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Dynamics of competing diffusion processes in a bias electric field: kinetic Ising model approach and phenomenological descriptions

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Abstract. The methodology of formulating spatio-temporal diffusion-migration equations in an applied electric field for two competing diffusion processes is outlined using kinetic Ising model versions with the help of spin-exchange dynamics due to Kawasaki. The two transport processes considered here correspond to bounded displacement of species attached to supramolecular structures and electron hopping between spatially separated electron transfer active centres. The dependence of the diffusion coefficient on number density as well as the microscopic basis underlying phenomenological diffusion-migration equations are pointed out.

1. Introduction

The description of spin-type Ising models involving different microscopic dynamical laws has proved valuable in diverse fields. The formalism of *spin-flip* between neighbouring spins originally introduced by Glauber [1] for studying time dependence of spin-spin correlation functions in magnetic systems has been subsequently demonstrated in the analysis of adsorption-desorption kinetics [2], critical dynamics in Ising chains [3] etc. Furthermore, the ingenuity of handling interactions between spins with the help of time-dependent *spin-exchange* processes for the calculation of transport properties, especially near the Curie point was advocated by Kawasaki [4]. In the context of the kinetic Ising model (KIM), the above spin-flip and spin-exchange processes are familiarly referred to as Glauber and Kawasaki rates, respectively. During the past few decades, the scope and applicability of Kawasaki dynamics has been further explored for studying diverse issues such as segregation in binary mixtures [5], polymer chain kinetics [6], phase transitions [7], percolation problems [8] etc. Among the advantages that KIM formalism offers we should mention the ease with which macroscopic phenomena can be understood in terms of microscopic transition probabilities [9]. This aspect is especially crucial in the analysis of statistical mechanics of interacting systems where microscopic details alone provide a clue to phenomenological observations. Furthermore, the exact mapping of such spin-type microscopic modelling into phenomenological coarse-grained versions as well as the powerful insights the fine-grained descriptions offer, are often not transparent.

The modelling of transport phenomena using KIM formalism has been studied from various perspectives. For instance, analysing the behaviour of the self-diffusion constant near the critical temperature constituted the first application of Kawasaki dynamics. The description of transport phenomena in the presence of a bias electric field using microscopic approaches has been extensively studied with objectives such as (i) onset of the non-diffusive

regime, (ii) dependence of the critical exponent on a bias electric field and, (iii) percolation behaviour, etc (cf [10–12]). However, the analysis based on the generalized master equation (GME) and the formulation of Kawasaki rates in the case of competing diffusion processes so as to decipher the origin of phenomenological equations has not yet been investigated. The starting point in this context usually consists in formulating an Ising model whose time-dependent behaviour is followed using the GME and expressing the transition probabilities in terms of the spin variables and appropriate frequencies.

The methodology proposed herein is especially pertinent to the study of charge transport through supramolecular systems [13] containing redox moieties, with potential applications to sensors [14], electrocatalysis [15], molecular electronics [16] and immobilization of enzymes onto electrode surfaces [17] etc. The charge propagation through macromolecular structures containing redox molecules occurs via (i) ‘bounded’ physical displacement of species and (ii) electron self-exchange from a reduced molecule to an oxidized one. In solutions, charge transport is usually dominated by the physical displacement of the redox molecules, whereas in the above-mentioned cases, redox moieties are bonded covalently, coordinatively or electrostatically with the macromolecular assembly, thereby movement of these particles in the lattice field is confined to a limited region in space (dictated by the polymer backbone). In addition to this bounded displacement, charge transfer also occurs by electron self-exchange, frequently referred as electron hopping between (nearest-neighbour) redox species which is also aided by an applied electrical potential.

In this paper, we propose a formalism for analysing the above competing diffusion processes in a bias electric field, namely diffusion of redox species via a vacancy mechanism and through electron hopping processes. We indicate the derivation of the spatio-temporal diffusion-migration equation using the KIM approach and demonstrate how this can be viewed as a generalization of either the classical Nernst–Planck equation for physical diffusion of charged species or of transport equations representing electron hopping between spatially separated redox centres. Apart from pointing out the dependence of the diffusion coefficient on the number density, we also demonstrate the significance of this methodology. We restrict ourselves to one-dimensional lattice system for brevity; however, we believe that the study will also be instrumental in extending such investigations to higher dimensions.

2. Model and analysis

The system we propose to investigate, consists of particles A, B and vacant sites randomly distributed. The charges of A and B are z_A and z_B respectively. At a given instant of time, A acts as a ‘donor’ of electrons while B as an ‘acceptor’ and hence B is considered to be the lattice point for electron hopping. $n (= z_A - z_B)$ represents the number of electrons involved in the hopping process. It is assumed that no interactions between particles and between particles and vacancies exist and multiple occupancy of a particular site by particles is prohibited. The system consisting of an ω lattice is the lattice populated by particles and vacant sites while an Ω sublattice is populated by particles A and B. A schematic sketch of the lattice under consideration is provided in figure 1(a).

