdot \vec{v}_a
\]  

[23]

If the transients caused by the perturbations from the moving hydronium ion vanish rapidly then a nonequilibrium stationary state, \( \rho(\vec{r}_a, \vec{p}, \vec{r}) \), is achieved by the solvent, which is mathematically given by allowing \( t \to \infty \) in Eq. [23]. We replace the full \( N+1 \) body distribution function in Eq. [13] with this more approximate version:

\[
\langle \vec{F}_a \rangle(\vec{r}_a) = \int d\vec{r} d\vec{p} \vec{F}_a(\vec{r}_a, \vec{r}) \rho(\vec{r}_a, \vec{p}, \vec{r})
\]  

[24]

The following identity is well known from nonequilibrium statistical mechanics (5):

\[
iL_0 \sum_{j=1}^{N} \vec{p}_j = \sum_{k=1}^{N} \frac{\partial V_{ax}(\vec{r}_a - \vec{r}_k)}{\partial \vec{r}_a} - \sum_{k=1}^{N} \frac{\partial V_{px}(\vec{r}_a)}{\partial \vec{r}_k} \equiv \vec{F}_a(\vec{r}_a, \vec{r}) + \vec{F}_p(\vec{r})
\]  

[25]

Substituting Eq. [25] in Eq. [23] and the result in Eq. [24] along with the definition of the force on the hydronium ion given in Eq. [12] one may calculate the average force \( \langle \vec{F}_a \rangle \). The friction coefficient is the quantity that relates this force with the hydronium ion velocity, \( \vec{v}_a \), in a linear manner and it can be easily seen that such a relationship is given by the second and third terms of Eq. [23]. The second term is, however, odd in the momentum components while Eq. [17] shows that \( \rho^f \) is even in these variables hence a zero contribution to the friction coefficient is made by this second term. The third term of Eq. [23] yields a finite friction tensor of second rank and is composed of four terms:

\[
\zeta = \beta \int_0^\infty dt \langle \vec{F}_a e^{-iL_0t} \vec{F}_a \rangle_0 + \beta \int_0^\infty dt \langle \vec{F}_a e^{-iL_0t} \vec{F}_{pt} \rangle_0 + \beta \int_0^\infty dt \langle \vec{F}_{pt} e^{-iL_0t} \vec{F}_a \rangle_0 + \beta \int_0^\infty dt \langle \vec{F}_{pt} e^{-iL_0t} \vec{F}_{pt} \rangle_0 \\
\equiv T_1 + T_2 + T_3 + T_4
\]  

[26]
where the symbol $\langle \rangle_0$ implies an average over the distribution function $\rho'$. The scalar friction coefficient can be extracted from the second rank tensor by taking one third of its trace, i.e.:

$$\zeta = \frac{1}{3} \sum_{i=1}^{3} \zeta_{ii}$$  \hspace{1cm} \text{[27]}

The four terms $T_1$, $T_2$, $T_3$, and $T_4$ in Eq. [26] can be given the following pictorial representations:

\begin{align*}
T_1 & \quad T_2 & \quad T_3 & \quad T_4 \\
\begin{array}{c}
p \\
\bullet \\
\bullet \\
\bullet \\
\bullet \\
\end{array} & \quad \begin{array}{c}
p \\
\bullet \\
\bullet \\
\bullet \\
\bullet \\
\bullet \\
\end{array} & \quad \begin{array}{c}
p \\
\bullet \\
\bullet \\
\bullet \\
\bullet \\
\bullet \\
\end{array} & \quad \begin{array}{c}
p \\
\bullet \\
\bullet \\
\bullet \\
\bullet \\
\bullet \\
\end{array}
\end{align*}

$p$ = pendant, $s$ = solvent, and $\alpha$ = the hydronium ion. The term $T_1$ corresponds to an average force experienced by the hydronium ion due to the solvent molecules, and $T_3$ 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. In $T_4$ both the solvent and the pendant groups interact directly with the hydronium ion. In this model we will assume that the last term is the most significant and absorb the first three terms in the friction coefficient $\zeta^{(0)}$ that is computed in traditional ion transport models. An example of this is to be seen in the work of Pintauro and Yang (18) in which the ionic mobility $u_i$ is related to the friction coefficient according to:

$$u_i = \frac{1}{\zeta^{(0)}}$$ \hspace{1cm} \text{[28]}

The correction term to the friction coefficient that we seek to calculate in this work is:

$$\zeta^{(c)} = \frac{1}{3} \text{Tr}[T_4]$$ \hspace{1cm} \text{[29]}

Prior to turning to the explicit calculation of the effects of the fixed anionic charges groups on the wall of the pore we point out that the derived results thus far still depend on the position of the hydronium ion with respect to the moving coordinate frame (i.e. $\vec{r}_\alpha$). This is a constant since the moving coordinate frame has the same velocity as the hydronium ion. This parameter is, therefore, set to zero either outright or after any parametric differentiation; implying that the origin of the frame of reference is on the hydronium ion.
Correction to Friction Coefficient

