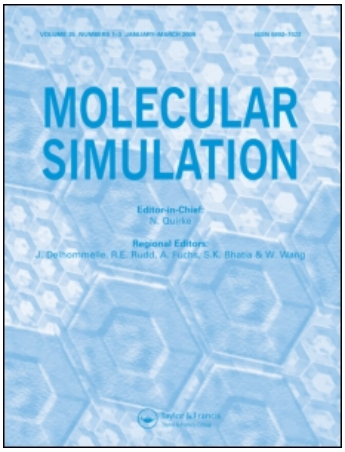

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Topological modelling of the hydrogen bond network of water cluster and proton hopping in a hydrated polyelectrolyte membrane

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The water cluster is characteristically constructed through the hydrogen bond formation in various types of aqueous solutions, especially in the pore of nano-materials such as polyelectrolyte membranes. The proton conduction in such a water cluster depends on the topology of the hydrogen bond network, since the movement of the proton is mainly driven by hydrogen bond exchange in the water cluster. The first-principle electronic state calculation should be straightforwardly adopted in order to estimate the proton conductivity because the change in hydrogen bond formation is associated with the change in the electronic states of the cluster. Although the first-principle calculations of proton conductivity are basically available to estimate the rate of proton hopping in the water clusters, it would be extremely time-consuming to simulate the dynamic structure in an inhomogeneous morphology of nanometre length scale such as in the polyelectrolyte membrane based on the electronic structure theory calculations. Here, the characterisation of the hydrogen bond network via a dynamically directed graph was evaluated to calculate the dynamical properties in the global structure of nanometre length scale inhomogeneous morphologies. The static and dynamic properties of the network structure were analysed by following the treatment of the graph theory. The mean rate of Hamming displacement (MHD) was defined to quantitatively express the dynamics of the hydrogen bond network. The average of the differences between the Hamming distances at different time steps, as the definition of the MHD, showed that the relaxation of the hydrogen bond network in polyelectrolyte membranes was slower than in the pure water because of the stronger clustering in a local area due to the mesoscopic morphology or confinement effect in nano-pores. Furthermore, proton hopping was modelled as a random walk on the dynamical hydrogen bond network, and then the diffusion coefficients of proton in the Nafion membranes were estimated as comparable results with the previous literatures.

Keywords: hydrogen bond network; graph analysis; proton conduction; random walk on a dynamical graph

1. Introduction

Recently, the fuel cell has become a very important technology for a variety of industrial applications such as next-generation low-emission vehicles, small devices like cell phones, etc., because of its efficient and eco-friendly power generation. Proton conductivity in a polyelectrolyte membrane is one of the key factors for the efficiency of the polyelectrolyte-type fuel cell. Thus, a method to estimate the proton conductivity in the polyelectrolyte membrane is necessary for the development of membrane materials. It would be possible to estimate the proton conductivity via the first-principle calculation as has been already reported in literature [1,2]. However, in the case of water clusters in inhomogeneous morphologies, it will be necessary to consider not only the local mechanism but also the global structure of the hydrogen bonds. It is well known that the inhomogeneous morphology at a nanometre length scale is formed in the hydrated polyelectrolyte membrane [3], and the structure of the hydrogen bond network should be influenced by this sort of mesoscopic morphology. This would be crucial for the global proton conductivity.

There are mainly two mechanisms for the proton conduction in water clusters: the vehicle and the Grotthuss mechanisms [4,5]. The former is the mechanism by which a positively charged proton diffuses, attaching to a water molecule as a hydronium ion. The Grotthuss mechanism, on the other hand, is explained as proton tunnelling from a protonated water molecule to the next water molecule throughout the hydrogen bond network. The high conductivity of the proton in aqueous solution is usually ascribed to the Grotthuss mechanism. In this sense, it is quite important to predict the global structure and dynamics of the hydrogen bond network of water cluster in a hydrated polyelectrolyte membrane.

Although the proton conduction is essentially related to the change in the electronic state and happens in a femtosecond time scale, the structure of the hydrogen bond network in aqueous solutions is characterised in a nanometre length scale, and the dynamics of the network occurs in a picosecond time scale. Therefore, a method based on the molecular dynamics is appropriate for detecting the hydrogen bond network in its characteristic time scale. As for the analysis of the network structures, the

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graph theory has a potential for one of the powerful tools because it has been developed for the analysis of networks. Recently, various types of networks have been analysed by the graph theory [6–8]. Therefore, we adopted the classical molecular dynamics for calculating the interaction between molecules and we analysed the hydrogen bond network by using the graph theory from the trajectory data of the classical molecular dynamics. This approach to analysing the molecular networks has been developed recently [9–11]. We do not focus on the details of mechanisms of proton conduction, but on the whole structure and dynamics of the hydrogen bond network. After the analysis of the network properties, we consider the pathway of proton transport based on the connectivity of the network. We analyse not only the global properties of the hydrogen bond network but also the local properties, since we regard the inhomogeneous structure as an important feature in the hydrated polyelectrolyte membrane.

