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Theoretical calculation of proton mobility for collective surface proton transport

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We present a theoretical study of surface proton mobility at a minimally hydrated array of protogenic surface groups. At dense packing, the array assembles into a 2D bicomponent lattice that is formed by sulfonate anions, which are only allowed to fluctuate about fixed equilibrium positions, and mobile hydronium ions. Proton transport on the lattice proceeds by collective translocations of hydronium ions. This type of motion is described within the framework of soliton theory. Our main objective in this article is to establish the relation between microscopic surface structure and effective proton mobility. To this end, we present an approach to calculate microscopic interaction parameters that determine hydronium ion motion. The developed formalism enables us to theoretically derive an expression for soliton mobility at a given surface structure and compare it with experimentally measured mobilities.

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I. INTRODUCTION

Proton transport is of vital interest for a wide range of phenomena in condensed matter physics, biochemistry, electrochemistry, and materials science [1–3]. However, the detailed mechanism of proton transport is often unknown or highly speculative, with bulk water being the main exception. Proton-conducting polymer electrolyte membranes (PEM) like Nafion® owe their high-proton conductivity to an extended network of water-filled channels [4]. Under sufficiently hydrated conditions, proton transport proceeds by structural diffusion of a protonic defect, which has been studied extensively for the case of bulk water [5]. Under conditions of very low relative humidity or elevated temperature $T > 90\,^{\circ}\mathrm{C}$, the conductivity of Nafion-type PEMs drop by several orders of magnitude due to dehydration, rendering virtually impossible the operation of polymer electrolyte fuel cells at higher temperatures [4]. On the other hand, for some materials a significant proton conductivity has been demonstrated even under very dry conditions [6]. Such findings allude to a different mechanism of proton transport involving surface water that is strongly bound to a polymeric host material. A similar mechanism might be relevant for lateral proton conduction at surfaces of biological membranes [7] or in recently explored polymer nanosheet assemblies [8]. Theoretical understanding of the mechanism of surface proton transport would deepen our knowledge of the nature of living organisms and it could enable a wider search for new proton-conducting materials for industrial use.

In [9], we presented a detailed *ab initio* molecular dynamics study of proton transport at a densely packed two-dimensional array of protogenic surface groups (SG) of the type CF_3-SO_3H. The terminating carbon atoms are fixed at vertices of a hexagonal lattice, allowing the side chains to tilt and rotate. One water molecule per SG is added to simulate minimal hydration. The water molecules form hydronium ions and bridge SGs with each other forming a bicomponent, honeycomb-like hydrogen-bonded network. Our metadynamics simulations in [9] showed that a collective motion of hydronium ions, which conserves the number of interfacial hydrogen bonds, exhibits a much smaller activation energy compared to a disconcerted motion, which involves a creation of local hydrogen bond defects. Therefore, we adopted a soliton transport mechanism, developed in the past for one-dimensional systems [10–13], for our two-dimensional system [14]. In the proposed mechanism, protons are transferred by solitary traveling waves of hydronium ion dislocations. This approach was not pursued further in the aforementioned one-dimensional case because it predicted a very low proton conductivity. The 2D lattice circumvents the main problem encountered in 1D systems. Our analytical results published in [14] nurture expectations that a soliton mechanism of surface proton transport is feasible. But questions remain concerning the applicability of the approach and evaluation of experimentally relevant parameters which would allow a comparison of theoretical predictions with experimental data. Some of these questions are addressed in the present paper.

In [14], we found expressions for soliton energy and mobility. However, one cannot compare them with experimental data since the soliton theory developed so far uses phenomenological constants such as a hydronium-hydronium interaction constant or a viscous friction coefficient. As long as those constants are unknown, it remains impossible to obtain any reliable estimate of soliton mobility.

In the present paper, we determine the required constants of microscopic interaction and use them to evaluate the mobility. The main asset of our approach is that we neither introduce new parameters nor run any specific simulations. New parameters would increase the complexity of the model. Computer simulations can give values only for a specific potential profile created by the surface groups. Our results are not based on any particular potential, rendering them rather universal and applicable to a wide range of systems. This follows the rationale suggested in [14] that all macroscopic properties should be expressed via a minimal number of microscopic parameters. In the ideal case, we should be able to evaluate the proton mobility solely based on the input information on the surface chemical composition and surface group spacing.