Since the pendant groups are treated in our model as fixed charged groups they produce an electrical field in the pore which is not affected by ensemble averaging in Eq. [26]. Therefore, with use of Eqs [6], [12], and [26], we may write for the correction term defined in Eq. [29]:

\[ \zeta^{(c)} = -\frac{2\pi V_0en\beta}{3L} \int_0^\infty dt C(t); \quad C(t) = \left< e^{-it\cdot\vec{F}_{\alpha\alpha}} \right>_0 \]  \hspace{1cm} [30]

where \( \vec{F}_{\alpha\alpha} \) is the z-component of the force \( \vec{F}_{\alpha} \). Eq. [30] is developed in the following steps:

1) The time displacement operator \( e^{-it\cdot\vec{F}} \) may be expanded as a power series according to:

\[ C(t) = \sum_{p=0}^\infty (-1)^p \frac{c_{2p}}{(2p)!} t^{2p} \] \hspace{1cm} [31]

where \( c_{2p} \) are the even moments of the distribution function \( \rho^f \). The moments of this correlation function are defined according to:

\[ c_p = (-i)^p \left< (-iL_0)^p \vec{F}_{\alpha\alpha} \right>_0 \] \hspace{1cm} [32]

and it can be shown that only the even moments do not vanish.

2) The Laplace transform of Eq. [31] is:

\[ \tilde{C}(s) = \sum_{p=0}^\infty (-1)^p \frac{c_{2p}}{s^{2p+1}} \] \hspace{1cm} [33]

where \( s \) is the Laplace transform variable.

3) Eq. [33] may be expressed in the form of a continued fraction (19):

\[ \tilde{C}(s) = \frac{a_0}{s + \frac{a_1}{s + \frac{a_2}{s + \frac{a_3}{s + \cdots}}}} \] \hspace{1cm} [34]

The coefficients of this continued fraction are related to the moments \( c_p \) in the following manner:

\[ a_0 = c_0, \quad a_1 = \frac{-c_2}{c_0}, \quad a_2 = \frac{c_4 + a_1 c_2}{a_0 a_1}, \quad a_3 = \frac{-c_6 - (a_1 + a_2) c_4}{a_0 a_1 a_2}, \quad \text{etc.} \] \hspace{1cm} [35]

4) Taking the simplest approximant from Eq. [34]:

\[ \tilde{C}(s) \approx \frac{a_0}{s + \frac{a_1}{s + \frac{a_2}{s + \frac{a_3}{s + \cdots}}}} \]
5) Laplace inversion of Eq. [36] gives:

\[
C(t) = -a_0 e^{-at}
\]  

[37]

6) Finally, substitution of Eq. [37] into Eq. [30] and employing the definitions in Eq. [35] gives for the friction coefficient the following expression:

\[
\zeta^{(c)} = \frac{2\pi V_0 e n \beta}{3L} \frac{c_0^2}{c_2}
\]  

[38]

Calculation of Moments

In order to calculation the correction to the friction coefficient we need to compute the two moments \( c_0 \) and \( c_2 \) appearing in Eq. [38]. The relevant definitions may be extracted from Eq. [32], i.e.:

\[
c_0 = -\langle F_{ax} \rangle_0
\]  

[39]

\[
c_2 = \langle L_0 F_{ax} \rangle_0
\]  

[40]

where \( F_{ax} \) is given by the negative gradient (along the z-axis) of \( V_{ax} \) (Eq. [5]), and \( L_0 \) is defined as indicated by Eq. [15]. Carrying out the relevant differentiation and setting \( \bar{r}_a = 0 \) as pointed out above, we obtain the following results:

\[
F_{ax} = \frac{\mu^2 e^2}{12\pi^2 \epsilon^2 m^2 kT} \sum_{i=1}^{N} \frac{z_i}{r_i^6}
\]  

[41]

\[
L_0^2 F_{ax} = Y_1 + Y_2 + U + Y_3
\]  