Although computer simulations sometimes introduce numerical artefacts, fast and low-cost estimations of physical properties using computational models are quite useful before real experiments for the design and development of materials are performed. After the validation of the adopted model through experimental results, the model will be available for understanding physical mechanisms. Also, it will be applicable to construct new scientific hypothesis. Hence, we consider mainly three aspects for the use of computational modelling in physics, as follows: predicting and understanding physical phenomena, and constructing a new hypothesis and theory. When we use a computational model in either scientific or engineering problems, we should always pay attention to the purpose of the computational modelling. In this paper, we mainly propose the analysis method for the global structure and the dynamics of the hydrogen bond network in aqueous solutions, and a computational model mainly for the prediction of proton conduction based on the network analysis without a time-consuming calculation.

In Section 2, the method for detecting and analysing the hydrogen bond network is explained. As an application of this method, the model of proton conduction is proposed. In Section 3, the static and dynamical properties of the hydrogen bond network in pure water and in the hydrated polyelectrolyte membrane having three different water contents are shown and compared. After that, we provide the calculation results of the proton conduction model and their discussion. Finally, the conclusions are summarised.

2. Method

To estimate the proton conductivity in the hydrated polyelectrolyte membrane, it is important to detect the global structure and dynamics of the hydrogen bond network. We apply the graph theory [9,10] to the analysis of the trajectory data from the calculation of classical molecular dynamics, because it is possible to evaluate and characterise quantitatively the global network structure and dynamics in a nanometre length scale. The classical molecular dynamics is a preferable method to calculate physical phenomena in larger length scales than the first-principles approach. Additionally, the use of the graph theory has an advantage for deducing the characteristics of complicated structures. As an application of this method, we propose a simple model for the proton conduction and estimate the proton diffusion coefficient. We take the following steps: calculating the system by using the classical molecular dynamics, extracting the hydrogen bond network as a directed graph from the trajectory data of the molecular dynamics calculation, and then analysing the graph data and applying it to a proton conduction model.

2.1 Classical molecular dynamics

The classical molecular dynamics was used for the calculation of pure water and hydrated polyelectrolyte membrane structures. We calculated Nafion®, produced by DuPont, as a polyelectrolyte, and used the COMPASS force field [12] and the Discover module in Material Studio® version 4.2, produced by Accelrys Inc. (San Diego, CA, USA), for the molecular dynamics calculation. The Nafion's chemical structure is given in Figure 1 with the construction of the segments adopted to the present calculation model. The pure water system contained 895 water molecules. As for the Nafion system, three kinds of Nafion systems with water contents, $\lambda = 10$, 6 and 3, were calculated. Here, λ means the ratio of water molecules to the sulphonic acid groups, H_2O/SO_3H. Every membrane system contained 30 Nafion molecules and the same number of hydronium ions (H_3O^+) as the number of sulphonic acid groups (SO_3^-). After the sufficiently long calculation to the equilibrium in the NVT ensemble with the time step $dt = 1.0$ fs, the trajectory data during 10 ps with the time step $dt = 0.5$ fs was analysed. The Nosé–Hoover thermostat [13] was applied to maintain the temperature at 358 K. The periodic boundary condition was adopted in every calculation.

2.2 Definition of the hydrogen bond

We distinguished the hydrogen bond by the distance between the hydrogen and oxygen atoms and by the

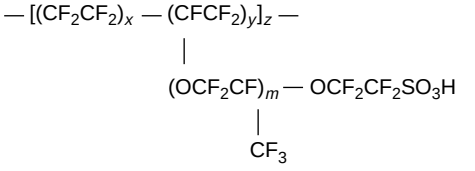

Figure 1. Chemical structure of Nafion. $x = 7$, $y = 1$, $z = 30$ and $m = 1$ are used in this study.

direction from a donor molecule to an acceptor one. The critical value of the hydrogen bond distance 0.237 nm was taken in this study. This value, 0.237 nm, was calculated from the distance of the intermolecular oxygen–hydrogen atom pair at the first minimum value of the radial distribution function in pure water at the temperature of 358 K. A hydrogen atom in a donor water molecule connects within 0.237 nm to the other oxygen atom which does not belong to the donor molecule. To indicate the acceptor molecule in this study, we chose to find the oxygen atom which is not a part of the donor molecule but close within 0.237 nm to the hydrogen atom without a covalent bond. The linkage information of the elements rather than the absolute coordinate of the atom is useful for the analysis of the hydrogen bond network. In particular, there are two important elements for expressing the topology of the network: vertex and edge. Concerning the hydrogen bond network, a vertex corresponds to an oxygen atom, and an edge corresponds to a hydrogen bond between the hydrogen and oxygen atoms. Conventional graph theory is employed to process this information. According to the above definition of the hydrogen bond, the hydrogen bond matrix M, which is the so-called adjacency matrix in the graph theory, can be defined as shown, for example, in Equation (1). Figure 2 represents the situation corresponding to Equation (1). In Figure 2, a solid line represents a covalent bond and a dotted line a hydrogen bond. Molecule 1 is a hydrogen donor to the molecule 2, which is an acceptor. Molecule 3 is a donor as well.