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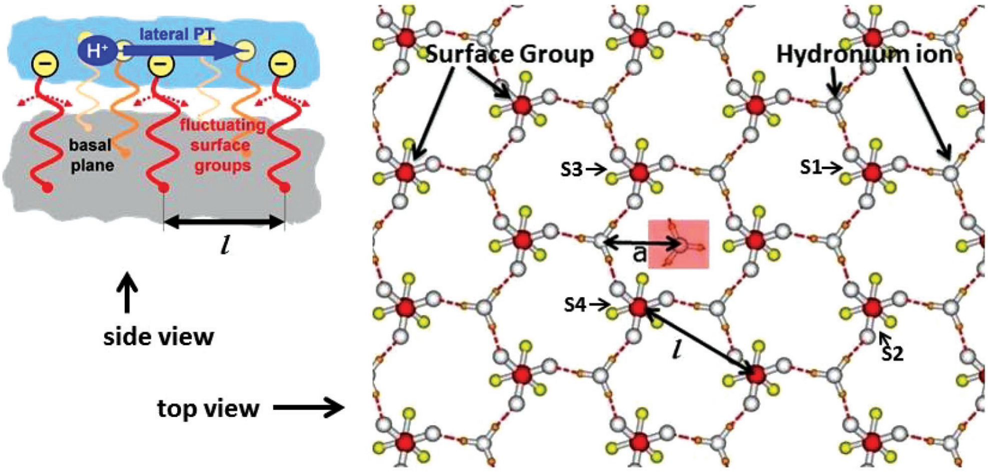

FIG. 1. (Color online) On the left is a schematic diagram of an interfacial system of end-grafted protogenic groups. On the right is a top view obtained from *ab initio* molecular dynamics studies in [15]. The shaded hydronium ion represents the position of the hydronium after a translocation. S1, S2, S3, and S4 are spectator SGs.

In Sec. II, we briefly review our surface soliton model and provide the main analytical results obtained in [14]. Then we discuss the physical origin of the phenomenological constants of interest and calculate them. In Sec. III, we evaluate the mobility and discuss its value. In the concluding parts, we point out some unexpected features of soliton dynamics.

II. PROTON TRANSPORT AND SOLITON MOBILITY

We consider a two-dimensional flat array of surface groups (SG) of the type R-SO_3H, where R represents a residual group or chain of fluorocarbon or hydrocarbon molecules, see Fig. 1. Terminating carbon atoms of SGs are anchored at positions of a hexagonal lattice with lattice constant l. One water molecule is added per SG, simulating minimally hydrated conditions. As discussed in [9], for most purposes a consideration of the simplest system with $R = CF_3$ is sufficient. For our analytical modeling the main feature of the model system is the symmetry of the ordered state, which controls the structure and dynamics in the hydrogen-bonded network.

Stable configurations and structural transitions were studied in [15–17]. At $l < 6.5$ Å, SGs assemble into an ordered state with a saturated number of hydrogen bonds, as shown in Fig. 1. At $l > 6.5$ Å, hydrogen bonds become too short relative to l, which makes a tilted structure energetically more preferable. At $l > 8.7$ Å, hydrogen bonds can no longer bridge the separation between SGs, which leads to incomplete dissociation. The disrupted hydrogen-bonded network at such large values of l renders interfacial proton translocations between SGs in the minimally hydrated system virtually impossible. At $l < 6.5$ Å, the system is too stiff which complicates a transition into the tilted structure. The ideal lattice constant for hydronium transport is in the range of $l = 6.5$ Å. At this SG density both the ordered and the tilted structure are energetically similar, increasing the propensity for fluctuations in SG and H bond density that could facilitate interfacial proton transitions. For the time being we will focus on this case. The influence of a distribution of SG density will be considered at a later stage.