The basic stochastic step involved in an ω lattice is ‘bounded’ displacement in which A and B can hop to empty sites under the influence of concentration and potential gradients (figure 1(b)). Here, bounded displacement implies that the physical movement of these particles becomes restricted and occurs between a few lattice sites in space. In addition to the motion of these particles in the lattice space ω , there exists an ‘apparent’ motion by the electron self-exchange mechanism between particles A and B. When an electron hop occurs from particle A at site j to the neighbouring particle B at site i , particles A and B

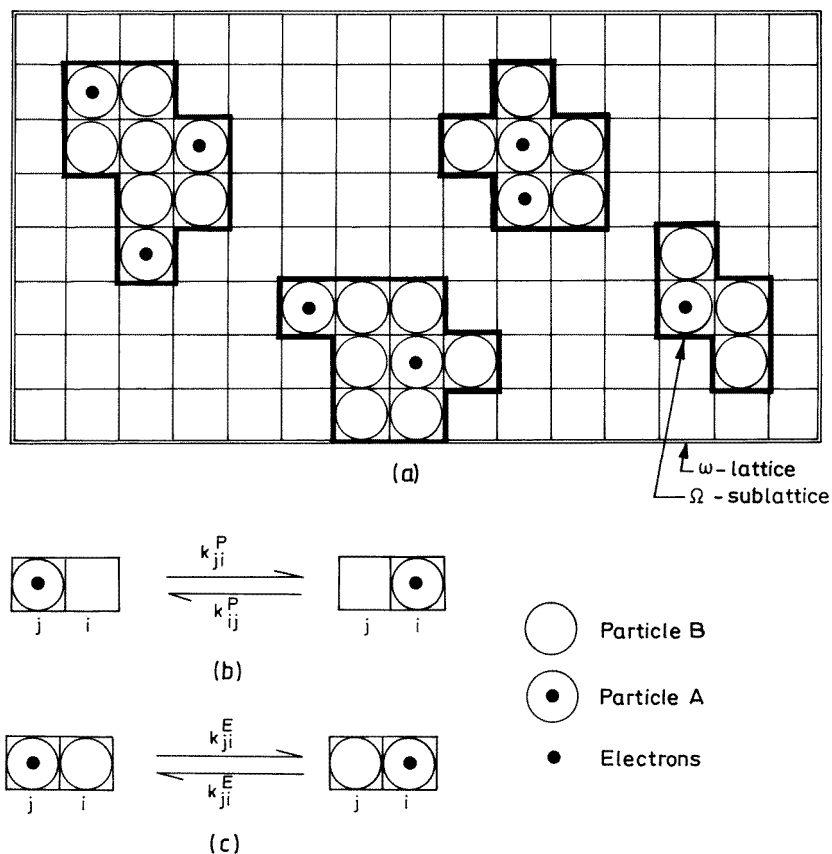


Figure 1. (a) A schematic sketch of ω -lattice and Ω -sublattice indicating state space partitioning (for ease of understanding the two-dimensional case is depicted). (b) Physical diffusion through the vacancy mechanism. (c) Electron hopping between nearest-neighbour sites.

become interchanged (figure 1(c)). Since A and B are interconverted on account of electron transfer, the movement of both species needs to be considered. Thus the sublattice for electron hopping is Ω .

While electron hopping occurs between A and B, counterions move accordingly in order to maintain electroneutrality in the system. We assume that the movement of counterions in the lattice is rapid in comparison with the physical motion and electron hopping. To focus our attention, we may consider A and B to be Os^{2+} and Os^{3+} , respectively, in the polymer $\text{poly}[\text{Os}(\text{bpy})_2(\text{vpy})_2]^{3+/2+}$ with a corresponding amount of ClO_4^- counterions (Os = Osmium; bpy = bipyridine; vpy = vinylpyridine). This polymer is coated onto the electrodes and the driving force for the transport is the applied electric potential which is felt over the entire interfacial region. Here, in view of the explicit dependences of the electric potential it is appropriate to call it a 'biased diffusion' problem.

Particle A attempts to move in the electric field at randomly selected location $j(i)$ with rate $k_{ji}^P(k_{ij}^P)$ and is successful only if the nearest-neighbour site $i(j)$ is vacant. This elementary event i.e. the jump from the j th lattice point to i covers a distance of Δx . And correspondingly when an electron hop occurs from particle A at site $j(i)$ to the neighbouring particle B at site $i(j)$ the rate constant involved is $k_{ij}^E(k_{ji}^E)$. The average

distance covered during this process δ is the centre-to-centre distance of closest approach between two adjacent particles; thus δ is comparable to or slightly greater than the molecular diameter.

