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Dynamics of electron hopping in redox polymer electrodes using kinetic Ising model

Abstract The analysis of diffusion-migration equations pertaining to electron hopping and physical displacement in redox polymer electrodes is carried out using kinetic Ising model formalism. It is shown that, by the appropriate choice of transition probabilities obeying detailed balancing conditions, a hierarchy of transport equations can be derived. Earlier transport equations due to Nernst-Planck and Savéant are derived as special cases. The dependence of apparent diffusion coefficient on number density of redox centres, polymer morphology etc. are pointed out. Several new insights concerning the microscopic basis underlying the hitherto known phenomenological equations are demonstrated.

Key words Kinetic Ising model · Electron hopping · Physical displacement · Diffusion-migration equation · Redox polymer electrodes

Introduction

The study of charge transport in redox polymer electrodes is a fascinating topic of research on account of its importance in diverse fields such as molecular electronic devices [1], biosensors [2], immobilization of enzymes onto electrode surfaces [3] etc. Further, transport of charges through these supramolecular structures may involve various processes such as diffusion of species, counterion movement, ion pair formation, electron transfer between spatially separated redox centers etc. Among these phenomena, analysis of electron transfer between redox centers is a challenging task on account of (1) non-validity of classical Nernst-Planck equation, (2) random distribution of molecules, (3) restricted physical

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displacement caused by the polymer backbone and (4) field-assisted electron hopping. Hence the preliminary step in the analysis of charge transport consists in formulating transport equations pertaining to nearest neighbor electron hopping, and this was first provided by Savéant [4] using chemical kinetic schemes and subsequently rediscovered by other methods (cf. [5]). Further, the methodology of incorporating long-distance electron transfer with rate constants exponentially decaying with distance was attempted [6]. In all the above endeavors, the focus of attention was the number density dependence of the electron diffusion coefficient. An issue that has not been extensively analyzed is the competition between electron hopping and physical displacement and the consequent dependence of the effective diffusion coefficient on concentration, potential difference etc. A recent Monte Carlo simulation in this context indicates a rich percolation behavior for two- and three-dimensional lattices [7].

The purpose of this communication is to report a time-dependent diffusion migration equation that takes into account the physical displacement as well as nearest-neighbor electron hopping. Our formalism makes use of the kinetic Ising model approach wherein explicit formulation of transition probabilities using Kawasaki rates is postulated.

Model and analysis

Let us consider a uniform regular lattice ω consisting of N lattice sites and over which N_T molecules of A and B are present, the number of vacant sites being N_V. Both particles A and B are assumed to be charged species, and the charges present in A and B are z_A and z_B respectively. The basic stochastic step involved in this ω lattice is the physical "bounded" displacement. Thus particle A attempts to move in the lattice field at a randomly selected location j with rate k_{ji}^P, and this is successful only if the nearest neighboring site i is vacant (the reverse jump