Hydronium ion motion consists of a sequence of elementary hops such as depicted in Fig. 1. As shown in [9], the activation energy of concerted motion of hydronium ions has about half the value found for a disconcerted single hydronium ion hop. Therefore, we consider a traveling solitary wave of dislocations of hydronium ions. As shown in [14], in this case it is sufficient to consider a one-dimensional Hamiltonian describing the part of the original two-dimensional system lying on the track of the 1D soliton. The relevant Hamiltonian reads

$$H = \sum_i \left(\frac{m}{2}\dot{u}_i^2 + \frac{k}{2}(u_{i+1} - u_i)^2 + V(u_i) \right), \tag{1}$$

where the index i labels hydronium ions along the soliton track, u is the displacement of the ith hydronium ion, m the hydronium ion mass, k the coupling constant between neighboring hydronium ions, and $V(u_i)$ the potential created by the lattice of SGs and acting on the ith hydronium ion. Due to the lattice order of the system, $V(u_i)$ is a periodic function consisting of equally spaced and equally deep potential wells centered at the equilibrium positions of hydronium ions. Assuming that the number of hydronium ions in a soliton is much larger than unity, we take the continuum limit. To describe a soliton, we introduce a wave coordinate $\xi \equiv x - vt$, where x is a coordinate along the soliton and v is the soliton velocity. Using the Euler-Lagrange formalism of classical mechanics we derived the equation of motion

$$\partial_\xi u = \pm\sqrt{2\Omega^2\,(V(u) + \epsilon)}, \tag{2}$$

where ϵ is a potential well depth and $\Omega^2 \equiv \frac{1}{m(v_0^2 - v^2)}$, with $v_0 \equiv \sqrt{\frac{ka^2}{m}}$ being the maximal soliton velocity.

In [14], based on Eq. (2), we derived an expression for the soliton energy,

$$E = \frac{E_0}{\sqrt{1 - \left(\frac{v}{v_0}\right)^2}}, \tag{3}$$

where $E_0 = \sqrt{\frac{2\epsilon k a^2}{3}}$ is the energy of a static soliton. This expression can also be derived by minimizing the action integral, as done in [7]. To find the soliton mobility we followed a standard approach: we added two terms representing a viscous friction and an external force acting on each hydronium into the equation of motion. Then we calculated the terminal drift velocity and took its ratio to the external force, f, in the limit $f \to 0$. Thereby, we obtained an expression for the mobility,

$$\mu = \frac{1}{b}\sqrt{\frac{ka^2}{2\epsilon}}, \tag{4}$$

where b is a viscous friction coefficient. It turned out that, up to a prefactor close to unity, Eqs. (3) and (4) are universal for different functional forms of the potential profile $V(u)$. For a detailed description of the model system, discussion of transport mechanisms, and derivation of the above equations the reader is referred to [14].

In the present paper, we use the previously obtained results as a starting point. The main objective is to develop a formalism for calculating the proton mobility. The ability to predict theoretically the proton mobility will be vital for evaluating the proposed concerted mechanism of proton transport in comparison to experimental data. Some of the parameters needed in Eq. (4) have been already determined. The elementary transfer distance of a hydronium ion, a, is related to the lattice constant l by $a = \frac{l}{\sqrt{3}}$, see Fig. 1. Since we consider specifically $l = 6.5$ Å, we have $a = 3.75$ Å. The parameter corresponding to the depth of the potential well, ϵ, was found in [9], $\epsilon = 0.3$ eV.

The constants b and k are still unknown. An estimate of k was provided in [14], $k \simeq 2$ kN m^{-1}. Therefore, we will focus on finding b. This constant describes viscous friction, i.e. the energy losses due to a particle motion in a viscous medium. Such losses can be calculated in two different but equivalent ways: phenomenologically and microscopically. To illustrate this aspect, let us consider a standard example—the motion of a sphere in still water. In this case, since the viscous friction force is known, one can calculate the work against the friction and thereby determine the associated energy loss. On the other hand, the resistance to the object's motion stems from molecular interactions between sphere and water molecules. If we could find a molecular-level description of this interaction, we could calculate the amount of energy transferred to water molecules from the sphere. This energy corresponds to the energy loss by friction. If there are no other sources of energy dissipation, the losses calculated by both methods must be the same. So, first we will express the phenomenologically calculated energy losses via b. Then, after comparison with the microscopically calculated losses, we will get an expression of b via microscopic parameters of the system.

