Predicted electric-field-induced hexatic structure in an ionomer membrane

Elshad Allahyarov

*Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106, USA and Joint Institute for High Temperatures,
Russian Academy of Sciences, Moscow 127412, Russia*

Philip L. Taylor

Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106, USA

Coarse-grained molecular-dynamics simulations were used to study the morphological changes induced in a Nafion®-like ionomer by the imposition of a strong electric field. We observe the formation of structures aligned along the direction of the applied field. The polar head groups of the ionomer sidechains aggregate into clusters, which then form rodlike formations which assemble into a hexatic array aligned with the direction of the field. Occasionally these lines of sulfonates and protons form a helical structure. Upon removal of the electric field, the hexatic array of rodlike structures persists and has a lower calculated free energy than the original isotropic morphology.

I. INTRODUCTION

The transport of protons through an ionomer membrane is at the heart of the operation of a polymer-electrolyte fuel cell, and any procedure that facilitates transport would thus be of value in improving this technology. The study of proton transport in aqueous ionomers has consequently received considerable attention [1–3]. For perfluorosulfonated ionomer membranes such as Nafion® [4] the structure is characterized by a long, hydrophobic, fluorinated main chain, and short sidechains terminating in hydrophilic sulfonate anion groups. The dissimilarity between the hydrophobic backbone and the hydrophilic sidechain terminations creates a phase-segregated morphology with sharp interfaces between the domains. The sulfonic-acid functional groups aggregate to form a hydrophilic domain that is hydrated upon absorption of water. It is within this continuous domain that ionic conductivity occurs when protons dissociate from their anionic counterions and combine with water to become mobile hydronium ions.

Beginning with a seminal paper by Eisenberg [5], a number of authors has suggested morphological geometries for this microphase separation. These include inverted globular micelles interconnected by a channel structure of cylindrical micelles [6] and lamellar sandwichlike structures. Other recent approaches are based on micelle-channel [7,8] and inverted micelle models [9]. There is, however, no complete consensus as to the structure of the percolating networks of sulfonate or water channels.

Lin and co-workers [10] investigated the field-induced morphological changes in poled Nafion. In order to increase mobility, poling fields were applied to solvent-cast Nafion at temperatures above its glass transition T_g. When the membrane was quenched back to room temperature it retained induced cylindrical aggregates of sulfonates. In Refs. [11,12] it was shown that poling Nafion at the membrane-electrode interface above T_g can lead to the alignment of carbon black particles perpendicular to the membrane surface and lead to improved electrodes for fuel cells.

In this Rapid Communication we describe simulations that indicate that application of a strong electric field could change the morphology of an ionomer membrane in such a way as to enhance proton transport appreciably. We have performed simulations of almost-dry Nafion-like ionomers with the goal of determining the morphological changes that would be produced by strong externally applied electric fields. We find that the sidechains self-organize into cylindrical clusters having their axes parallel to the applied field and that these clusters form a hexatic array in the plane perpendicular to the field direction. At very strong fields each of the rodlike clusters has an ordered inner core consisting of distinct wires of sulfonate head groups and their attendant protons. The stable cylindrical cluster structures that emerged included an unusual spiral arrangement of three sulfonic wires with four protonic chains. The structural changes resulting from the poling process appear irreversible.

II. MODEL

We employ a united-atom representation for Nafion [13–16], where the CF_2 and CF_3 groups of the backbone and sidechains, and the sulfur atom S and oxygen group O_3 of the sulfonate head groups are modeled as Lennard-Jones (LJ) monomers with a universal diameter $\sigma = 0.35$ nm. We assume that the number λ of water molecules per sulfonate is small ($\lambda < 5$) and that a proton detached from a sulfonate captures a water molecule and becomes a hydronium ion.