$$M = (m_{v_i v_j}) = \begin{array}{c} \\ v_1 \\ v_2 \\ v_3 \end{array} \begin{array}{c} \begin{array}{ccc} v_1 & v_2 & v_3 \end{array} \\ \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \end{array}, \tag{1}$$

where v_n is the vertex of the graph (Figure 2 (right)), where the number corresponds to the number of the molecule (Figure 2 (left)). In this case, there are two hydrogen bonds, one from the molecule 1 to the molecule 2 and the other from the molecule 3 to the molecule 2. Here, the elements

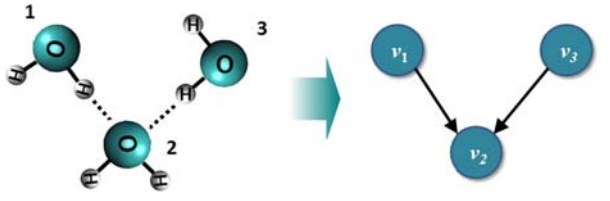

Figure 2. An example for the definition of the hydrogen bond. Each water molecule corresponds to a vertex in the graph. When the distance between the hydrogen atom belonging to the water molecule 1 and the oxygen atom of the water molecule 2 is less than 0.237 nm, $(v_1, v_2) \in E$, i.e. the element of the hydrogen matrix $m_{12} = 1$. $(v_3, v_2) \in E$ and $m_{32} = 1$ as well. Solid lines indicate covalent bonds in the water molecule, dotted lines show hydrogen bonds.

m_{12} and m_{32} of matrix M equal to 1. In the conventional graph theory, this directed graph G is represented as Equation (2):

$$G = (V, E), \tag{2a}$$

$$V = \{v_1, v_2, v_3\}, \tag{2b}$$

$$E = \{(v_1, v_2), (v_3, v_2)\}, \tag{2c}$$

where V is the vertex set and E is the edge set of the graph. Note that generally $(v_i, v_j) \neq (v_j, v_i)$ because a hydrogen bond has a direction, so that the hydrogen bond network becomes a directed graph. By the definition of the hydrogen bond matrix above, the network structure becomes the binary digit data which represents the network topology, so that many useful algorithms in the graph theory are applicable to the analysing of the structure and dynamics of the hydrogen bond network.

2.3 *Proton hopping model*

We represent the Grotthuss mechanism of the proton diffusion approximately by a random walk on a dynamical graph. The proton hopping is in fact not at random, but we consider that it is sufficient for the global and statistical measure. For a confirmation of this assumption, the results of the calculation are compared with the first-principle calculation and experimental data in Section 3. In this model, a virtual proton randomly hops from the position of an oxygen atom to the next oxygen atom at a random hopping frequency via hydrogen bonding towards the direction. The random hopping frequency of $0.69\,\mathrm{ps}^{-1}$ is considered, which is obtained from a first-principle calculation [1]. Because the graph changes every moment according to the molecular motion, the virtual proton always changes its position by the translational motion of a water molecule, even if the hopping does not occur. That is why the vehicle effect is also considered in this model. The transition probability matrix P is defined as follows by Equation (3):

$$P = (p_{ij}) \in [0, 1]^{V \times V}, \tag{3a}$$

$$p_{ij} = \begin{cases} \frac{1}{d(i)} & ((v_i, v_j) \in E \vee (v_j, v_i) \in E), \\ 0 & ((v_i, v_j) \notin E \wedge (v_j, v_i) \notin E), \end{cases} \tag{3b}$$

$$d(i) = \sum_j m_{j,i} + \sum_j m_{i,j}, \tag{3c}$$

where $d(i)$ denotes the number of degree at the vertex v_i. The $d(i)$ also means the number of hydrogen bonds connecting to the water molecule v_i. The hopping direction is randomly selected at the same probability for the connected hydrogen bonds in Equation (3).

A detailed picture of proton hopping in Nafion membranes has been proposed based on the results of first-principle calculations by Choe et al. [14]. After an elemental hopping, it becomes easier for the hopped hydrogen to get

back to the previously connected water molecule because the inverse situation occurs along with the asymmetric hydrogen bond formation. The elemental proton hopping is therefore not always effective for the global proton diffusion. When a sequential hopping through different water molecules (at least three molecules) occurs, the hopping motion can be effective for the global diffusion. Choe et al. called this process 'constructive' hopping which is to be distinguished from non-effective proton transfer between two identical water molecules which can be called as 'non-constructive' transfer. The probability of 'constructive' proton transfer to occur, strongly depends on the connectivity of the hydrogen bond network, therefore the water-content dependence of the proton diffusion can be ascribed to the confinement of water cluster in the inhomogeneous morphologies in Nafion membranes. When we should take into account all the elementary processes in the proton transfer, the transition probability of proton hopping should be treated as a conditional probability which depends on the history of the itinerancy of the proton. Under such a restriction, the assumption of the random-direction hopping in the previous sentence would be unsuitable for the description of the process. On the other hand, the 'constructive' proton transfer could evenly occur to every following hopping-site after several non-effective oscillational motions of the proton. It would be a support of the assumption of the random-direction hopping in the estimation of global proton diffusion, even though the degree of randomness of 'constructive' proton transfer has still been an open question. Here, we introduced the assumption to the present proton hopping model in order to estimate the diffusion of protons in the globally defined hydrogen bond network structures.