A. Phenomenological calculation

Let us consider a soliton traveling with velocity v. According to Eq. (3), an energy loss leads to a change of velocity. To avoid this complication we will consider a differential energy loss, dE_b, since an infinitesimal change of the energy should not change the soliton velocity noticeably. The subscript b points out that the value is found in the framework of the phenomenological approach. At each instant, hydroniums in the soliton have a certain displacement, u. The differential energy loss is

$$dE_b = \frac{1}{3a}\int_{-\infty}^{\infty}(F du)dx, \tag{5}$$

where $3a$ is the distance between hydroniums, see Fig. 1. $F du$ is the energy lost by one hydronium ion overcoming the distance du. F is the viscous friction force, $F = b\dot{u}$. Here, to simplify the notation, we omitted the minus sign indicating that the energy is lost but not gained due to friction. Hence, dE_b is positive. The integration sums up the contributions from all the hydronium ions. Then, replacing du by $\dot{u}dt$, inserting the expression for F, and dividing the equation by dt gives

$$\dot{E}_b = \frac{b}{3a}\int_{-\infty}^{\infty}\dot{u}^2 dx. \tag{6}$$

To obtain the final expression we introduce the traveling wave coordinate $\xi = x - vt$, which leads to

$$\dot{E}_b = \frac{bv^2}{3a}\int_{-\infty}^{\infty}(\partial_\xi u)^2 d\xi. \tag{7}$$

This is a general expression; it holds for an arbitrary potential function $V(u)$. To evaluate the integral for a particular $V(u)$, one can use the equation of motion, Eq. (2).

We note that $\dot{E}_b$ is proportional to v^2. This is consistent with the result for motion of a sphere in water.

B. Microscopic model of energy dissipation

Let us consider a soliton traveling with velocity v. If we were to neglect the energy loss by friction, the soliton would continue to travel over infinite time and distance. To describe a realistic soliton motion, a microscopic mechanism must exist by which the soliton loses energy. One requirement for such a mechanism is that the energy loss rate should be proportional to v^2, as remarked at the end of the previous subsection.

The soliton model considered so far assumes an energetically isolated hydronium ion subsystem which does not exchange energy with the surroundings. A possible mechanism for energy losses is the energy transfer from the hydronium ion subsystem to the SG subsystem. Such a transfer should be conducted by a change in the SG subsystem caused by the soliton motion. To accommodate the soliton motion, two SG located at the soliton sides should tilt. These SG, indicated in Fig. 2, are called spectator SG. While tilting, they pull neighboring hydronium ions and SGs, which will shift and pull their next neighbours, and so on. In other words, each tilting spectator SG generates a propagating spherical wave of dislocations in the coupled hydronium ion and SG subsystems. Each emitted wave consumes a portion of the soliton energy, comprising the mechanism of energy loss.

In the following, we assume that the soliton velocity remains constant during the time of one hydronium ion relocation. We will justify this assumption *a posteriori* in Sec. III. The energy lost by one hydronium ion during a single relocation step is e_l. The energy loss rate is, therefore,

$$\dot{E}_l = \frac{v}{3a}e_l, \tag{8}$$

where the subscript l shows that the value is calculated in the frame of the microscopical approach. We will evaluate only the energy transmitted from the soliton to the SG subsystem. The energy transmitted from the soliton to the hydronium

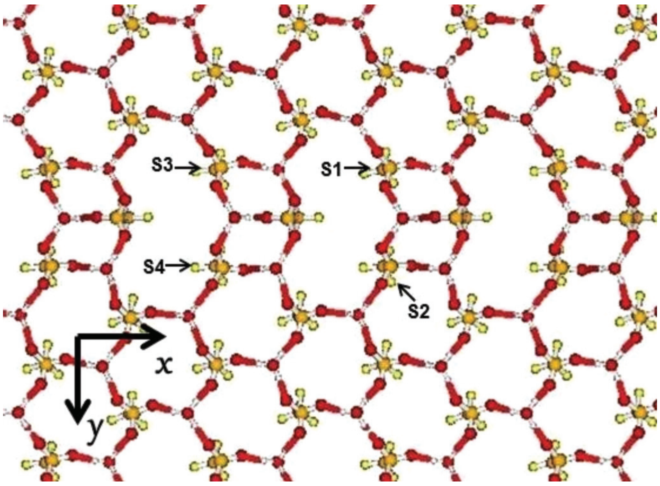

FIG. 2. (Color online) Defect structure on an ordered bicomponent lattice of hydronium ions and SGs, created by collective hydronium ion translocations along a 1D chain. Obtained from *ab initio* molecular dynamics studies [22], it demonstrates a propagation of a 1D soliton. S1, S2, S3, and S4 are spectator SG shown in Fig. 1. The soliton run from left to right.

ion subsystem, i.e., to hydronium ions that do not lie on the soliton track, could be calculated using the same formalism and added afterwards. However, this energy is smaller because hydronium ions are easy to relocate whereas SG motions are restricted by grafting their endpoints; therefore, their motion requires more energy.