2.1. Generalized master equation description

The time dependence of this model is described in terms of a master equation which governs the time evolution of the probability distribution. Denoting the normalized N spin distribution function at time t by $P_N(\{\sigma\}_N; t)$ the GME can be written as

$$\begin{aligned} \frac{d}{dt} P_N(\{\sigma\}_N; t) = & \sum_{\langle ij \rangle} W_{ij}(\sigma_i \sigma_j \{\sigma\}_{ij}) P_N(\{\sigma\}_N^{ij}) - \sum_{\langle ij \rangle} W_{ij}(\sigma_j \sigma_i \{\sigma\}_{ij}) P_N(\{\sigma\}_N) \\ & + \sum_{\langle jk \rangle} W_{jk}(\sigma_k \sigma_j \{\sigma\}_{jk}) P_N(\{\sigma\}_N^{jk}) - \sum_{\langle jk \rangle} W_{jk}(\sigma_j \sigma_k \{\sigma\}_{jk}) P_N(\{\sigma\}_N) \end{aligned} \quad (1)$$

where i and k are the site indices of the nearest neighbours of j , $\{\sigma\}_N^{ij}$ and $\{\sigma\}_N^{jk}$ are the spin configurations in which σ_j , σ_i and $\sigma_j \sigma_k$ are interchanged with respect to $\{\sigma\}_N$. $\langle ij \rangle$ and $\langle jk \rangle$ implies the pair of nearest-neighbour spins. The notations are as in [2]. Through a single elementary step the configuration $\{\sigma\}_N^{ij}$ or $\{\sigma\}_N^{jk}$ can evolve to $\{\sigma\}_N$ only if $\{\sigma\}_N^{ij}$ or $\{\sigma\}_N^{jk}$ differ from $\{\sigma\}_N$ at most by the state of *two nearest-neighbour spins* at locations i and j or j and k . The transition probabilities of the individual spins are dependent on the transient values of the neighbouring spins as well as on the influence of the bias electric field.

σ^ω and σ^Ω represent the spin variables for the ω lattice and Ω sublattice respectively. In this analysis, we consider a two-state Ising model where the spin variable σ^ω can have a value of either $+1$ or -1 in the ω lattice depending on whether that site is occupied (by A or B) or vacant. Similarly for the Ω sublattice σ^Ω can take two possible values $+\chi$ and $-\chi$ depending on whether the site has particle A or B. Thus in the main lattice ω , we do not distinguish whether a site is occupied by A or B; rather, we differentiate between occupancy and vacancy of a given site, whereas in the Ω sublattice, this difference is explicitly taken into account. Thus, a complete description of a given site requires specification of the value of the spin variable *as well as* the lattice type (ω or Ω).

On the basis of this definition, we introduce the macroscopic variables χ_A , χ_B and χ_V , which represent the fraction of the sites occupied by A ($= N_A/N$), B ($= N_B/N$), and vacant sites respectively, where N_A and N_B are the number of particles of A and B present and N is the total number of lattice sites. In lattice ω ,

State of occupancy	σ^ω	χ_T	χ_V
Occupied	$+1$	1	0
Vacant	-1	0	1

Thus we can write

$$\chi_T = \left(\frac{1 + \langle \sigma^\omega \rangle}{2} \right) \quad (2)$$

where $\chi_T = \langle \chi \rangle = \chi_A + \chi_B$ and $\chi_V + \chi_T = 1$. In the sublattice Ω

State of occupancy	σ^Ω	χ_A	χ_B
Occupied by A	$+\chi$	χ	0
Occupied by B	$-\chi$	0	χ

In general

$$\chi_A = \left(\frac{\langle \chi \rangle + \langle \sigma^\Omega \rangle}{2} \right) \tag{3}$$

and analogously for χ_B and χ_V . For further analysis, we need the first moment $\langle \sigma_j \rangle$ of the probability distribution $P_N(\{\sigma\}_N; t)$ which can easily be obtained from equation (1) as (cf [1])

$$\frac{d\langle \sigma_j \rangle}{dt} = -2 \sum_{\langle ij \rangle \in j} \langle \sigma_j W_{ij}(\sigma_j \sigma_i \{\sigma\}_{ij}) \rangle - 2 \sum_{\langle jk \rangle \in j} \langle \sigma_j W_{jk}(\sigma_j \sigma_k \{\sigma\}_{jk}) \rangle \tag{4}$$

where, $\langle \sigma_j \rangle = \sum_i \sigma_j P_N(\{\sigma\}_N; t)$ is obviously the expectation value of σ_j , $\langle ij \rangle \in j$ and $\langle jk \rangle \in j$ implies that the sum is over those bonds $\langle ij \rangle$ and $\langle jk \rangle$ which involve j as the terminal site.