3. Results and discussion

3.1 Connectivity

In order to quantitatively compare the connectivity of the hydrogen bonds in different conditions, the average number of hydrogen bond per water molecule both in pure water and in the Nafion is shown in Figure 3. The cluster size distributions of the hydrogen bond network are shown in Figure 4. The cluster size is calculated as the number of vertices connected by the hydrogen bonds. It is found that three hydrogen bonds are averagely counted in pure water. As expected, the average is less in the polyelectrolyte membrane than in pure water, and the less the water content, the less are the hydrogen bonds.

In the pure water system, most of the hydrogen bonds are connected and build up one large cluster. On the other hand, the network does not percolate in the hydrated Nafions, and the cluster sizes are distributed decreasing exponentially, but some large clusters are detected with low probabilities.

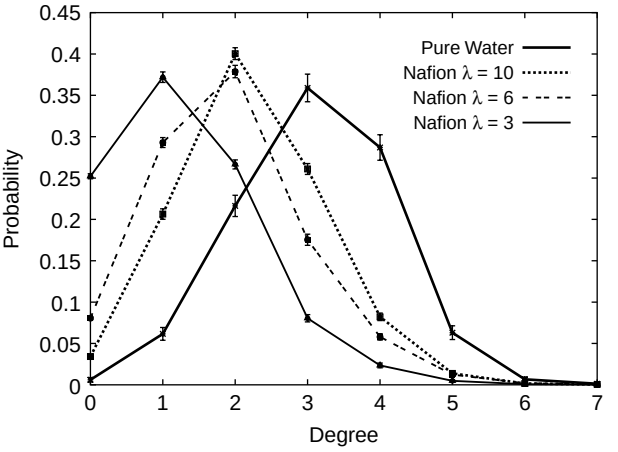

Figure 3. The results of the average number of hydrogen bonds per water molecule for pure water and Nafion membranes at $\lambda = 10$, 6 and 3.

3.2 Mean rate of Hamming displacement

To quantitatively examine the changes in the network, we introduce the mean rate of Hamming displacement (MHD), which shows the ensemble average of differences between the networks during the time t. The MHD, D_{H}, is defined here as:

$$D_{\mathrm{H}}(t) = \frac{\langle D(0,t)\rangle}{\langle S(0,t)\rangle}. \tag{4}$$

The Hamming distances D and S are defined as:

$$D(t_1,t_2) = \sum_{i,j} |m_{ij}(t_1) - m_{ij}(t_2)|, \tag{5a}$$

$$S(t_1,t_2) = \sum_{i,j} (m_{ij}(t_1) - m_{ij}(t_2)), \tag{5b}$$

where $m_{ij}(t)$ is the element of the hydrogen bond matrix M, which expresses a directed graph at time t (see Equation (1)). The Hamming distance is originally named after Richard Hamming, who introduced it in his fundamental paper on *Hamming Codes* in 1950 [15]. The Hamming distance in this study is defined as the number of different elements between the hydrogen bond matrices at the time t_1 and t_2. If the MHD value equals to zero, the two graphs between the time interval Δt are totally the same. On the other hand, if the value equals to 1, the graphs are entirely different. The MHD of the hydrogen bond network in pure water and in the Nafions is shown in Figure 5. The data is fitted to the stretched exponential function $C(t)$ defined by:

$$C(t) = 1 - \alpha \exp[-(t/\tau)^{\beta}], \tag{6}$$

where t is the time, τ is the relaxation time, and α and β are the amplitude of the second term at $t = 0$ and the parameter which indicates the inhomogeneity of a system, respectively. The relaxation time τ in pure water is 0.889 ps calculated by the least-squares fitting of the MHD to Equation (6), and in the hydrated Nafions is