As defined above, u is a displacement of a hydronium ion in the soliton. In the same manner, n is defined as a displacement variable of SGs in the emitted wave. Both n and u are functions of spatial coordinates and time. For convenience, these dependences will be shown explicitly only when necessary. Because details of the tilting dynamics of the spectator SGs are unknown, we assume that they move simultaneously with hydronium ions, which is reasonable due to the strong hydrogen bonds between these species. This gives a boundary condition for the emitted wave,

$$n(y=0) = \frac{\delta}{a}u(x=0), \tag{9}$$

where x denotes a coordinate in the direction of solution propagation, y a coordinate perpendicular to the direction of soliton propagation, and δ is the maximal displacement of the SG, i.e., the difference of its coordinates in the tilted and up-right structures.

Another simplifying assumption concerns the emitted wave propagation. Despite the emitted wave propagates over a 2D network of SG, we will consider a 1D string of SGs connected by springs. In other words, instead of considering a spherical wave, we will consider a 1D wave traveling perpendicular to the soliton along the $y-$axis. This simplifies the mathematical treatment significantly but gives out approximately the same value of the lost energy, because in the vicinity of the soliton both spherical and plain waves should look similar and possess same energies. The perturbation propagates according to the wave equation,

$$\ddot{n} = c^2 n'', \tag{10}$$

where c is the sound velocity, $c^2 = \frac{Kl^2}{M}$, K is an elastic constant describing the interaction of SGs with each other in nearest neighbor approximation, and M is the mass of a SG. One should be aware that M is an effective mass introduced for the sake of the spring-mass model. In reality, SGs do not move but tilt. However, if the magnitude of the SG oscillations is small, M should not differ much from the actual SG mass.

With these preparations, we can calculate e_l. The solution of the wave equation is well known, $n = G(\eta)$, where G is an arbitrary function, and $\eta = y - ct$ is a traveling wave coordinate similar to $\xi = x - vt$. We do not consider a wave coming from the infinity to the soliton which corresponds to an unphysical solution. The function $G(\eta)$ is defined by the initial condition Eq. (9),

$$n(y-ct) = \frac{\delta}{a}u\left(\frac{v}{c}(y-ct)\right). \tag{11}$$

This equation defines a functional relation between n and u, valid for any arbitrary potential $V(u)$. The energy of the emitted wave can be found in exactly the same way as the energy of the soliton was found in [14],

$$\frac{e_l}{2} = \frac{M}{2l}\int_{-\infty}^{\infty}\dot{n}^2 dy + \frac{Kl}{2}\int_{-\infty}^{\infty}(n')^2 dy = Kl\int_{-\infty}^{\infty}(\partial_\eta n)^2 d\eta. \tag{12}$$

The factor two on the left-hand side comes from the fact that each hydronium has two spectator SGs and, therefore, emits identical waves to either side of the soliton. The two terms in the central part represent the kinetic and potential energies of the emitted wave. The limits of integration could be 0 to ∞ because there is no wave at $y < 0$. However, the limits $-\infty$ to ∞ make the treatment simpler. To obtain the expression on the right of Eq. (12), we changed variables from y and t to η. The integral is similar to the integral in Eq. (7). Inserting the functional relation between n and u from Eq. (11) and using Eq. (8), we can transform Eq. (11) into

$$\dot{E}_l = \frac{2Kv^2}{\sqrt{3}c}\frac{\delta^2}{a^2}\int_{-\infty}^{\infty}(\partial_z u(z))^2 dz, \tag{13}$$

where z is a new integration valuable. This equation is valid for an arbitrary potential $V(u)$ and it gives a dependence on v^2, as required.