Fig. 1 Schematic representation of various processes taking place at sites i, j and k. Any loss to the particle A at site j due to electron hopping (adjacent site is B) or particle displacement (adjacent site is vacant) is represented by a *dotted line* with the indicated field-dependent jump frequency. Any gain for particle A at site j is represented by a *full line*
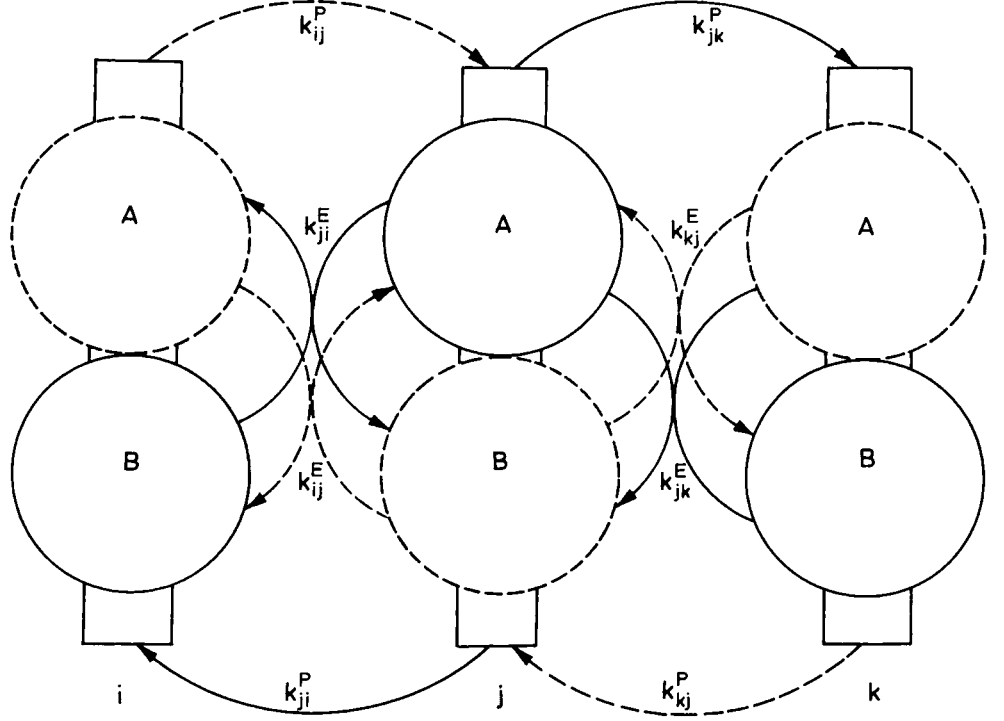
from site i to j takes place with a rate k_{ij}^{P}). This elementary displacement covers a distance of ΔX, which is assumed to be the distance between the centers of the two adjacent lattice points.

In addition to the "bounded" physical displacement, electron hopping takes place on the sublattice Ω provided by particle B with field-dependent rates. For brevity, particle A is considered as electron donor (electron) and B as an electron acceptor (hole),[1] and hence particle B is the lattice point for the electron hopping. For the electron hopping to take place between any adjacent sites i and j the pre-requisite is that one of the two sites in the sublattice should be occupied by particle A. When an electron hops from site $i(j)$ to the neighboring particle B at site $j(i)$ with rate k_{ij}^{E} (k_{ji}^{E}) the particles A and B get interconverted. The average distance covered during this exchange process is δ, which is the center-to-center distance of closest approach between the two adjacent particles.

Under the Ising model formalism, individual sites in the regular and sublattices have been assigned a spin variable σ^{Ω} and σ^{ω}, which can take a multiplicity of possible values corresponding to the state that particular site may be in. In this model we restrict ourselves to a two-state Ising model, where the spin variable σ_{j}^{ω} at site j in the regular lattice takes the value of either $+1$ or -1, depending on whether the jth site is occupied (by A or B) or vacant. Here we do not distinguish between particles A and B, but it will be done explicitly when we consider

the sublattice using spin variable σ^{Ω}. The possible values σ^{Ω} can take are $+\chi$ and $-\chi$, corresponding to the site being occupied by A and B respectively.

The Generalized Master Equation

The time evolution of the normalized N spin distribution function at time t, viz. $P_{N}(\{\sigma\}_{N};t)$, is

$$
\begin{aligned}
\frac{d}{dt} P_{N}(\{\sigma\}_{N};t) = &\sum_{\langle ij \rangle} W_{ij}(\sigma_{i}\sigma_{j}\{\sigma\}_{ij})P_{N}(\{\sigma\}_{N}^{ij}) \\
&- \sum_{\langle ij \rangle} W_{ji}(\sigma_{j}\sigma_{i}\{\sigma\}_{ij})P_{N}(\{\sigma\}_{N}) \\
&+ \sum_{\langle jk \rangle} W_{kj}(\sigma_{k}\sigma_{j}\{\sigma\}_{jk})P_{N}(\{\sigma\}_{N}^{jk}) \\
&- \sum_{\langle jk \rangle} W_{jk}(\sigma_{j}\sigma_{k}\{\sigma\}_{jk})P_{N}(\{\sigma\}_{N})
\end{aligned}
\tag{1}
$$