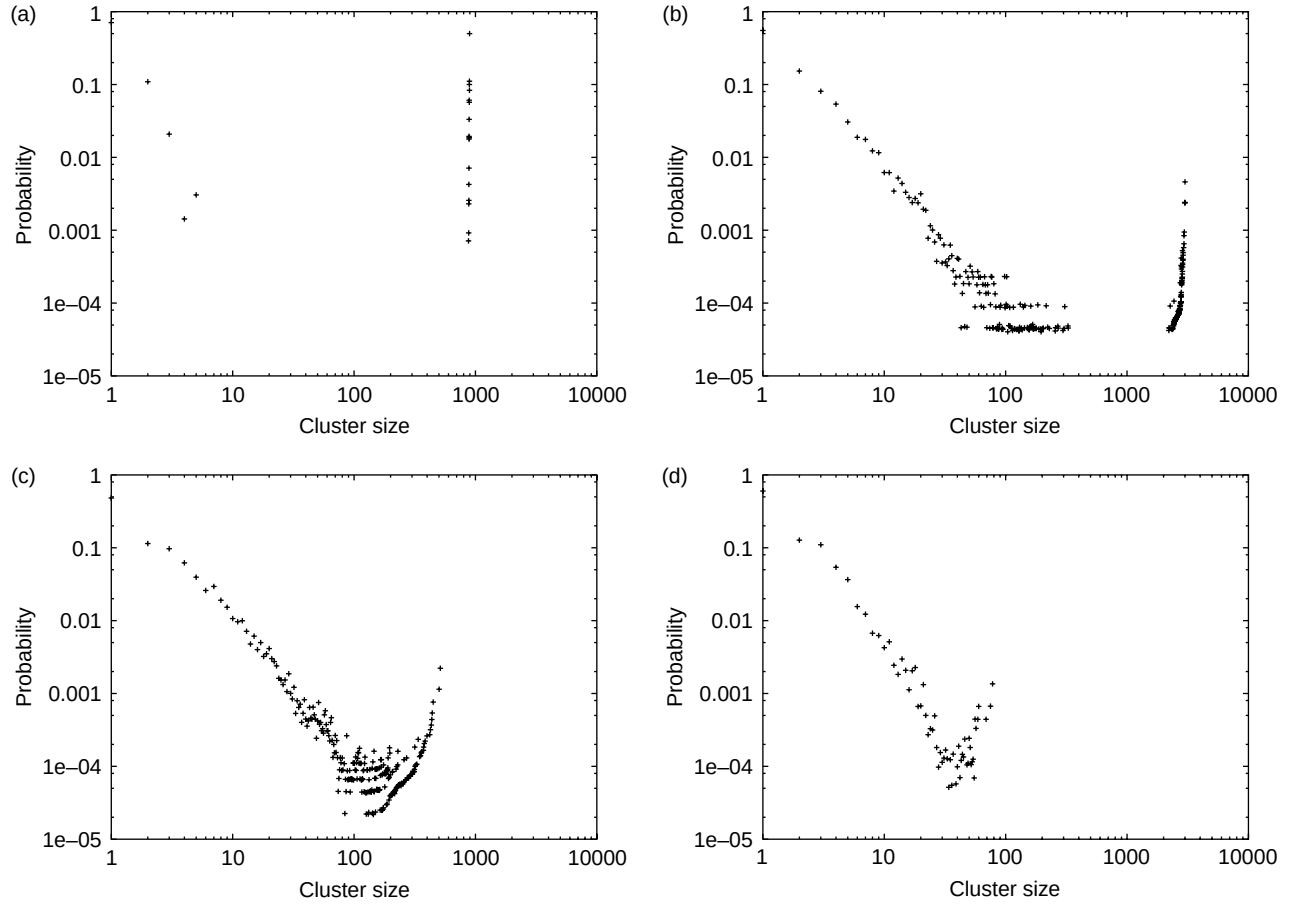

Figure 4. The results of cluster size distributions. (a) Pure water system, (b) Nafion system at $\lambda = 10$, (c) Nafion system at $\lambda = 6$ and (d) Nafion system at $\lambda = 3$. The cluster is defined as the number of vertices which are linked with each other by the hydrogen bonds.

14.7, 8.83×10^2 and 1.87×10^6 ps for $\lambda = 10$, 6 and 3, respectively.

The stretched exponential function has been phenomenologically introduced to predict the effect of the distribution of lifetimes in inhomogeneous systems in 1847 by R. Kohlrausch, and after that this has been applied widely to systems which have a large number of relaxation processes. The parameter β should be assigned to what expresses the time dependences or distribution of the relaxation processes in a tagged system. When β equals to 1, Equation (6) becomes a simple exponential function and expresses a completely homogeneous system. The meaningful region of the β value is $0 < \beta \leq 1$ and a decreasing β value from 1 means the decreasing homogeneity of the system. As can be seen in Figure 5, the β values decreased while α and τ increased following decreasing water contents. It is fairly acceptable that the structures of water clusters are widely dispersed in their forms in the polyelectrolyte membranes of inhomogeneous morphologies because the structures of the hydrogen bond network in small pores could be more unsettled than in larger spaces at larger water contents. The characteristic time scales of the relaxation τ are longer for smaller water contents. This result is quite understandable because larger contents of the polymer slow down the entire relaxation process in the membrane. The results of fitting displayed in Figure 5 could indicate that Equation (6) of the stretched exponential function is qualitatively meaningful. We actually tried to fit the data in Figure 5 by other types

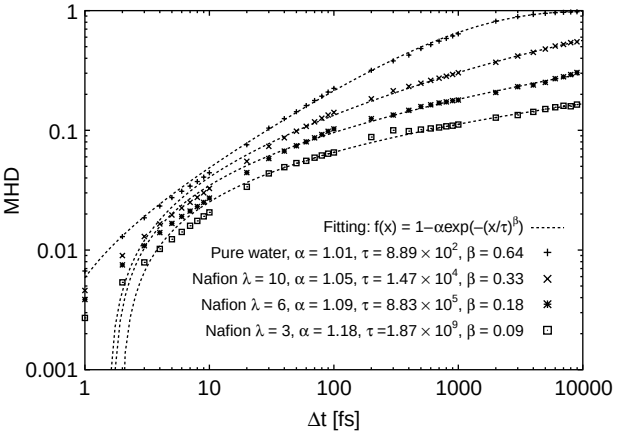

Figure 5. MHD in the systems of pure water and the Nafion at $\lambda = 10$, 6 and 3.

and/or combinations of decay functions. Even though it could be found that the root mean square deviations were small in several cases, we have still not found any physically meaningful fitting results than those displayed in Figure 5. The processes in polyelectrolyte membranes might be more complicated than as described by Equation (6) only. However, the use of the stretched exponential function for describing the dynamical processes in the present tagged materials could be an acceptably suitable qualitative analytical approach.