The force-field parameters for the ionomer are chosen to agree in most instances with the Nafion model of Paddison [17] and are given in our recent paper [18]. All the partial charges on the ether oxygen, carbon, and fluorine atoms of the side chain and on the fluorocarbon groups of the backbone skeleton are set to zero. Electrostatic charge is located on the sulfur atom (charge $+e$) and oxygen group (charge $-2e$), such that the total charge of the sulfonate head group SO_3^- is $-e$. The hydrogen ion H^+ is considered as part of a hydronium complex of charge $+e$. For the low water contents ($\lambda < 5$) considered in this work, the remaining water molecules are mostly in an immobile state near the pore walls. One can then effectively integrate out their degrees of

freedom by introducing an effective proton diameter σ =0.35 nm and a distance-dependent dielectric permittivity [18], which implicitly accounts for the nonpolar nature of all the interaction sites considered as neutral blocks in this work. Aside from these two approximations, our approach is equivalent to the consideration of a membrane with $\lambda = 1$ with all its sulfonic groups dissociated to form hydronium ions [19,20].

The total potential energy of the membrane is taken to be

$$U(\vec{r}) = \sum_i U_b^i + \sum_j U_\theta^j + \sum_m U_\varphi^m + \sum_{k,l} U_{nb}(|\vec{r}_k - \vec{r}_l|), \quad (1)$$

where $(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ are the three-dimensional position vectors of the N particles in the system. In Eq. (1), i runs over all bonds, j runs over all bond angles, m runs over all torsional angles, and k, l run over all nonbonded (Lennard-Jones and Coulomb) force-center pairs in the system. For lightly humidified membrane materials, the protons are mostly energetically bound to their host sulfonate groups [21,22]. The resulting SO$_3$H groups are electrostatically neutral and have zero dipole moment in the absence of an applied field. The dipole moment induced by a field depends on the field strength, on the bending and dihedral forces acting on the sidechain tip, and on the position of the hydrogen ion relative to the charged SO$_3^-$ dipole. These induced dipoles experience no net force in a uniform applied external field but are subject to torques. In direct current experiments, the electrostatic field E inside the polymer is assumed uniform [23]. In nonequilibrium molecular-dynamics simulations the current flow is usually induced by applying such a field E [24], the scalar proton conductivity χ being defined from the relation $\vec{j} = \chi \vec{E}$ between the applied field and the induced current density $\vec{j}$. When the external field is applied along the z axis, $j = \Sigma q_i v_{i,z} / V$, where $v_{i,z}$ is the axial component of the velocity of the ith proton, $i = 1, \ldots, N_s$, with N_s as the total number of protons and V as the sample volume. The conductivity can also be related to the diffusivity D through the Nernst-Einstein relation $\chi = N_S e^2 D / V k_B T$ in equilibrium molecular-dynamics simulations. However, this method is less accurate for phase-separated systems, where confinement effects, such as proton trapping in the water-sulfonate clusters, strongly affect the overall diffusion constant D.

At low λ we expect Grotthuss proton shuttling to be negligible and surface hopping to be the leading contribution to the current through the membrane. This assumption is based on the fact that at low water content the hydronium ions are close to sulfonates and the sulfonate-sulfonate distance is at its minimum value [25]. In this case the protons move in the electrostatic energy landscape of the sulfonate ions. Proton hopping is expected to occur at sulfonate-sulfonate separations 0.7–0.8 nm [26] with an energy barrier less than 2.1 kcal/mol [22,26–28]. Contributions to the current arising from en-masse proton diffusion in bulklike water are small for $\lambda \leq 5$ when almost all water molecules are in a frozen state near pore walls [29].

III. SIMULATION RESULTS

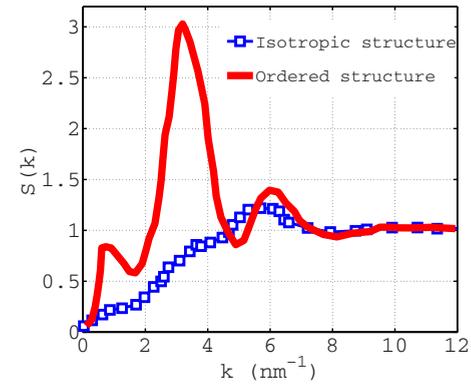Molecular-dynamics simulations were performed for coarse-grained membranes kept at constant volume

FIG. 1. (Color online) The structure factor for sulfur atoms is markedly changed by the application of a strong field from its unstructured isotropic form to an ordered aligned structure.