where i and k are indices of the nearest neighbor j, $\{\sigma\}_{N}^{ij}$ and $\{\sigma\}_{N}^{jk}$ denote the spin configurations in which $\sigma_{j}\sigma_{i}$ and $\sigma_{j}\sigma_{k}$ are interchanged in their configuration with respect to $\{\sigma\}_{N}$ (cf [8, 9]). W denotes transition probability. The above GME can be reduced by substituting,

$$
h_{ji} = W_{ji}(\sigma_{j}\sigma_{i}\{\sigma\}_{ij})P_{N}(\{\sigma\}_{N};t)
\tag{2}
$$

and

$$
h_{jk} = W_{jk}(\sigma_{j}\sigma_{k}\{\sigma\}_{jk})P_{N}(\{\sigma\}_{N};t)
\tag{3}
$$

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[1] In the terminology of solid state physics, particle A and B can be termed as electron and hole respectively

and putting P_{ji} and P_{jk} as the spin exchange operators, which changes the configuration of the spin variable, i.e. P_{ji} changes $\{\sigma\}_N$ to $\{\sigma\}_N^{ij}$, hence

$$\frac{\partial}{\partial t}P_N(\{\sigma\}_N; t) = \sum_{\langle ij \rangle}[P_{ji}h_{ji} - h_{ji}] + \sum_{\langle jk \rangle}[P_{jk}h_{jk} - h_{jk}] \quad (4)$$

$$= \sum_{\langle ij \rangle}[P_{ji} - 1]h_{ji} + \sum_{\langle jk \rangle}[P_{jk} - 1]h_{jk} \quad (5)$$

Multiplying both sides in the above equation by σ_j

$$\frac{\partial}{\partial t}P_N(\{\sigma\}_N; t) = \sum_{\{\sigma\}_N} \sigma_j \sum_{\langle ij \rangle}[P_{ji} - 1]h_{ji}$$
$$+ \sum_{\{\sigma\}_N} \sigma_j \sum_{\langle jk \rangle}[P_{jk} - 1]h_{jk} \quad (6)$$

Since the summation operators commute with each other, one can write,

$$\frac{\partial \langle \sigma_j \rangle}{\partial t} = \sum_{\{\sigma\}_N} \sum_{\langle ij \rangle} \sigma_j[P_{ji} - 1]h_{ji}$$
$$+ \sum_{\{\sigma\}_N} \sum_{\langle jk \rangle} \sigma_j[P_{jk} - 1]h_{jk} \quad (7)$$
$$= \sum_{\{\sigma\}_N \in j} \sum_{\langle ij \rangle} \sigma_j[P_{ji} - 1]h_{ji}$$
$$+ \sum_{\{\sigma\}_N \notin j} \sum_{\langle ij \rangle} \sigma_j[P_{ji} - 1]h_{ji}$$
$$+ \sum_{\{\sigma\}_N \in j} \sum_{\langle jk \rangle} \sigma_j[P_{jk} - 1]h_{jk}$$
$$+ \sum_{\{\sigma\}_N \notin j} \sum_{\langle jk \rangle} \sigma_j[P_{jk} - 1]h_{jk} \quad (8)$$

For $\langle ij \rangle \notin j, P_{ji}$ and σ_j commute and for $\langle ij \rangle \in j, P_{ji}$ and σ_j anticommute i.e., one can elaborate it as shown below:

for $\langle ij \rangle \notin j \qquad P_{ji}\sigma_j = P_{ji}\sigma_j$

and for $\langle ij \rangle \in j \quad P_{ji}\sigma_j = -P_{ji}\sigma_j$

This is so because the P_{ij} operator changes the sign of the configuration when it operates on the appropriate function. So the above equation becomes,

$$\frac{\partial \langle \sigma_j \rangle}{\partial t} = \sum_{\{\sigma\}_N \in j} \sum_{\langle ij \rangle} \sigma_j[-P_{ji} - 1]h_{ji}$$
$$+ \sum_{\{\sigma\}_N \notin j} \sum_{\langle ij \rangle} \sigma_j[P_{ji} - 1]h_{ij}$$
$$+ \sum_{\{\sigma\}_N \in j} \sum_{\langle jk \rangle} \sigma_j[-P_{jk} - 1]h_{jk}$$
$$+ \sum_{\{\sigma\}_N \notin j} \sum_{\langle jk \rangle} \sigma_j[P_{jk} - 1]h_{jk} \quad (9)$$