[42]

where:

\[
Y_1 = \frac{\mu^2 e^2}{12\pi^2 \epsilon^2 m^2 kT} \sum_{i=1}^{N} \left[ \frac{42 p_{ad}^2 z_i}{r_i^8} - \frac{12 p_{ad}^2}{r_i^7} \right]
\]  

[43]

\[
Y_2 = \frac{\mu^2 e^4}{144\pi^4 \epsilon^4 m(kT)^2} \sum_{i=1}^{N} \frac{(r_i - x_i)z_i}{r_i^{13}}
\]  

[44]
In Eqs. [41] – [46] \(x_r, y_l,\) and \(z_i\) are the Cartesian coordinates of the solvent molecule \(l\) with respect to a frame located on the hydronium ion and \(r_i\) the radial distance of the solvent molecule from the origin of this frame. In the same manner, \(p_u, p_y,\) and \(p_d\) are the momenta of an arbitrary solvent molecule along the respective axis.

In computing the averages of the five functions listed in Eqs. [41] to 1461 we recognize the fact that all these terms with the exception of \(U\) are sums of one body functions while the latter involves summation of a two body function. The ensemble averaging in Eqs. [39] and [40] involves the \(N\)-body distribution function \(p_f\) defined in Eq. [19] and since all solvent molecules are treated as identical, the following simplifications result:

\[
\langle F_{\alpha \gamma} \rangle_0 = \frac{\mu^2 e^2 N}{12 \pi^2 e^2 kT} \int d\vec{r} \frac{Z}{r_6^2} P_0(\vec{r}) \tag{47}
\]

\[
\langle K \rangle_0 = \frac{7 \mu^2 e^2 N}{2 \pi^2 e^2 mT} \int d\vec{r} \frac{Z}{r_6^2} P_0(\vec{r}) \tag{48}
\]

\[
\langle Y_2 \rangle_0 = \frac{\mu^4 e^2 N}{144 \pi^2 e^4 mkT} \int d\vec{r} \frac{Z}{r^{13}} P_0(\vec{r}) \tag{49}
\]

\[
\langle U \rangle_0 = \frac{\mu^6 e^2}{24 \pi^4 e^4 m(kT)^2} \frac{N(N-1)}{2} \int d\vec{r} d\vec{r}' u(\vec{r}, \vec{r}') P_2(\vec{r}, \vec{r}') \tag{50}
\]

\[
u(\vec{r}, \vec{r}') = \frac{1}{|\vec{r} - \vec{r}'|^8} \left[ \frac{(x-x')x - (z-z')z}{r^7} - \frac{(x-x')x - (y-y')y}{r^7} \right] \]

\[
\langle Y_3 \rangle_0 = \frac{\mu^6 e^2 n^2 V_o N}{3 mkT L^2 \varepsilon^2} \int d\bar{r} \sin \left(\frac{2n\pi L}{L} \right) \frac{1}{r_6^6} P_1(\bar{r}) \tag{51}
\]

From henceforth \(\vec{r}\) and \(\vec{r}'\) will be coordinate vectors of single molecules. \(P_n\) is an \(n\)-body reduced distribution function given by:

\[
P_n(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n) = \int d\vec{r}_{n+1} \ldots d\vec{r}_N P_N(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n) \tag{52}
\]

At this stage of the development the integrals over the momenta and coordinates of the \(N\) solvent molecules have been reduced to integrals over the coordinates of either one or two molecules.
In order to make further progress with these equations we must calculate explicit forms for the two distribution functions $R_1(\bar{r})$ and $R_2(\bar{r}, \bar{r}')$. In principle this can be done by using Eq. [52] along with the definition of $P_N(\bar{r}_1, \bar{r}_2, \ldots \bar{r}_N)$ given in Eq. [20]. It is, however, easier to obtain these functions as functional derivatives of the configuration integral (20). Written explicitly, Eq. [18] with $\bar{r}_a = 0$, is of the form:

$$Z = \int \cdots \int d\bar{r}_1 d\bar{r}_2 \cdots d\bar{r}_N \prod_{i=1}^N \exp \left[ -\beta \left( a_1 \frac{n_i}{r_i^4} + a_2 \cos \left( \frac{2n\pi z_i}{L} \right) \right) \right] \prod_{i<j}^N \exp \left[ -\beta \frac{a_2}{|\bar{r}_i - \bar{r}_j|^6} \right]$$  \[53\]

where:

$$a_1 = -\frac{\mu^2 e^2}{48\pi^2 e^2 kT}; \quad a_2 = \frac{2\mu^4}{3(4\pi\varepsilon)^2 kT}; \quad a_3 = V_0 e$$  \[54\]