3.3 Clustering of the hydrogen bond network

In order to detect the dense part of the hydrogen bond network, we calculate the clusters by using the Markov CLuster (MCL) algorithm which is one of the so-called hard clustering methods [16,17]. The MCL algorithm was created for graph clustering by Stijn van Dongen in 2000 [18]. The hydrogen bond network in pure water is totally connected and one large cluster is built up as shown in Section 3.1. However, there must be some dense and sparse parts even in pure water. The MCL algorithm simulates random walks on a graph by the alternation of two operators, which are called expansion and inflation. One of the advantages of the MCL algorithm is that it is able to detect the clusters even if the network is totally percolated. Another advantage is the fast calculation. According to Dongen [18], the calculation cost is $O(Nk^2)$, where N is the number of vertices and k is the average number of edges per vertex. The average number of hydrogen bonds per water molecule is approximately 3 as shown in Figure 3. Therefore, the cost is $O(N)$ in the case of analysing the hydrogen bond network. The general algorithm is described as follows:

Algorithm 1:

(1) $P = P_G$
(2) Do
$P = P_2$ (expansion operation)
$P = \Gamma_r P$ (inflation operation)
While $(P^2 \neq P)$,

where P is the Markov matrix which means the transition probability matrix of the Markov process given by Equation (3) on the graph G, and Γ_r is called inflation operation which is defined by Equation (7):

$$(\Gamma_r P)_{ij} = \frac{(P_{ij})^r}{\sum_k (P_{kj})^r}, \tag{7}$$

where r is a parameter for the inflation operation and equals to 2 in this study. The network is divided into a set of separate subnetworks after this calculation. The lifetimes of each cluster in pure water and Nafion with $\lambda = 10$, 6 and 3 are shown in Figure 6, and the lifetime distributions of each cluster size are shown in Figure 7. The lifetime of the cluster is calculated as the length of time in which a subnetwork maintains the same topological structure.

The average lifetime in Nafion is twice or more higher than in pure water, and the standard deviation of the lifetime in hydrated Nafion is also larger than in pure water (Figure 6). The lifetime was found to be distributed by a power law in every cluster (Figure 7). Some clusters sometimes live over 100 ps, which is several times longer than the average.

The lifetimes of the cluster detected by the MCL algorithm are shorter than the ones expected for the actual hydrogen bonds in pure water, about 1 ps, obtained from experiments [19,20] and simulations [21,22]. The fact is that the cluster of the MCL algorithm is not corresponding to a real hydrogen bond cluster; therefore, more information about the cluster of the MCL algorithm is given below.

According to Algorithm 1, P_G corresponds to the Markov matrix for graph G. Therefore, P_G can be viewed as a transition probability matrix of the Markov process, while P_{ij} means the transition probability from node i to node j. The transition probability matrix after k steps of the Markov chain is expressed as P_k. Then, the transition probability (P_{ij}) increases when the density (connectivity) of the network is high around the local area where both node i and j exist. The main idea of the MCL algorithm is the emphasis on this property by the two operations, i.e. the expansion and inflation.

It should be pointed out next that the MCL algorithm refers to the operation that extracts the relatively dense part of a network. Therefore, the clusters of the MCL algorithm would be classified, even if there is a link between clusters when the density of links is relatively sparse around the clusters. In hydrated Nafions, the clusters of the MCL algorithm correspond to the aggregates of the hydrogen and oxygen atoms, but the clusters do not correspond to the real hydrogen bond clusters, since the clusters of the MCL algorithm change, depending not only on the connections inside the clusters but also the outside connections near the clusters. Also, of course, the lifetime of the cluster of the MCL algorithm depends on the definition of the hydrogen bond. That is why lifetimes of the cluster of the MCL algorithm are estimated to be shorter than those of the real hydrogen bond clusters.

As for the physical significance of the use of the cluster of the MCL algorithm, the prediction of localisation of excess protons should be noticed. The lifetime of the cluster is evaluated in order to detect how long the dense parts of the hydrogen bond network are maintained, since the global proton diffusion is mainly governed by two factors: the average time of proton hopping and the connectivity of the hydrogen bond network. In this study, the lifetimes of the cluster of the MCL algorithm are estimated to be shorter than those of the real hydrogen bond clusters due to, for example, transient breaking of the hydrogen bonds with thermal fluctuation, since the cluster of the MCL algorithm