The reduced form of the master equation is obtained by substituting back the h_{ji} and h_{jk} values and also taking into account
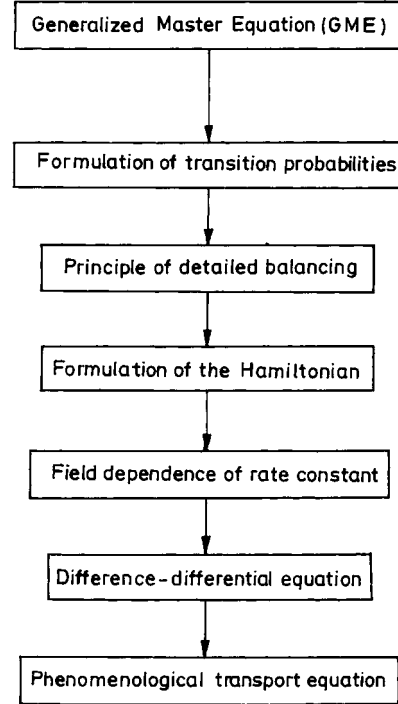
Fig. 2 Steps involved in the conversion of GME into continuum diffusion migration versions [10]

$$\sum_{\{\sigma\}_N} P_{ji} = \sum_{\{\sigma\}_N} P_{jk} = 1$$

The first moment of the probability distribution, $\langle \sigma_j \rangle$ can thus be given as

$$\frac{\partial \langle \sigma_j \rangle}{\partial t} = -2 \sum_{\langle ij \rangle \in j} \langle \sigma_j W_{ji}(\sigma_j \sigma_i \{\sigma\}_{ij}) \rangle$$
$$- 2 \sum_{\langle jk \rangle \in j} \langle \sigma_j W_{jk}(\sigma_j \sigma_k \{\sigma\}_{jk}) \rangle \quad (10)$$

Equation 10 is also called the reduced master equation. The conversion of the above microscopic equation into gross phenomenological versions amenable for experimental analysis involves several steps as indicated in Fig. 2.

It is imperative at this stage to decipher the meaning of a few terminologies employed above. The W_{ij}s appearing in the generalized master equation (GME) are transitional rates which are intrinsically coupled to rate constants that one encounters in chemical kinetics. The Ising model version appears while expressing the transition probabilites in terms of (pseudo) spin variables, and usually is described using a two-state model (± 1). Because of the above subtle points, it has become customary to call such approaches as based on kinetic Ising model version (or equivalently non-equilibrium Ising model). Such transitional rates are of two types, viz.: (1) Spin flip in the case of the adsorption-desorption problem where one usually deals with a *single* site. This rate is known as Glauber dynamics. (2) Spin-exchange em-
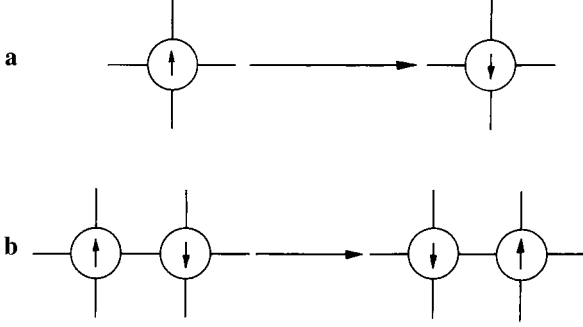
Fig. 3a, b Illustration of (a) spin flip and (b) spin exchange processes. Upward and downward arrows indicate the instantaneous configurations of site(s), viz. $+1$ and -1 respectively

ployed for kinetic processes where *two types of sites* are involved at any given instant. This time dependence of the configurational change involved in these *two-site* exchanges is referred to as Kawasaki rate.