Now we have to understand how we could estimate K, the coupling constant of SG displacements. If a SG is displaced, it pulls the neighboring hydronium ion due to a strong H bond connection. The hydronium ion pulls the neighboring SG, accomplishing the coupling. We refer to this as a SG-hydronium-SG coupling. Using similar reasoning, the coupling between hydronium ions, described by k, corresponds to a hydronium-SG-hydronium coupling. The coupling constants K and k are therefore derived from the same elementary steps, taken, however, in different sequence. For small relative displacements, the system is linear and the sequence of coupling steps is irrelevant. In this case, we expect $K = k$. As a matter of fact, the assumption of linearity was already invoked in the definition of the Hamiltonian, Eq. (1), when the term $k(u_{i+1} - u_i)^2$ was introduced.

There are two problems with the reasoning showing above. First of all, other interactions, neglected so far, may contribute to the coupling like, for example, Coulomb interactions. However, the mechanism described above should be predominant due to an exceptional strength of H bonds. Moreover, the contribution of Coulomb interaction will affect the values of K and k equally, due to the same charges of SGs and hydronium ions. In the linear approximation, due to the symmetry of the system, SG and hydronium ions are interchangeable and their Coulombic coupling must preserve $K = k$.

The second problem is that K is assumed to describe the interaction between the neighboring SGs separated by l. On the other hand, in the Hamiltonian Eq. (1), k describes the coupling between hydroniums in the soliton, whose separation is $\sqrt{3}l$, as can be easily seen from the geometry shown in Fig. 1, which should lead to a different value of the coupling constant. However, $\sqrt{3}$ is not much different from unity and, if we consider the pathways which pass on the interaction between hydroniums in the soliton, one can expect that they are not very different from the once connecting two SGs. Therefore, we believe that the reasoning is correct up to a factor close to unity. Note, the original equations, Eqs. (3) and (4), are also approximate up to a prefactor close to unity. Currently we are running simulations to obtain k and K, which will evaluate the assumptions made. For the time being, we could rely on the assessment made in [13]. The authors were facing the same problem of defining the constants in a similar 1D model. Different from our approach, they represent each constant as a product of a mass and a corresponding frequency in order to make clear a connection with spectroscopic data. So, instead of our k and K they use $m\omega_1^2$ and $M\Omega_1^2$. To find ω_1, they used a similar approach as we did. To find Ω_1, they considered a range of possible reasonable displacements of atoms in the system and found a window of corresponding frequencies. It turned our that ω_1 does not belong to the window for Ω_1. However, the treatment in terms of frequencies obscured the fact that $m\omega_1^2$ falls in the middle of the window for $M\Omega_1^2$.

Finally, summarizing the reasoning and discussion above, Eq. (13) reads

$$\dot{E}_l = \frac{2kv^2}{\sqrt{3}c}\frac{\delta^2}{a^2}\int_{-\infty}^{\infty}(\partial_z u(z))^2 dz. \tag{14}$$

III. MOBILITY OF SOLITONS

In the previous section we found $\dot{E}_b$ and $\dot{E}_l$. From equating the expressions obtained, $\dot{E}_b = \dot{E}_l$, we can determine the viscous friction coefficient,

$$b = 2\sqrt{kM}\frac{\delta^2}{a^2}. \tag{15}$$

We did not use an explicit expression for u which is determined by $V(u)$, therefore b is the same for any potential $V(u)$. This is a consequence of the soliton adaptation to a change of $V(u)$. In [14], we found that a soliton changes its shape in response to a change of $V(u)$ in order to minimize its energy. Now we see that this adaptation also minimizes the energy loss rate.