2.2. Choice of transition probabilities

The energy required for the particle and electron hop in the lattice ω and sublattice Ω respectively, can be expressed using the Ising Hamiltonian [18]. Assuming no interaction between the particles, the Hamiltonian at site j can be formulated as

$$\mathcal{H}_j^\omega = - \sum_j h_j^\omega \left(\frac{1 + \sigma_j^\omega}{2} \right) \tag{5}$$

$$\mathcal{H}_j^\Omega = - \sum_j h_j^\Omega \left(\frac{\chi + \sigma_j^\Omega}{2\chi} \right) \tag{6}$$

where $h_j^\Omega = ne\phi_j$ and $h_j^\omega = z_j e\phi_j$, apart from an additive constant, ϕ_j is the electric potential at j , n being the number of electrons involved in the hopping, while $z_j e$ indicates the charge of the diffusing species at site j . These Hamiltonians are constructed in such a way that when a particle or electron resides on a site j the Hamiltonian exists, otherwise it vanishes. For example, when a particle is at site j in the ω lattice, the spin variable σ_j^ω takes a value of $+1$ and hence the Hamiltonian exists or else σ_j^ω becomes -1 and \mathcal{H}_j^ω will vanish. Similarly for the non-vanishing of the Hamiltonian at the Ω sublattice, σ_j^Ω should be $+\chi$.

Though equations (5) and (6) pertain to a non-interacting system, interactions can be effortlessly incorporated at the mean-field level so as to give the familiar nearest-neighbour Ising Hamiltonian [18]. Applying the condition of detailed balancing to the master equation we obtain

$$W_{ij}(\sigma_j \sigma_i \{\sigma\}_{ij}) P_N^e(\{\sigma\}_N; t) = W_{ij}(\sigma_i \sigma_j \{\sigma\}_{ij}) P_N^e(\{\sigma\}_N^{ij}; t) \tag{7}$$

$$W_{jk}(\sigma_k \sigma_j \{\sigma\}_{jk}) P_N^e(\{\sigma\}_N^{jk}; t) = W_{jk}(\sigma_j \sigma_k \{\sigma\}_{jk}) P_N^e(\{\sigma\}_N; t). \tag{8}$$

At equilibrium, the probability that the spin configurations $\{\sigma\}_N^{ij}$ and $\{\sigma\}_N^{jk}$ will interchange their configurations with respect to $\{\sigma\}_N$ is proportional to the Maxwell-Boltzmann factor $\exp(-\mathcal{H}/k_B T)$ namely,

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

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

$$P_N^e = \frac{\exp(-\mathcal{H}_{ij}/k_B T)}{Z} \tag{9}$$

where Z represents the partition function.

It is necessary at this stage to decipher the nature of physical displacement and electron hopping and some subtle differences that exist between the two. First, at lattice ω , the probability of physical displacement increases with the ‘blocking factor’ $(1 - \sigma^\omega)/2$, which means that as the probability of a site adjacent to the particle under consideration being empty increases, the probability of diffusion by the vacancy mechanism also increases. Similarly the rate of electron hopping increases if the probability of B occupying a site adjacent to A increases. Second, as discussed earlier, the physical motion of the molecules at the ω lattice is not free in that the redox molecules are bound to the underlying supramolecular structure. Due to this inherent restriction, the tendency of the particle to back track to the site just vacated by it is enhanced. Moreover, if a particle has just moved from site j to site i , site j is more likely to be unoccupied than any other site adjacent to i . Therefore, an attempt to return to site j is more likely to be successful because the field is not strong enough to restrict the backward motion as compared to the attempted movement to other sites (cf [19,20]). Thus the transition probability predicted in terms of spin variables and rate constants will be more than the observed transition rate. Hence a correlation factor f is needed to account for the retarded motion of the particle under consideration. We consider the correlation factor effect to be significant for the vacancy diffusion mechanism, although for a more accurate description the detailed dependence of the correlation factor on both processes needs to be investigated.

As mentioned earlier, the transition probabilities in equation (1) are dependent on the neighbouring spin values and on the electric field. These can be constructed from the spin variables and field-dependent particle jump frequencies $k_{ij}^P, k_{ji}^P, k_{kj}^P$ and k_{jk}^P and the electron hopping frequencies $k_{ij}^E, k_{ji}^E, k_{kj}^E$ and k_{jk}^E using the condition of detailed balancing. Taking into account the above factors, the transition probabilities satisfying detailed balancing are as follows:

$$W_{ij}^E(\sigma_i \sigma_j \{\sigma\}_{ij}) = k_{ji}^E \left(\frac{\chi - \sigma_i^\Omega}{2\chi} \right) \left(\frac{\chi + \sigma_j^\Omega}{2\chi} \right) + k_{ij}^E \left(\frac{\chi - \sigma_j^\Omega}{2\chi} \right) \left(\frac{\chi + \sigma_i^\Omega}{2\chi} \right) \quad (10)$$

$$W_{jk}^E(\sigma_j \sigma_k \{\sigma\}_{jk}) = k_{kj}^E \left(\frac{\chi - \sigma_j^\Omega}{2\chi} \right) \left(\frac{\chi + \sigma_k^\Omega}{2\chi} \right) + k_{jk}^E \left(\frac{\chi - \sigma_k^\Omega}{2\chi} \right) \left(\frac{\chi + \sigma_j^\Omega}{2\chi} \right) \quad (11)$$