Formulation of transition probabilities

In order to formulate transition probabilities, the number of occupied and vacant sites needs to be determined. In this two-state version,

$$\chi_A + \chi_B = \left(\frac{1 + \langle \sigma^\omega \rangle}{2}\right) \tag{11}$$

$$\chi_V = \left(\frac{1 - \langle \sigma^\omega \rangle}{2}\right) \tag{12}$$

in the case of ω-lattice. Similarly, for Ω-sublatttice,

$$\chi_A = \left(\frac{\langle \chi \rangle + \langle \sigma^\Omega \rangle}{2}\right) \tag{13}$$

$$\chi_B = \left(\frac{\langle \chi \rangle - \langle \sigma^\Omega \rangle}{2}\right) \tag{14}$$

Using the above definitions, the transition probabilities that obey detailed balancing conditions may be written.

We have already mentioned that the transition probability is dependent on the neighboring spin value of the site under consideration. For example the presence and absence of a particle in a particular site is indicated in terms of the spin variable. Thus the transition probabilities for the electron hopping and particle displacement occurring between sites i and j can be written in terms of the spin variable σ^Ω and σ^ω as

$$W_{ji}^E(\sigma_j \sigma_i \{\sigma\}_{ij}) = k_{ji}^E \left(\frac{\chi - \sigma_i^\Omega}{2\chi}\right)\left(\frac{\chi + \sigma_j^\Omega}{2\chi}\right)$$
$$+ k_{ij}^E \left(\frac{\chi - \sigma_j^\Omega}{2\chi}\right)\left(\frac{\chi + \sigma_i^\Omega}{2\chi}\right) \tag{15}$$

$$W_{ji}^P(\sigma_j \sigma_i \{\sigma_j\}_{ij}) = k_{ij}^P f\left(\frac{1 - \sigma_j^\omega}{2}\right)\left(\frac{\chi + \sigma_i^\Omega}{2\chi}\right)$$
$$+ k_{ji}^P f\left(\frac{1 - \sigma_i^\omega}{2}\right)\left(\frac{\chi + \sigma_j^\Omega}{2\chi}\right) \tag{16}$$

where f is the correlation factor. Analogous expressions for W_{jk}^E and W_{jk}^P can be written. The electron transfer rate constants appearing in the above equations from the Hamiltonian can be derived as shown in the appendix.

$$k_{jj}^E = k_E \exp\left[\frac{\alpha' n e(\phi_j - \phi_i)}{k_B T}\right] \tag{17}$$

and

$$k_{ji}^E = k_E \exp\left[\frac{-\alpha n e(\phi_j - \phi_i)}{k_B T}\right] \tag{18}$$

where k_E represents the standard heterogeneous rate constant. Substitution of the rate constants into the transition probabilities expression and then into the reduced GME (Eq. 10) finally leads to

$$\frac{\partial \chi_A}{\partial t} = D_{ap}\left\{\frac{\partial^2 \chi_A}{\partial x^2} + \frac{D_{ap}^{nz} e}{D_{ap} k_B T}\left[\frac{\partial}{\partial x}\left(\chi_A \frac{\partial \phi}{\partial x}\right)\right.\right.$$
$$\left.\left. - \frac{n D_E \chi_T}{D_{ap}^{nz}}\frac{\partial}{\partial x}\left(\chi_A^2 \frac{\partial \phi}{\partial x}\right)\right]\right\} \tag{19}$$

where

$$D_{ap} = D_P f(1 - \chi) + D_E \chi \tag{20}$$
$$D_{ap}^{nz} = z_A D_{ap} + (n - z_A)D_E \chi$$

with $D_E = k_E \delta^2$ and $D_P = k_P \Delta X^2$; z_A represents charge of the species and n denotes the number of electrons transferred.