With the following definitions:

$$z(\bar{r}) = \exp \left[ -\beta \left( a_1 \frac{n_i}{r_i^4} + a_3 \cos \left( \frac{2n\pi z_i}{L} \right) \right) \right]; \quad f(\bar{r}_i, \bar{r}_j) = \exp \left[ -\beta \frac{a_2}{|\bar{r}_i - \bar{r}_j|^6} \right] - 1$$  \[55\]

the configuration integral may be written:

$$Z[z] = \int \cdots \int d\bar{r}_1 d\bar{r}_2 \cdots d\bar{r}_N \prod_{i=1}^N z(\bar{r}_i) \prod_{i<j}^N \left[ 1 + f(\bar{r}_i, \bar{r}_j) \right]$$  \[56\]

where $f(\bar{r}_i, \bar{r}_j)$ in Eqs. [55] and [56] is the Mayer Cluster function. The symbol $Z[z]$ is used to indicate the functional dependence of the configuration integral on the function $z$.

We now approximate $Z[z]$ by the simplest cluster integral:

$$Z[z] \approx \int \cdots \int d\bar{r}_1 d\bar{r}_2 \cdots d\bar{r}_N \prod_{i=1}^N z(\bar{r}_i) + \int \cdots \int d\bar{r}_1 d\bar{r}_2 \cdots d\bar{r}_N \prod_{i=1}^N z(\bar{r}_i) \sum_{i<j}^N f(\bar{r}_i, \bar{r}_j)$$

$$= \left[ \int d\bar{r} z(\bar{r}) \right]^N + \frac{N(N-1)}{2} \left[ \int d\bar{r} z(\bar{r}) \right]^{N-2} \int d\bar{r} d\bar{r}' f(\bar{r}, \bar{r}') z(\bar{r}) z(\bar{r}')$$

$$= g_1(z)^N + \frac{N(N-1)}{2} g_1(z)^{N-2} g_2(z)$$  \[57\]

The one and two body distribution functions are given by:

$$p_1(\bar{r}) = \frac{1}{Z} \frac{\delta Z}{\delta z(\bar{r})}$$  \[58\]
Carrying out these functional differentiations gives for the distribution functions:

\[ P_1(\vec{r}, \vec{r}') = \frac{N g_1(z)^{N-3}}{Z} \left[ g_1(z)^2 + \frac{(N-1)(N-2)}{2} g_2(z) + (N-1)g_1(z)\chi(\vec{r}) \right] z(\vec{r}) \]

\[ P_2(\vec{r}, \vec{r}') = \frac{N(N-1)g_1(z)^{N-4}}{Z} \left[ g_1(z)^2 + \frac{(N-2)(N-3)}{2} g_2(z) + (N-2)\{\chi(\vec{r}) + \chi(\vec{r}')\} g_1(z) + g_1(z)^2 f(\vec{r}, \vec{r}') \right] z(\vec{r})z(\vec{r}') \]

where use has been made of the following relations:

\[ \frac{\delta g_1(z)}{\delta \epsilon(\vec{r})} = 1; \quad \frac{\delta g_2(z)}{\delta \epsilon(\vec{r})} = 2 \chi(\vec{r}); \quad \chi(\vec{r}) = \int d\vec{r}' f(\vec{r}, \vec{r}'); \quad \frac{\delta \chi(z)}{\delta \epsilon(\vec{r}')} = f(\vec{r}, \vec{r}') \]

Since \( N >> 3 \) the one and two body functions undergo simplification to yield:

\[ P_1(\vec{r}) = \frac{N}{g_1(z)} z(\vec{r}) + \frac{N^2}{Z'} \chi(\vec{r}) z(\vec{r}) \]

\[ P_2(\vec{r}, \vec{r}') = \frac{N^2}{g_1(z)} z(\vec{r}) z(\vec{r}') + \frac{N^3}{Z'} \left[ \chi(\vec{r}) + \chi(\vec{r}') \right] z(\vec{r}) z(\vec{r}') + \frac{N^2}{Z'} f(\vec{r}, \vec{r}') z(\vec{r}) z(\vec{r}') \]

where \( Z' = 1 + \frac{N^2}{2} g_2(z) \). Now inserting Eqs. [62] and [63] into Eqs. [47] --[51] we obtain:

\[ c_0 = \sum_{i=1}^{2} D_i j_i; \quad c_2 = \sum_{i=1}^{9} C_i l_i \]

where the various coefficient and integrals appearing in Eq. [64] are as follows:

\[ D_i = -\frac{\mu^2 e^2 N^2}{12\pi^2 e^2 kT g_1}; \quad D_2 = -\frac{\mu^2 e^2 N^3}{12\pi^2 e^2 kT Z'}; \quad J_1 = \int d\vec{r} \frac{z}{r^6} \chi(\vec{r}) z(\vec{r}); \quad J_2 = \int d\vec{r} \frac{z}{r^6} \chi(\vec{r}) z(\vec{r}) z(\vec{r}); \]

\[ C_1 = \frac{7\mu^2 e^2 N^2}{2\pi^2 e^2 m g_1}; \quad C_2 = \frac{7\mu^2 e^2 N^3}{2\pi^2 e^2 m Z'}; \quad I_1 = \int d\vec{r} \frac{z}{r^8} \chi(\vec{r}) z(\vec{r}); \quad I_2 = \int d\vec{r} \frac{z}{r^8} \chi(\vec{r}) z(\vec{r}); \]

\[ C_3 = \frac{\mu^4 e^4 N^2}{144kT\pi^4 e^4 m g_1}; \quad C_4 = \frac{\mu^4 e^4 N^3}{144kT\pi^4 e^4 m Z'}; \quad I_3 = \int d\vec{r} \frac{(r-x)z}{r^{13}} \chi(\vec{r}) z(\vec{r}); \quad I_4 = \int d\vec{r} \frac{(r-x)z}{r^{13}} \chi(\vec{r}) z(\vec{r}); \]
The contribution to the friction coefficient made by the pendant groups is given by Eq. [29] and is therefore:

$$\zeta^{(c)} = \frac{2\pi V_0 e n \beta \left( \sum_{i=1}^{2} D_i J_i \right)}{3L \sum_{i=1}^{9} C_i I_i}$$  \hspace{1cm} [65]$$

The total friction then becomes:

$$\zeta = \zeta^{(c)} - \frac{2\pi V_0 e n \beta \left( \sum_{i=1}^{2} D_i J_i \right)}{3L \sum_{i=1}^{9} C_i I_i}$$  \hspace{1cm} [66]$$

The result has been expressed in terms of one and two body integrals which will have to be evaluated numerically. The most convenient frame of reference for evaluating these integrals is a cylindrical frame.

Conductivity of Pore

Under the influence of the electric field $\vec{E}$ (due to the potential difference between the anode and cathode) the hydronium moves through the pore and may be assumed to obey Newton second law according to:

$$m_a \frac{d\vec{v}_a}{dt} = -\zeta \vec{v}_a + e\vec{E}$$
where friction has been included explicitly. When a stationary state has been achieved $\bar{v}_a$ becomes the drift velocity. Assuming that the electric field acts along the pore axis (z-axis) the drift speed becomes:

$$v_a = \frac{eE}{\zeta}$$

The current density in the pore may be expressed in terms of the concentration of the hydronium ions, $c$, according to:

$$J = \mathcal{F}cv_a = \frac{\mathcal{F}c}{\zeta} E = \kappa E$$

where $\mathcal{F}$ is the Faraday constant and $\kappa$ the conductivity. The molar conductivity, $\Lambda$, may then be expressed in terms of our derived correction to the friction coefficient according to:

$$\Lambda = \frac{e\mathcal{F}}{2\pi V_0 \alpha \beta \left( \sum_{i=1}^{2} D_i J_i \right)}$$

$$\left( \zeta^{(c)} \right) = \frac{3L \sum_{i=1}^{2} C_i J_i}{\zeta^{(v)}}$$

If the contribution of the pendant groups is ignored ($V_0 = 0$) then the conductivity is simply as derived by Pintauro and Yang (6).

CONCLUDING REMARKS

We have derived a mathematical model that describes the transport of a molecule of water (vehicle-type mechanism) via the displacement of an hydronium ion through a cylindrical pore in a PEM with incorporated molecular structural potentials due to pendant side chains along the inside of the walls. This is essentially the first attempt at combining features of continuum mechanics with statistical mechanics into a unified theory. Numerical work is currently being undertaken to calculate the conductivity of a Nafion® pore as a function water content.

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REFERENCES

* DuPont registered trademark polymer.
Figure 1 Schematic of idealized membrane pore used in model.