$$W_{ij}^P(\sigma_i \sigma_j \{\sigma\}_{ij}) = k_{ij}^P \left(\frac{1 - \sigma_j^\omega}{2} \right) \left(\frac{\chi + \sigma_i^\omega}{2\chi} \right) + k_{ji}^P f \left(\frac{1 - \sigma_i^\omega}{2} \right) \left(\frac{\chi + \sigma_j^\omega}{2\chi} \right) \quad (12)$$

$$W_{jk}^P(\sigma_j \sigma_k \{\sigma\}_{jk}) = k_{jk}^P f \left(\frac{1 - \sigma_k^\omega}{2} \right) \left(\frac{\chi + \sigma_j^\omega}{2\chi} \right) + k_{kj}^P f \left(\frac{1 - \sigma_j^\omega}{2} \right) \left(\frac{\chi + \sigma_k^\omega}{2\chi} \right). \quad (13)$$

These are written in a manner analogous to the Ising Hamiltonian (6) whereby a particle or electron jumps from i to j or j to i depending on the value of the spin variables σ_i and σ_j in the appropriate lattice. For electron hopping to take place from site i to j in the Ω sublattice, A has to be present in site i and B at site j , i.e. $\sigma_i^\Omega = +\chi$ and $\sigma_j^\Omega = -\chi$ then $W_{ij}^E(\sigma_i \sigma_j \{\sigma\}_{ij}) = k_{ij}^E$. Similarly for the transfer of an electron from site j to i , $\sigma_i^\Omega = -\chi$ and $\sigma_j^\Omega = +\chi$ and hence $W_{ij}^E(\sigma_i \sigma_j \{\sigma\}_{ij}) = k_{ji}^E$. For particle A to hop from i to j , a vacant site should be present at site j , $\sigma_j^\omega = -1$ and $\sigma_i^\omega = +\chi$ then $W_{ij}^P(\sigma_i \sigma_j \{\sigma\}_{ij}) = k_{ij}^P f$. When both the electron hop and particle displacement are operative, equations (7) and (8) still hold for the detailed balance, with [21]

$$W_{ij}(\sigma_i \sigma_j \{\sigma\}_{ij}) = W_{ij}^E(\sigma_i \sigma_j \{\sigma\}_{ij}) + W_{ij}^P(\sigma_i \sigma_j \{\sigma\}_{ij}). \quad (14)$$

The choice of the transition probability W_{ij} in (10)–(13) is not entirely unique, and the

condition of detailed balancing essentially puts a minimal constraint on the general form of W_{ij} whereby rejection of a large number of functional forms for W_{ij} is made possible.

2.3. Phenomenological diffusion-migration equations

By imposing the condition of detailed balancing for W_{ij}^E and W_{jk}^E , we can write the ratio of electron jump frequencies using equations (7)–(13)

$$\frac{k_{ji}^E}{k_{ij}^E} = \exp[ne(\phi_i - \phi_j)/k_B T] \quad (15)$$

$$\frac{k_{kj}^E}{k_{jk}^E} = \exp[ne(\phi_j - \phi_k)/k_B T] \quad (16)$$

and analogously for physical displacement frequencies. This suggests

$$k_{ij}^E = k_0^E \exp(-\xi_1^E/k_B T) \quad (17)$$

$$k_{ji}^E = k_0^E \exp(-\xi_2^E/k_B T). \quad (18)$$

In order for equations (17) and (18) to satisfy equation (15) we further demand that

$$\xi_2^E - \xi_1^E = ne(\phi_j - \phi_i). \quad (19)$$

Equation (19) implies the following form for ξ_1^E and ξ_2^E :

$$\xi_1^E = \xi_0^E - \alpha' ne(\phi_j - \phi_i) \quad (20)$$

$$\xi_2^E = \xi_0^E + \alpha ne(\phi_j - \phi_i) \quad (21)$$

and $\alpha + \alpha' = 1$. Even in the absence of applied electrical potential the spin-exchange is possible due to ξ_0^E which is constant independent of potential but may depend upon polymer morphology, solvent effects, etc. The segmental motion of the polymer chains aided by the solvent dynamical effects are implicitly incorporated through ξ_0^E . Now the exchange rate constant becomes

$$k_{ji}^E = k_E \exp[-\alpha ne(\phi_j - \phi_i)/k_B T] \quad (22)$$

$$k_{ij}^E = k_E \exp[\alpha' ne(\phi_j - \phi_i)/k_B T]. \quad (23)$$

Similarly from equation (16) we obtain

$$k_{kj}^E = k_E \exp[\alpha ne(\phi_j - \phi_k)/k_B T] \quad (24)$$

$$k_{jk}^E = k_E \exp[-\alpha' ne(\phi_j - \phi_k)/k_B T] \quad (25)$$

where

$$k_E = k_0^E \exp(-\xi_0^E/k_B T). \quad (26)$$

It is easy to recall that equations (22)–(25) represent the potential dependence of electron hopping frequencies [22]. Analogously, we can write for the physical displacement process, equations similar to (22)–(25).