Discussion

Equation 19 represents the spatio-temporal diffusion equation in a bias electric field when electron hopping and physical displacement occur simultaneously. It may be noted that when $\chi_T \to 1$, Eq. 19 leads to the transport equation for nearest neighbor electron hopping originally derived by Savéant [4]. Similarly, when $\chi_T \to 0$, the classical Nernst-Planck equation is recovered from Eq. 19. This is not all. By modelling mean square displacements δ^2 and ΔX^2 in terms of concentration of species, diverse patterns of number density dependence of effective diffusion coefficient may be analyzed. A chief merit of kinetic Ising model formalism consists in the formulation of the diffusion migration equation along with the concentration dependence of the diffusion coefficient. Furthermore, Eq. 19 itself can be subjected to analysis of transient electrochemical experiments in order to decipher the influence of system parameters on the observed current.

A few comments about the significance of Eq. 20 are in order here. This equation is identical to that derived by Savéant using the method of random flights and was shown to hold good with Monte Carlo simulations below the percolation threshold. We emphasise here that the correlation factor f is in principle capable of taking into account the diverse concentration dependence of D_{ap}. Furthermore, Eq. 19 represents a non-steady state diffusion-migration equation when two competing transport processes occur simultaneously (hitherto unknown).

A few salient features of such microscopic models may be pointed out here. In the present analysis we have focussed our attention on systems where both the oxidized and the reduced form of the redox species are electron transfer active. However, as suggested by Savéant [11], ion aggression can also take place between the redox-active species (A and/or B) and the supporting electro inactive counterion (C) leading to an electron transfer inactive species (D). Thus, in addition to the electron hopping and "bounded" physical displacement, ion pairing can also take place and affect the charge propagation rate. The introduction of ion pairing into the present formalism is possible.

A description of the electron hopping and physical displacement when interaction between sites is present may also be attempted within the kinetic Ising model formalism. However, this involves incorporation of interaction energy J in the Ising Hamiltonian and introducing it into the transport equation through the spin exchange jump frequencies. The Ising Hamiltonian then becomes,

$$\mathscr{H}^{\Omega} = -\sum_j h_j^{\Omega}\left(\frac{1-\sigma_j^{\Omega}}{2}\right) - J\sum_{\langle ij\rangle}\left(\frac{1-\sigma_j^{\Omega}}{2}\right)\left(\frac{1-\sigma_i^{\Omega}}{2}\right)$$

(21)

However, products of spin variables $\sigma_i\sigma_j$ need a decoupling. At the simplest level, the molecular field approximation provides a primitive methodology, viz. $\langle\sigma_i\sigma_j\rangle = \langle\sigma_i\rangle\langle\sigma_j\rangle$. Higher level approximations such as "Bethe Ansatz" may also be employed but will make the analysis quite tedious.

Summary

The methodology of deriving spatio-temporal diffusion migration equations for electron hopping coupled with physical displacement process using kinetic Ising model formalism is studied using a two-state lattice model.

Appendix

Consider the energetics involved in electron hopping and physical displacement. Let the potential at a site j be ϕ_j.

When there is no interaction between particles the total Hamiltonian pertaining to electrostatic terms can be represented as follows:

$$\mathscr{H}_j^{\omega} = -\sum_j h_j^{\omega}\left(\frac{1+\sigma_j^{\omega}}{2}\right)$$

(A1)

$$\mathscr{H}_j^{\Omega} = -\sum_j h_j^{\Omega}\left(\frac{\chi+\sigma_j^{\Omega}}{2\chi}\right)$$

(A2)

Under molecular field approximation the above Hamiltonian can be modified by incorporating terms such as $J\langle\sigma_i\rangle\langle\sigma_j\rangle$, where J represents the composite interaction energy parameter. The postulate of detailed balancing enables us to formulate equalities among the transition probabilities as given below,

$$W_{ji}(\sigma_j\sigma_i\{\sigma\}_{ij})P_N^e(\{\sigma\}_N;t) = W_{ij}(\sigma_i\sigma_j\{\sigma\}_{ij})$$
$$\times P_N^e(\{\sigma\}_N^{ij};t)$$