$V = (11 \text{ nm})^3$ and constant temperature $T = 300$ K. Each sidechain contains two hydrophilic and seven hydrophobic monomers, and there were 14 hydrophobic backbone monomers between adjacent sidechains. There were 1400 sidechains, each comprising nine monomers and 1400 backbone segments each comprising 14 monomers between adjacent sidechains. The sidechain terminal groups were neutralized by 1400 protons. In total the simulation box contained 33 600 membrane particles and no explicit water molecules. The system temperature was controlled by a Langevin thermostat with a friction coefficient $\gamma = 0.1$ and Gaussian noise $6k_B T \gamma$. The equations of motion were integrated using the velocity Verlet algorithm with a time step of 0.2 fs. Periodic boundary conditions and Lekner summation [30] of long-range electrostatic interactions were used.

We temporarily detached the sidechains from the backbone skeleton [31] and cut the backbone into 14-monomer segments [32] for initial equilibrating runs of 50 ps, after which the polymer was reassembled and equilibrated with another 50 ps run. Statistically averaged quantities were gathered during the next 5–10 ns. The ionomer was seen to undergo partial phase separation on the nanometer scale into a polymer phase consisting of backbone with pendant sidechains and a hydrophilic phase of loosely connected clusters of sulfonate head groups, mostly composed of compact multiplets of about 12 sulfonates.

Application of a strong electric field of the order of 10^9 V/m gives rise to a change in morphology, as indicated by the structure factor for sulfur atoms shown in Fig. 1 and the structure shown in Fig. 2(a). The field strength was increased step by step, giving the system enough time to relax into a state with a minimal free energy for a given poling field. The original isotropic system of clusters is now replaced by a system of cylinders aligned along the z axis. The sulfonates form the walls of these cylinders, which have a diameter of about $5\sigma(\approx 1.8$ nm) and a separation of roughly $8–10\sigma$. As the field strength is increased, these cylinders form a hexatic array. At the same time, the internal structure of the cylinders self-organizes into an array of distinctive "wirelike" chains of sulfonates or, to be more precise, chains of oxygens and sulfurs, and parallel chains of protons. Although the number of sulfonic wires per cylinder varies be-
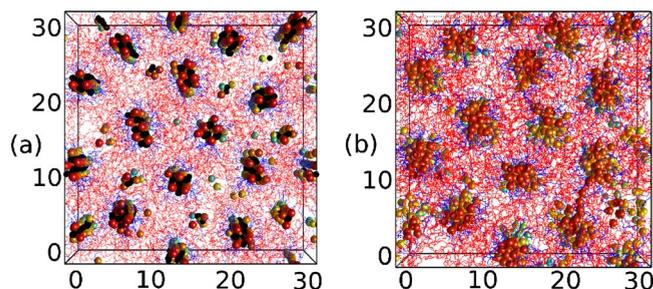
FIG. 2. (Color online) View from above of the simulation system for applied fields of (a) $E=8.2\times10^6$ kV/m and (b) remnant structure in a membrane after removal of the applied field. The colors of the spheres represent altitudes with light gray at the base and dark gray at the top of the simulation box. Protons are shown as black dots in (a).

tween 1 and 5, nearly half of the structures have a three-wire structure. All of the other structures observed consist of an equal number of sulfonate and proton wires, an example for a five-wire structure being given in Fig. 3(a). The mean SO_3^--SO_3^- group spacing along the chains is about 0.65–0.80 nm, which is close to the separation distance expected for Nafion-like membranes [26]. The cylinders composed of three sulfonic wires accommodate four protonic wires, as shown in Fig. 3(b) for the special case of a spiral cylindrical cluster. The apparent stability of this structure may be an artifact of the periodic boundary conditions.