Inserting Eq. (15) into Eq. (4) we obtain an expression for the soliton mobility,

$$\mu = \frac{a^3}{\delta^2\sqrt{8\epsilon M}}. \tag{16}$$

Note that the mobility does not depend explicitly on the coupling constant between hydronium ions, k, nor on the hydronium ion mass, m; but it depends on the SG mass, M. This is due to the fact that we expressed k and b via K and M. We thus managed to get rid of k and K which are the only constants we do not know from simulations yet. M is estimated as the mass of an SO_3^- ion, for which we use $M = 80m_p$, where m_p is the proton mass. An estimate of ϵ was obtained in [9], $\epsilon = 0.3$ eV. The parameter δ represents the SG dislocation by tilting during hydronium ion transfer and can be found by a simple geometry optimisation simulation, $\delta = 0.09a$, [22]. These parameter estimates provide a mobility $\mu \approx 2 \times 10^{14}$ m $(\mathrm{Ns})^{-1} \approx 3 \times 10^{-5}$ m^2 $(\mathrm{Vs})^{-1}$ which corresponds to a proton diffusion coefficient $D \approx 10^{-2}$ cm^2 s^{-1} at $T = 100\,^\circ$C. This value is quite large in comparison to the diffusion coefficient in bulk water at room temperature, 9.3×10^{-5} cm^2 s^{-1}, as well as it is larger than experimentally found values [18–21] observed, though, in chemically different systems.

We have considered an idealized model without any defects at the optimal interfacial density of SGs. These conditions will provide the optimal value of proton mobility. Nonidealities in real experimental systems due to variations in interfacial SG spacing and SG lengths diminish the efficiency of interfacial proton transport and lead to smaller values of proton mobility. We will consider the influence of these factors in our later publications. So far we have found the mobility for our "perfect" system and theoretically demonstrated the benefit of optimal density of SGs for proton transport.

Many parameters of solitons depend on the constant k which is still unknown. In [14] we used an estimation $k \approx 2$ kN. Using Eq. (3) one can calculate the energy of a static soliton, $E_0 \approx 18$ eV. The energy is high due to a large number of hydronium ions in the soliton. It is still unclear what makes all those hydroniums move simultaneously, and we will discuss it in our next paper. For now, we can specify the rate of energy loss of a soliton and use it to estimate the the soliton life time. The rate of energy loss can be found by taking the integral in Eq. (14) or, which is the same, in Eq. (7). The integration was performed in [14] where it was shown that the result does not depend on the potential $V(u)$. Hence, Eq. (14) becomes

$$\dot{E}_l = \frac{v^2\delta^2}{3a^3}\sqrt{\frac{8\epsilon M}{1-\left(\frac{v^2}{v_0^2}\right)^2}}. \tag{17}$$

One can see that the rate of energy loss is strongly dependent on soliton velocity, $\dot{E}_l \sim v^2$. Fast solitons lose energy more rapidly. To simplify the formalism, we will consider a slow soliton having energy $E(t) = E_0 + A(t)$, where $A(t) \ll E_0$ for each t. Expressing $\frac{v}{v_0}$ via E from Eq. (3), Eq. (17) gives a simple differential equation for $A(t)$. Its solution is

$$\begin{aligned} A(t) &= A(0)\exp\left(-\frac{4\delta^2 v_0^2\sqrt{2\epsilon M}}{3a^3 E_0}t\right) \\ &= A(0)\exp\left(-\frac{2b}{\sqrt{3}m}t\right) \equiv A(0)\exp(-\lambda t), \end{aligned} \tag{18}$$

where $\lambda \equiv \frac{2b}{\sqrt{3}m} \approx 10^{13}$ s^{-1}. Assume for estimation $A(0) = 3k_BT \approx 0.1$ eV which corresponds to $v \approx 0.1v_0 \approx 10^4$ m s^{-1}

as seen from Eq. (3). Note that this amount of energy is distributed over the whole soliton, so each hydronium will lose only a tiny portion of energy. Let us find the distance s that a soliton overcomes until it loses its energy:

$$s = \int_0^\infty v(t)dt \approx v_0\sqrt{\frac{2}{E_0}}\int_0^\infty \sqrt{A(t)}dt = \frac{v_0\sqrt{8A(0)}}{\lambda\sqrt{E_0}}. \quad (19)$$

Inserting the values we find that during its lifetime a soliton can overcome only $\frac{s}{l} \approx 100$ hydronium ions which is comparable with the size of the static soliton estimated in [14], $N_0 > 50$. This is an unexpected result because in the literature solitons are thought of as a more or less long-living perturbation running without changes with a constant velocity, hence the coined term soliton. However, it turns out that such kinks lose their energy very fast and stop moving after overcoming a relatively short distance. Note that the proposed mechanism of energy loss is essentially two-dimensional. Therefore, in one-dimensional systems solitons might lose energy slower and live longer due to a different mechanism of energy losses. Concerning our two-dimensional system, we believe that we found the most relevant, i.e., most efficient, mechanism of energy losses. Indeed, there is only a very narrow window for b. If b were much smaller than we found, then the mobility would be unreasonably large, see Eq. (4). On the other hand, if b were much larger than we found, then solitons would not move in the system at all due to a very short live time, see Eq. (18).