(A3)

$$W_{kj}(\sigma_k\sigma_j\{\sigma\}_{jk})P_N^e(\{\sigma\}_N^{jk};t) = W_{jk}(\sigma_j\sigma_k\{\sigma\}_{jk})$$
$$\times P_N^e(\{\sigma\}_N;t)$$

(A4)

where P_N^e represents the probabilities of the spin exchange under the equilibrium condition and it is related to the Hamiltonian in the following manner

$$\frac{P_N^e(\{\sigma\}_N^{ij};t)}{P_N^e(\{\sigma\}_N;t)} = \exp\left(\frac{-\mathscr{H}_{ij}}{k_B T}\right)$$

(A5)

where $\mathscr{H}_{ij} = \mathscr{H}_j - \mathscr{H}_i$. In general, P_N^e is given by

$$P_N^e = \frac{\exp(-\mathscr{H}_{ij}/k_B T)}{Z}$$

(A6)

where Z represents the partition function. On account of the independence of the electron hopping and physical displacement process the transition probability can be considered as a sum of those due to the individual phenomena [11]. Hence

$$W_{ji}(\sigma_j\sigma_i\{\sigma\}_{ij}) = W_{ji}^E(\sigma_j\sigma_i\{\sigma\}_{ij}) + W_{ji}^P(\sigma_j\sigma_i\{\sigma\}_{ij})$$

(A7)

The electric potential dependence of rate constant follows from Eqs. A3–A9, 15 and 16 as

$$\frac{k_{ji}^E}{k_{ij}^E} = \exp[ne(\phi_i - \phi_j)/k_B T]$$

(A8)

$$\frac{k_{kj}^E}{k_{jk}^E} = \exp[ne(\phi_j - \phi_k)/k_B T]$$

(A9)

Since the above equation gives the ratio of the electron transfer frequencies it seems appropriate to introduce the parameter k_0^E which is independent of potential.

$$k_{ij}^E = k_0^E \exp(-\xi_1^E/k_B T)$$

(A10)

$$k_{ji}^E = k_0^E \exp(-\xi_2^E/k_B T)$$

(A11)

On account of Eqs. A10 and A11 we may write

$$\xi_2^E - \xi_1^E = ne(\phi_j - \phi_i) \tag{A12}$$

Note that the above Eq. A12 gives the difference between ξ_1^E and ξ_2^E, which is still inadequate for our purpose since we need explicit forms for these two separately. Hence we introduce a factor α and α' which may be considered analogous to transfer coefficient in the electrochemical literature.

$$\xi_1^E = \xi_0^E - \alpha' ne(\phi_j - \phi_i) \tag{A13}$$

$$\xi_2^E = \xi_0^E + \alpha ne(\phi_j - \phi_i) \tag{A14}$$

and $\alpha + \alpha' = 1$. In the above equations ξ_0^E are introduced for the sake of generality to take into account any morphological changes brought about in the polymer. Now the exchange rate constants become

$$k_{ji}^E = k_E \exp[-\alpha ne(\phi_j - \phi_i)/k_B T] \tag{A15}$$

$$k_{ij}^E = k_E \exp[\alpha' ne(\phi_j - \phi_i)/k_B T] \tag{A16}$$

Similarly from Eq. A9 we obtain

$$k_{kj}^E = k_E \exp[\alpha ne(\phi_j - \phi_k)/k_B T] \tag{A17}$$

$$k_{jk}^E = k_E \exp[-\alpha' ne(\phi_j - \phi_k)/k_B T] \tag{A18}$$

where

$$k_E = k_0^E \exp(-\xi_0^E/k_B T) \tag{A19}$$

It is easy to recall that Eqs. A15–A18 represent the potential dependence of electron hopping frequencies (see for example [10]). Analogously, we can write for the physical displacement process equations similar to Eqs. A15–A18.

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