Using the above expressions for electron transfer and particle movement rates and substituting in the transition probability occurring in the GME (4) and invoking the definition of $\langle \sigma_\omega \rangle$ and $\langle \sigma_\Omega \rangle$, we derive a difference-differential equation. Converting it to the corresponding differential equation, we obtain the transport equation for C_A which is the fraction of sites occupied by A out of the total number of occupied sites ($= \chi_A/\chi_T$), namely

$$\frac{\partial C_A}{\partial t} = D_{\text{ap}} \left\{ \frac{\partial^2 C_A}{\partial x^2} + \frac{e}{D_{\text{ap}} k_B T} \frac{\partial}{\partial x} \left[C_A (D_{\text{ap}}^{nz} - n D_E \chi_T C_A) \frac{\partial \phi}{\partial x} \right] \right\} \quad (27)$$

where D_{ap} refers to the apparent diffusion coefficient,

$$D_{\text{ap}} = D_{\text{Phys}} f(1 - \chi_{\text{T}}) + D_{\text{E}} \chi_{\text{T}} \quad (28)$$

and

$$D_{\text{ap}}^{nz} = z_{\text{A}} D_{\text{ap}} + (n - z_{\text{A}}) D_{\text{E}} \chi_{\text{T}}. \quad (29)$$

D_{E} and D_{P} follows as

$$D_{\text{E}} = k_0^{\text{E}} \delta^2 \exp(-\xi_0^{\text{E}}/k_{\text{B}}T) \quad (30)$$

$$D_{\text{Phys}} = k_0^{\text{P}} \Delta x^2 \exp(-\xi_0^{\text{P}}/k_{\text{B}}T). \quad (31)$$

It is pertinent to note here that diverse dependences of mean-square displacement on time have been explicitly reported in the literature (cf diffusion-to-drift crossover). In competing diffusion processes such as the one analysed here, non-diffusive movement as well as percolation effects also need to be considered. However, since our objective in this investigation has been to unravel the microscopic origins of macroscopic transport equations the above improvisations have been ignored.

3. Perspectives

Equations (27)–(29) constitute the central results of the analysis. In hindsight, the structure of equation (28) is not entirely unanticipated, as the combined diffusion coefficient essentially represents the individual effects due to physical displacement and electron hopping taking account of the correlation factor f . As indicated earlier, the basis behind the introduction of f is to incorporate the correlated movement of the particle and it is customary to invoke the dependence of f on site occupancy in studies involving tracer diffusion [19]. The dependence of the diffusion coefficient D_{ap} on number density has been the topic of current investigations [23] in the study of charge transport through supramolecular assembly. For example, since the correlation factor f is a function of site occupancy, equation (28) predicts nonlinear variation of D_{ap} with respect to fractional occupancy χ_{T} in accordance with the Monte Carlo simulation of restricted diffusion (cf [24]). Further, juxtaposition of n and z_{A} occurring in equation (29) for D_{ap}^{nz} is quite non-trivial. If $n = z_{\text{A}} = 1$, $D_{\text{ap}}^{nz} = D_{\text{ap}}$ and equation (16) of [24] follows from (28).

As $\chi_{\text{T}} \rightarrow 1$ (which implies the absence of vacancies), physical diffusion cannot occur and D_{ap} is governed only by the electron hopping diffusion coefficient D_{E} given by (30). Analogously when $\chi_{\text{T}} \rightarrow 0$, electron hopping is negligible, because of the increased spatial separation between the redox moieties. Under this condition, equation (31) implies that the physical motion of the redox molecules is governed essentially by three parameters namely ξ_0^{P} , k_0^{P} and Δx^2 . ξ_0^{P} may be considered as arising from the conformational behaviour of the polymer†. The parameter k_0^{P} characterizes the jump frequency while the spatial restriction of a redox molecule away from its equilibrium position is taken into account through Δx .

The interesting solvent dependence of D_{E} (and D_{Phys}) arising from equations (30) and (31) should be noted. In particular, a major component of ξ_0^{E} is the solvent reorganization energy of Marcus, pertaining to electron transfer reactions [25] and has entered naturally

† Even though equation (27) has been derived assuming a one-dimensional lattice its extension to three-dimensional systems is straightforward. Since the electrode potential varies in one direction in chemically modified electrodes the expected alteration as far as higher dimensions is concerned will essentially be in concentration gradient terms. Thus we anticipate that terms such as ξ_0^{P} , will still exist in three-dimensional systems. The retarded motion arising from detailed structural changes in polymer morphology will require extensive study and is at present not considered.

from the structure of charge transfer rate constant *vis à vis* transition probabilities and could not have been foreseen except on empirical considerations. Furthermore Δx^2 and δ^2 of equations (30) and (31), respectively, may be modelled[†] as a function of number density for point molecules [26] even if k_0^E and k_0^P are constants for a given system and thus various types of concentration dependence of D_E and D_{Phys} critically analysed. In the analysis of charge transport through supramolecular structures nonlinear variation of the diffusion coefficient with number density involving percolation effects are noticed. This aspect is also amenable for investigations within this framework.