A remarkable result of the simulations was that this field-induced morphology remains after the removal of the applied field. Figure 2(b) shows the ordered structure that persists after the field has been removed from the system shown in Fig. 2(a). The persistence of the hexatic structure suggests that it might in fact have a lower free energy than the isotropic structure. To verify this, we used Kirkwood's coupling-parameter method [33] to evaluate the free-energy difference between the isotropic and remnant hexatic structures. This is achieved by tracing the free-energy difference $\Delta A_I=A_I-A_I^0$ that occurs as the strength of Coulomb interactions U_c^{ij} between head groups i and j is gradually reduced to zero in the isotropic structure. A similar evaluation of $\Delta A_{II}=A_{II}-A_{II}^0$ is then done for the hexatic structure. It is then verified that the
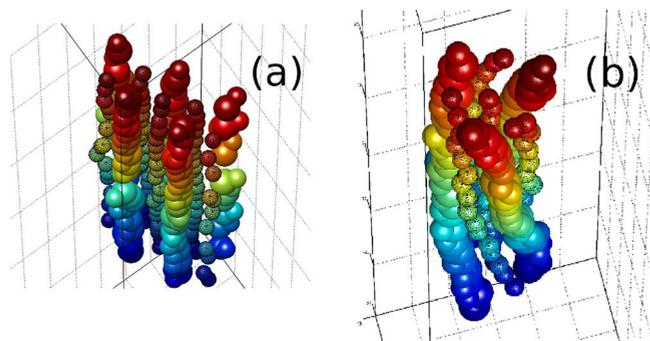

FIG. 3. (Color online) A perspective view of a single rodlike cluster with (a) a five-wire structure and (b) a spiral three-wire structure from Fig. 2(b). Small spheres attached to oxygens represent sulfurs and netted small balls are protons. Note that there are four protonic wires for a triplet of sulfonic wires.
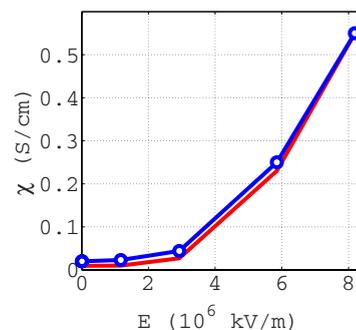

FIG. 4. (Color online) Proton conductivity χ of the membrane as a function of applied field E. Line without or with circles depicts increasing or decreasing field.

two final structures reached are identical, making $A_I^0=A_{II}^0$ $=A_0$. In this approach a coupling parameter ξ characterizes the strength of Coulomb interactions U_c^{ij} between head groups i and j so that the configurational part of a parametrized Hamiltonian $H(\xi)$ is $U(\xi,\vec{r})=U(\vec{r})+(\xi-1)\Sigma_{i>j}U_c^{ij}$. The integral $\int_{\xi=0}^{\xi=1}\langle\partial H(\xi)/\partial\xi\rangle d\xi$ then gives the free-energy difference ΔA_I. The integral was evaluated by gradual decharging of the membrane by decreasing the coupling parameter ξ in 20 steps. Precautions were taken to ensure proper equilibration at each step. The same procedure was followed to obtain ΔA_{II}. We found values of $\Delta A_I=-223k_BT$ per sulfonate for an isotropic membrane and $\Delta A_{II}=-233k_BT$ per sulfonate for a system with remnant hexatic order, showing the latter to have a lower free energy by about $10k_BT$. The morphological changes induced by the strong external field thus appear to be irreversible.

Proton conduction is strongly enhanced by the conducting path provided by the formation of the sulfonate cylinders along the current direction, as indicated in Fig. 4, which shows that the effective conductivity $\chi(E)$ increases rapidly with field strength. Because the effect of high fields is irreversible, there is hysteresis in the current-field plot. Both the small-field conductivity $\chi=9.5\times10^{-3}$ S/cm of the isotropic membrane and the value of $\chi=2\times10^{-2}$ S/cm for our comparatively dry poled membrane are understandably smaller than the experimental values $\chi=0.1$ S/cm for highly humidified Nafion but are much larger than the theoretically predicted surface hopping conductivity $\chi\sim10^{-5}$ S/cm [34].

We thus conclude from our simulations that application of a strong applied electric field to a Nafion®-like ionomer may induce the formation of rodlike structures of sulfonate groups, which assemble into a hexatic array aligned with the direction of the field. On the basis of our free-energy calculation, we conclude that this distinctive morphology should persist after the removal of the field.

The induced agglomeration of hydrophilic head groups into long rods appears to reduce the percolation threshold for ion conductance [10]. Simulations also indicate that strong correlations between the sulfonate head groups and protons inside the rods create wirelike structures of charged particles. The geometry of these structures is very rich and includes stable spiral-like three-wire clusters. These effects, if confirmed experimentally, may have an impact on the industrial applications of Nafion-like membranes.

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