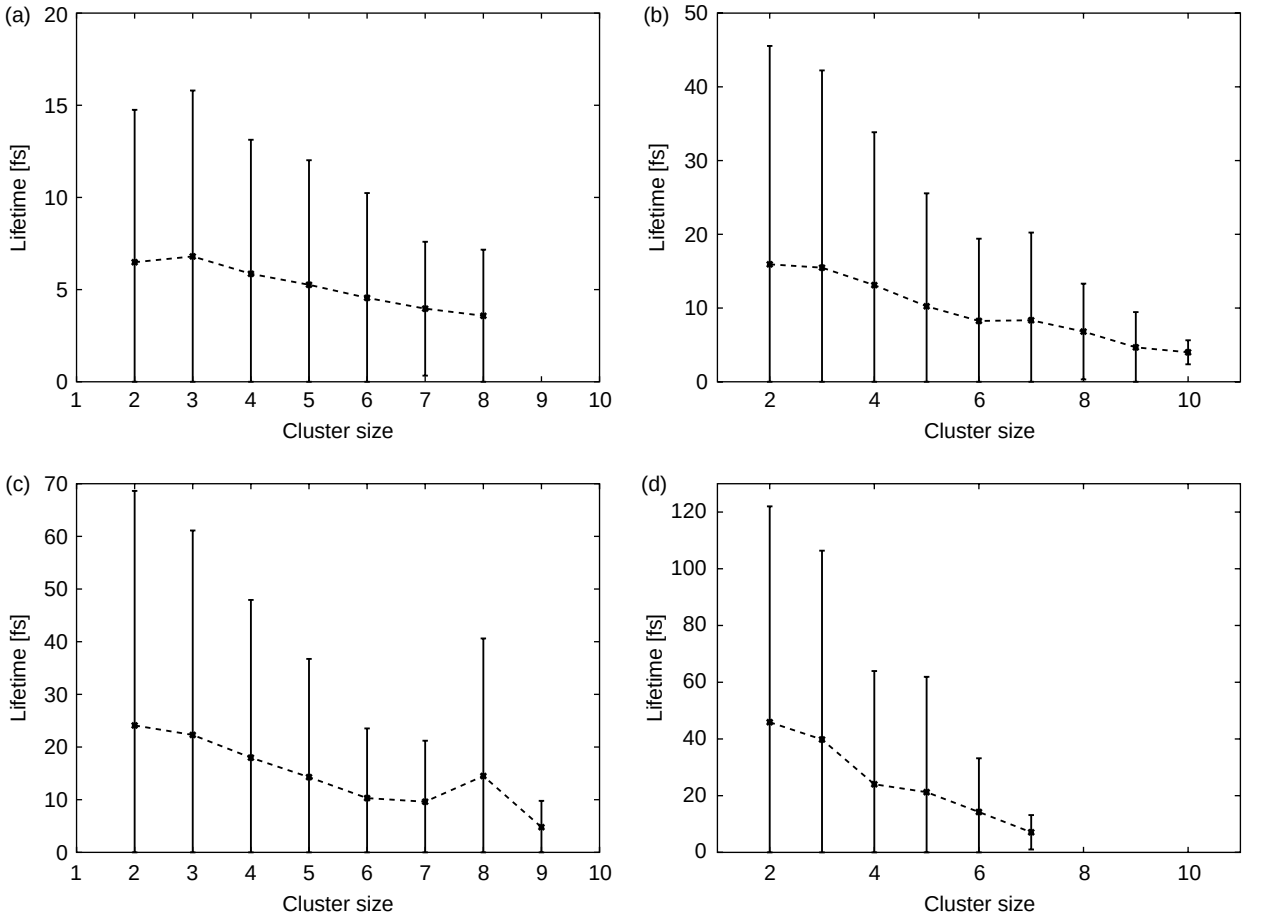

Figure 6. Average lifetimes of water clusters with error bars. A dot means the average of the lifetimes and a vertical solid line shows the standard deviation of the lifetimes of each cluster. (a) Pure water, (b) Nafion system at $\lambda = 10$, (c) Nafion system at $\lambda = 6$ and (d) Nafion system at $\lambda = 3$.

depends on the definition of the hydrogen bond. However, in the case of the evaluations of the proton localisation on a longer time scale, the detailed process of proton migration is not important, and it is not necessary to fit the lifetimes of real hydrogen bond formation in detail. It is important to study more quantitatively the dense parts of the hydrogen bond network for understanding the detailed mechanism of the dynamical structures. We leave it for a future work because it needs other analyses, which are beyond the aim of the present article.

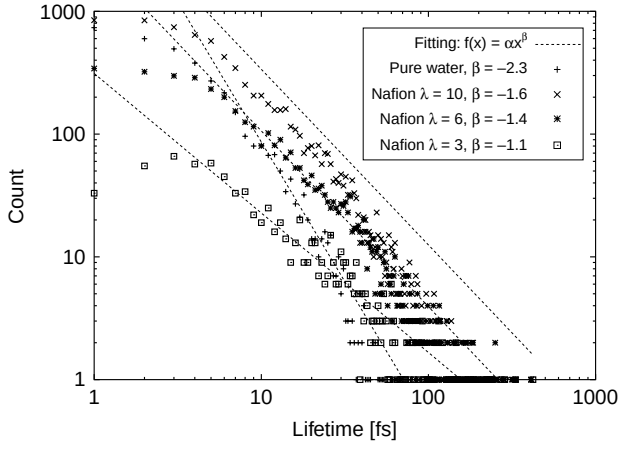

Figure 7. Distributions of the lifetime of the cluster at size 4.