Even more interesting is the time-dependent diffusion-migration equation (27) when two different dynamical processes, namely conventional ‘bounded’ diffusion and electron hopping between redox centres, occur. When $\chi_T \rightarrow 0$, the second term of equation (27) vanishes and the classical Nernst–Planck equation [27], namely

$$\frac{\partial C_A}{\partial t} = D_{\text{Phys}} \left\{ \frac{\partial^2 C_A}{\partial x^2} + \frac{z_A e}{k_B T} \frac{\partial}{\partial x} \left[C_A \frac{\partial \phi}{\partial x} \right] \right\} \quad (32)$$

is obtained[‡] and $D_{\text{Phys}} = k_0^P \Delta x^2 \exp(-\xi_0^P/k_B T)$ since $f = 1$. Analogously, when $\chi_T \rightarrow 1$, there are no vacant sites (whereby the physical diffusion is absent) and hence equation (27) becomes

$$\frac{\partial C_A}{\partial t} = D_E \left\{ \frac{\partial^2 C_A}{\partial x^2} + \frac{ne}{k_B T} \frac{\partial}{\partial x} \left[C_A(1 - C_A) \frac{\partial \phi}{\partial x} \right] \right\} \quad (33)$$

where $D_E = k_0^E \delta^2 \exp(-\xi_0^E/k_B T)$. Equation (33) was first derived by Savéant [28] and its generalization to include interaction between particles has also been discussed [18]. Thus, equation (27) can be considered either as a generalization of the classical Nernst–Planck equation for diffusion of charged particles or of the transport equation for electron hopping between nearest-neighbour redox centres[§].

The methodology of deriving the combined diffusion coefficient D_{ap} for two competing transport phenomena, namely physical displacement and electron hopping, in itself can be accomplished by other approaches, such as the use of random walks [24], random flights [26], lattice gas models [29], etc. However, the chief merit of the KIM approach expounded here consists in the *simultaneous* determination of the diffusion-migration equation and the corresponding diffusion coefficient. For example, the availability of equation (28) by other procedures does not lead to the structure of the diffusion-migration equation *per se*. The latter aspect is especially important in experimental evaluation of the current by transient electrochemical techniques. However, solving equation (27) either analytically or by using numerical techniques is a profound exercise because of the spatially varying electric field. It should be mentioned here that even the solution of Nernst–Planck equation ((32) above) pertaining to diffusion of ions in membranes, is a non-trivial exercise (cf [30]).

For electric field driven *fluctuating* systems a transport equation of the form (27) does not suffice, because diffusion becomes anomalous. This issue becomes crucial especially if our objective is to analyse the dynamical behaviour of $\langle x^2(t) \rangle$ *vis à vis* D_{ap} . A vast amount of literature exists on this aspect (cf [31]). Our emphasis, however, is to indicate how the GME equation coupled with Ising Hamiltonian leads to a hierarchy of phenomenological transport equations which can be subsequently employed to analyse the ‘output’ of electrochemical

[†] By considering the transition probabilities W_{ij} to be random, it is possible to introduce $\langle \delta^2 \rangle$ and $\langle \Delta x^2 \rangle$, mean-square estimates of the hopping distance and physical displacement, respectively. We ignore this aspect here.

[‡] Recall that a Kramers–Moyal expansion of the continuum version of GME leads to the Fokker–Planck equation containing the potential energy of the system instead of the applied electric field.

[§] If we ignore the spatial variation of the electric potential ϕ , equation (32) is isomorphic with Burgers’ equation.

experiments. We reiterate here that other conventional global approaches based on chemical kinetic schemes, irreversible thermodynamics, electrolyte solution theory, etc are not directly amenable to model electron hopping and particle diffusion processes occurring simultaneously in an electric field. Hence the present methodology using KIM versions is especially attractive in so far as the mapping of phenomenological descriptions using microscopic basis is concerned.

It is interesting to enquire whether the above formalism can be studied using the spin 1 Ising model version with $\{\sigma\}$ values $+1$, -1 and 0 for A, B and vacancy. However, the formulation of transition probabilities and the subsequent substitution in the reduced GME becomes tedious. Nevertheless, the final algebraic structure of the diffusion-migration equation is not expected to alter since the physical description remains the same. Furthermore, one may ask whether the GME itself can be subjected to further analysis obviating the need to derive phenomenological transport equations. There exist two possibilities: the first is the evaluation of the mean-square displacement by Monte Carlo simulation (cf [32]) which leads to a microscopic dependence of the diffusion coefficient on system parameters. The second option consists in recognizing the nature of the hopping particle as an electron and thereby resorting to methodologies such as effective medium approximations [37] to evaluate the current in the time domain. Furthermore, the incorporation of distance-dependent electron transfer rates using the continuum version of equation (1) *vis á vis* transition probabilities, is feasible and will be discussed elsewhere.