So far we assumed that there is a soliton in the system and we found the energy loss rate. But what happens when the soliton loses all its energy and stops? In fact, static solitons are unlikely to exist since their formation involves the creation of local hydrogen bond defects which carry a huge energy burden, as determined in [9]. On the other hand, as we just saw, even a few k_BT per soliton, so a very tine amount of energy per each hydronium in the soliton, can make the soliton overcome a noticeable distance. Therefore, once appeared, solitons will always be in motion due to thermal fluctuations. In other words, we have a number of mobile thermal excitations transferring protons and responsible for a high conductivity.

All the results mentioned in the present paper are based on the assumption made after Eq. (8) that the velocity of a soliton is constant within the time slot corresponding to a single hop of one hydronium ion. However, as we just saw, a soliton loses its energy very fast. Therefore, the assumption must be verified. Let us consider a soliton traveling with a velocity v. Provided v is constant, the time necessary for a relocation of one hydronium ion $\tau = \frac{a}{v}$. We will evaluate whether the velocity change due to the energy loss corresponding to this value of τ is indeed negligible. From Eq. (18) we have

$$\Delta A = A(0)\exp\left(-\frac{\lambda a}{v}\right), \quad (20)$$

where ΔA is the energy lost during one hop. Using the relation between A and v in Eq. (3), we obtain

$$\Delta v = v\exp\left(-\frac{\lambda a}{v}\right), \quad (21)$$

where Δv is the change of velocity during a hop. Our assumption requires $\frac{\Delta v}{v} \ll 1$ which holds if $v < 0.1v_0$. As we pointed out in [14], it is unlikely to have a soliton with a velocity close to v_0. Therefore, despite solitons losing energy very fast, all the results presented here and in [14] are applicable.

IV. CONCLUSIONS

In the present paper we have made further strides in the theoretical analysis of the collective mechanism of interfacial proton transport at a dense array of protogenic surface groups (SG), started in [14]. The model system is described by a Hamiltonian which contains unknown interaction constants and other coefficients that should be found separately. In [14] we solved the equation of motion and expressed the soliton mobility through microscopic parameters. In the present paper we showed how to treat the unknown constants in this theory. To evaluate the mobility, we proposed and explored a microscopic mechanism of energy loss. It involves perturbations of the SG subsystem caused by the traveling soliton. Values of soliton mobility, estimated with this theory, are in reasonable agreement with experimental results. However, because we consider an idealized defectless system, the theoretical formalism overestimates the proton mobility. Nevertheless, we consider the reasonable value of mobility as an argument in favour of the proposed collective transport mechanism.

Within the formalism, we could also estimate the soliton lifetime. In our model, solitons lose energy rapidly and are able to overcome a distance only a few times larger than their our size. However, static solitons are unstable and tend to move at slightest thermal excitations. Therefore, the system contains a number of very mobile perturbations transmitting protons.

Despite the reasonable value of the calculated mobility and the overall consistency of the collective transport mechanism with molecular simulations and relevant experimental data for interfacial systems, unresolved problems remain. First of all, each soliton consists of a relatively large number of hydronium ions corresponding to the total soliton energy exceeding 18 eV. Therefore, the mechanism of soliton creation is of foremost interest since spontaneous accumulation of this amount of energy is problematic. Also the number of solitons in the system is important because it can link the mobility to the conductivity. We will address this problem in the paper devoted to a soliton statistics.

There are two last constants we have not found yet—k and K. Knowledge of these constants will allow us to evaluate any parameter of a soliton. Currently we are performing molecular dynamics simulations to find them. In the Hamiltonian we assume a harmonic coupling between hydroniums and between SGs as well. In fact, this assumption is made throughout the literature but has not been verified. However, as we showed earlier, if $k \approx K$, the coupling must be harmonic, which proves the assumption.

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