3.4 Proton diffusion coefficient

Here, random walk on the hydrogen bond network is evaluated to estimate the global proton conduction in the polyelectrolyte membranes. A typical trajectory of the random walk of the proton and the movement of the water molecule are shown in Figure 8. It can be found that the proton moves several times faster than the water molecule. In order to evaluate the proton conductivity quantitatively, the diffusion coefficient D_c of the proton is calculated from the mean square displacement (MSD) through the Einstein relation:

$$D_c = \lim_{t\to\infty} \frac{M(t)}{6t}, \tag{8}$$

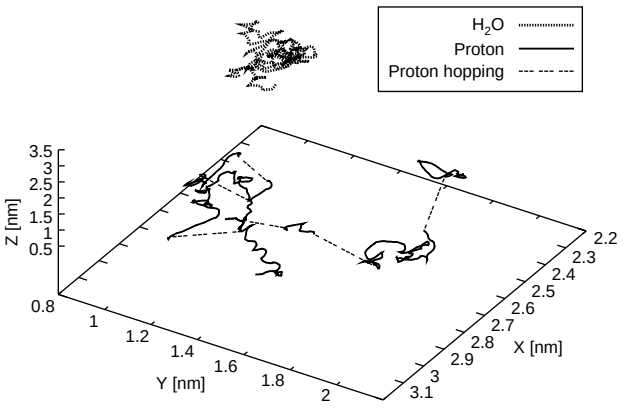

Figure 8. A typical trajectory of a proton and of a water molecule. While the solid lines and the dotted lines represent the translational trajectories of a proton and a water molecule, respectively, the thin dotted line between the solid lines represents the hopping of a proton in the 3D area for 10 ps in the pure water system.

where t is the time and $M(t)$ is the MSD. $M(t)$ is calculated by Equation (9):

$$M(t) = \frac{1}{N}\sum_{i}^{N} |r_i(t) - r_i(0)|^2, \tag{9}$$

where r_i is the centre of mass position of molecule i and N is the total number of molecules. r_i of the proton in Equation (9) is obtained from the model described in Section 2.3, but that of the water molecule is obtained from classical molecular dynamics calculations. The diffusion coefficients of the proton and water molecule are summarised in Table 1. These results are comparable to the first-principle calculations and the experimental results [2,14,23,24]. The calculated self-diffusion coefficient of water molecules in pure water is several times larger than the experimental result (2.15×10^{-5} cm^2/s at 298 K) as expected due to the higher simulation temperature of 358 K. The experiments of Zawodzinski et al. [23–25] show that the water diffusion coefficients in Nafion over a whole range ($\lambda = 2$–22) are about 10^{-6} cm^2/s and those of the proton in Nafion are 4.4×10^{-6} cm^2/s ($\lambda = 9$) and 5.8×10^{-6} cm^2/s ($\lambda = 14$). Choe et al. [14] reported by using the first-principle calculation that the diffusion coefficients of protonic defects were calculated to be 0.3×10^{-5} and 7.1×10^{-5} cm^2/s in Nafion at $\lambda = 4.25$ and 12.75, respectively. Even though the total calculation time of the classical molecular dynamics is short compared to the characteristic time of the hydrogen bond network change, it is possible to estimate effective diffusion coefficients. This is due to many trials of random hopping of virtual protons and to the calculation of the ensemble average of the hopping trials.

Table 1. Diffusion coefficients of proton and water molecule.

System	H_2O ($\times 10^{-5}$ cm^2/s)	Proton ($\times 10^{-5}$ cm^2/s)
Pure water	8.70	17.3
Nafion ($\lambda = 10$)	1.23	5.90
Nafion ($\lambda = 6$)	0.357	3.93
Nafion ($\lambda = 3$)	0.041	1.70

4. Conclusions

We analysed the hydrogen bond networks in pure water and in the hydrated polyelectrolyte membrane with different moisture contents by using graph theory. We characterised the hydrogen bond network as a dynamical directed graph, based on the results of classical molecular dynamics. In order to detect and evaluate the global structure of the hydrogen bond network in a nanometre length scale, the cooperation of classical molecular dynamics and graph theory was quite useful.

The density of the hydrogen bonds and the global connectivity in the system can be understood roughly from the average number of hydrogen bonds per water molecule and cluster size distribution (Figures 3 and 4). Although the hydrogen bond network in the pure water system percolates and a large cluster builds up, the hydrogen bond network is not entirely linked in the Nafion system.

The dynamics of the hydrogen bond network is fitted to a stretched exponential function in a picosecond time scale, which is found through the MHD calculation (Figure 5). The parameters β and τ in the stretched exponential function were found to reflect inhomogeneous and complicate relaxation mechanisms in the dynamics of the hydrogen bond network in the hydrated Nafion systems. The fact that the dynamics in the hydrated Nafion system is slower than that in the pure water system is also detected quantitatively from the MHD calculation. The reason for the slower dynamics in the Nafion system would be stronger clustering in a local area due to the mesoscopic morphology or confinement effect (Figure 6) [26]. Taking into account the fact that not only the static network structure but also the global network dynamics must influence the Grotthuss mechanism of the proton transport, this result should be quite important to study proton transport mechanisms.

As for the proton hopping model, it is very simple but at the same time appropriate to estimate the proton conductivity in the global structure. We found, by comparing with the experimental results, that it is quite reasonable to estimate the proton conductivity as an average quantity in nanometre length scale inhomogeneous morphologies. This method is quite general and easy to apply to the other network systems.

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