Appendix A

In formulating the spatio-temporal diffusion-migration equation using KIM it is essential to decipher whether the electron hopping or particle motion takes place at adjacent sites i and j . Accordingly the transition probability has to incorporate necessary changes to account for the spin exchange. It should be noted here, that at any given instant of time, only one process, either electron hopping or physical motion, can take place between these two sites. There are two methodologies using which the final diffusion-migration equation can be arrived at. Firstly the spin exchange due to electron and particle hopping can be incorporated at the GME itself whereby the master equation is expressed with eight terms, four for electron hopping and four for physical 'bounded' displacement. Another method is to incorporate, the transition probabilities in general at first, and then splitting into two separate forms using the 'addition' property as used by Bellon and Martin in [21]. Both these methods do not violate the condition of detailed balancing and do not alter the final equation. In this paper we have resorted to the methodology of Bellon and Martin.

A few comments concerning the significance of the final equation (28) may be pointed out here: the limiting behaviours and their origin. First, when the electron hopping is set to zero i.e. $\chi_T \rightarrow 0$, the unoccupied adjacent site for hopping to occur will be far away. In this case, $D_{ap} = D_{Phys}f$, where f becomes a constant (since $\chi_T \rightarrow 0$) and hence the diffusion coefficient becomes a constant as shown by Kutner [34] provided Δx is constant. Second, when the occupancy is below the percolation threshold, for electron hopping to take place the molecules have to reach the 'encounter distance' i.e. the molecular separation has to be less than δ . However, for the case under consideration here, fractional occupancy is less than percolation threshold, hence the probability for the molecules to come within the encounter distance decreases. For this reason the time taken for electron hopping will be high and hence D_E is lowered. Thus the particle density is indirectly related to D_E .

Appendix B

In statistical models such as the one being analysed here, the notion of correlation factor enters quite explicitly. For example, if an electroactive species has exchanged its position with a vacant site, the probability of it returning to the vacant site is higher than the probability of any other jump. This implies that some of the jumps prove to be ineffective; hence the correlation factor is less than one. This intuitive picture has given rise to a whole set of rules to determine the correlation factor as a function of number density and lattice geometry in solid state physics [19].

The particle jump frequency that appears in equations (12) and (13) along with the correlation factor is the total rate at which the particle hops to the adjacent site (k_{ij}^T), which can be represented as,

$$k_{ij}^T = k_{ij}^P f \quad (\text{B1})$$

where k_{ij}^P is potential dependent and the correlation factor f is independent of potential. Hence, by writing k_{ij}^P and f instead of k_{ij}^T we have essentially separated potential-independent and -dependent terms. Now it should be noted that the total rate of particle jumps in a redox polymeric system is a function of both time and distance [23, 24]. The time dependence can be represented by

$$k_{ij}^T = \frac{1}{2\tau}. \quad (\text{B2})$$

Let us consider the distance travelled by the particle after n jumps which is

$$x = \sum_{m=1}^n x_m \quad (\text{B3})$$

where x_m is the displacement of the particle in the m th jump. The ensemble average of $\langle x^2 \rangle$ can be represented as

$$\langle x^2 \rangle = \sum_{m=1}^n \langle x_m^2 \rangle + 2 \sum_{p=1}^{n-1} \sum_{m=1}^{n-p} \langle x_{m+p} x_m \rangle. \quad (\text{B4})$$

Thus to satisfy equations (B1) and (B2) the following forms were suggested for k_{ij}^P and f ,

$$k_{ij}^P = \frac{\sum_{m=1}^n \langle x_m^2 \rangle}{2 \langle x^2 \rangle t} \quad (\text{B5})$$

and

$$f = \frac{\langle x^2 \rangle}{\sum_{m=1}^n \langle x_m^2 \rangle} \quad (\text{B6})$$

or using equation (B4),

$$f = 1 + \frac{2 \sum_{p=1}^{n-1} \sum_{m=1}^{n-p} \langle x_{m+p} x_m \rangle}{\sum_{m=1}^n \langle x_m^2 \rangle}. \quad (\text{B7})$$

Equation (B7) can also conveniently be written in its equivalent three-dimensional form by considering the vector displacement of the particle in its jump. However, such a step is unnecessary since the transport equation here is also derived only for the one-dimensional case. If after any one jump of a particle, say A, all possible directions for its next jump

were equally possible, then the factor f would be unity, because all the $\langle y_{m+p}y_m \rangle$ would be zero. The extent to which f departs from unity is a measure of the correlations between successive jumps of the particle i.e. $\langle y_{m+p}y_m \rangle$. The dimensionless factor, f is therefore known as the correlation factor and its value varies between 0 and 1. Correspondingly, k_{ij}^p would be the particle hopping rate constant if no account were taken of the occurrence of these correlations.

In the competing diffusion process under consideration here, a similar argument holds for electron exchange as well. A rigorous solution of the problem would then require either formulating a system of equations and some sort of 'closure' assumptions or probability distribution of transition rates, taking these correlations into account. Since this has not been carried out here, the derivation of macroscopic transport equation from the microscopic picture is in a sense 'unsatisfactory'.

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