

A molecular Debye-Hückel approach to the reorganization energy of electron transfer reactions in an electric cell

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Electron transfer near an electrode immersed in ionic fluids is studied using the linear response approximation, namely, mean value of the vertical energy gap can be used to evaluate the reorganization energy, and hence any linear response model that can treat Coulomb interactions successfully can be used for the reorganization energy calculation. Specifically, a molecular Debye-Hückel theory is used to calculate the reorganization energy of electron transfer reactions in an electric cell. Applications to electron transfer near an electrode in molten salts show that the reorganization energies from our molecular Debye-Hückel theory agree well with the results from MD simulations. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4896763>]

I. INTRODUCTION

Electron transfer (ET) reactions are ubiquitous in chemistry and biology.¹ In this report we address one of the fundamental issues of electron transfer reactions in electrochemistry where an electron transfer reaction happens at the interface between an electrode and an electrolyte solution.²⁻⁴ According to the Marcus theory,⁵⁻⁷ the reaction rate for a nonadiabatic ET is determined by three major parameters: the reorganization energy λ , which captures the ability of the dielectric environment to promote the reaction, the free energy difference ΔA for the reactant and product states as the thermodynamic driving force, and the coupling strength between the donor and the acceptor electronic states. In this report we will present a theoretical framework to accurately calculate the reorganization energy of an electron transfer reaction in an electric cell.

Almost fifty year ago, Marcus derived an analytical formula for the reorganization energy of an electron transfer reaction near an electrode in an electrolyte solution using the Debye-Hückel (DH) theory.⁸ However, this formula is rarely used to electron transfer reactions in an electric cell due to the well-known limitation of the DH theory at high coupling strength of ionic fluids. Motivated by recent simulation studies on the reorganization energy in an electric cell⁹⁻¹¹ and our work on the extension of the DH theory to ionic fluids with high coupling strength¹²⁻¹⁴ we developed a general theoretical formulation to calculate the reorganization energy of an ET reaction in an electric cell and successful comparisons with simulation results demonstrate the accuracy of derived reorganization energy formula.

In short, our extension of the DH theory to ionic fluids with an arbitrary coupling strength, called molecular Debye-Hückel (MDH) theory,¹²⁻¹⁴ is to express the mean potential of a tagged ion in an ionic fluid as a linear combination of multiple Debye modes $e^{-k_l r}/r$, $\{l = 1, 2, \dots\}$ where the effective Debye screening length k_l are the roots of the dielectric function of the ionic fluids, which can be obtained either ex-

perimentally or theoretically. The traditional DH theory is just the single mode limit of our formulation with the conventional Debye screening length k_D , which is valid only for low coupling strength situations, namely, $k_D \rightarrow 0$. Using the traditional DH theory Marcus showed that the reorganization energy near an electrode is $\lambda = \frac{e^2}{2} \left\{ \frac{k_D}{1+k_D a} + \frac{1}{R} \frac{e^{-k_D(R-a)}}{1+k_D a} - \frac{1}{R} \right\}$ for $k_D \rightarrow 0$, where a is the radius of the spherical donor/acceptor and R is the distance of the reactant to the electrode. Our theory yields $\lambda = \frac{e^2}{2} \sum_l C_l \left\{ \frac{k_l}{1+k_l a} + \frac{1}{R} \frac{e^{-k_l(R-a)}}{1+k_l a} - \frac{1}{R} \right\}$, where $\{C_l, k_l\}$ can be determined from the dielectric function of the ionic fluid. Hence, our theoretical formulation leads to a simple extension of the Marcus result and is valid for any ionic fluid in an electric cell. Furthermore, as our formulation is based the linearized Poisson-Boltzmann equation extension to donor/acceptor with arbitrary molecular shape is straightforward.

This study provides a bridge between one of the crucial quantities, the reorganization energy, in electron transfer reactions and the dielectric properties of the ionic fluid in an electric cell, which are experimentally accessible. As such a connection does not rely on the detailed molecular model of the electric cell, thus our study presents a useful tool that can relate one type of experimental measurements such as current-voltage relation to another type of experimental properties, the dielectric function of the ionic fluid and capacitance of an electric cell.

II. A MICROSCOPIC MODEL OF AN ELECTRON TRANSFER PROCESS NEAR AN ELECTRODE

In order to show how the reorganization energy of an ET reaction between an electrode and a solute in ionic fluids can be obtained from our molecular Debye-Hückel theory,¹³ theoretical development of the Marcus free energy profiles from the linear response theory will be presented. As electron transfer processes in an electric cell occur near an electrode under a constant potential and recent molecular simulations⁹ of such a

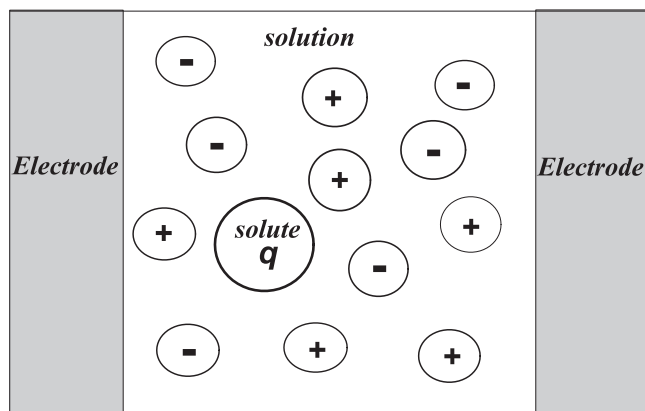


FIG. 1. A schematic diagram for ET at an electrode immersed in an ionic fluid. The particle labelled as *solute* represents an electron donor or acceptor.

process were performed under a constant potential condition, our theoretical formulation will be presented in a manner that is consistent with the constant potential condition. The starting point of our theoretical formulation is a molecular model of an ionic fluid, a solute and an infinitely long electrode under the donor-accepter picture.¹⁵

Consider a model electric cell that consists of an ionic fluid confined between two parallel electrodes which are separated by a distance L and are held at a constant potential. As shown in Fig. 1, we have two types of particles in the system, namely, solvent particles and a solute particle, which acts as the donor of the electron transfer reaction. Using cartesian coordinate $\mathbf{r} = (x, y, z)$, the electrode plane is defined as the x - y plane, and thus z -axis is perpendicular to the electrode plane. Denote the distance between the solute and the left electrode by z_0 , and the charge of the j th particle of the solvent as q_j . For such a reaction, we assume that the solute o has a charge q_R in the reactant state and a charge $q_P = q_R + \Delta q$ in the product state. The i th and j th particles interact via a pairwise additive potential,

$$u_{ij}(r_{ij}) = \frac{q_i q_j}{r_{ij}} + u_{ij}^s(r_{ij}), \quad (1)$$

where u_{ij}^s is a short ranged interaction, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between two particles. For a particular configuration of solvent particles denoted by $\mathbf{R}^N = \{\mathbf{r}_i, i = 1, 2, \dots, N\}$, the total energy for the system in state M ($M = R$ for the reactant state and $M = P$ for the product state) is

$$E_t(\mathbf{R}^N, M) = \frac{1}{2} \sum_{i,j=s} u_{ij}(r_{ij}) + \sum_{j=s} u_{jo}^s(r_{jo}) + \sum_{i=s} q_i \phi_w(\mathbf{r}_i) + q_M \Phi_o(\mathbf{R}^N), \quad (2)$$

where the subscript s and o denote the solvent and solute species, respectively. The induced potential Φ_o at the center of the solute o is defined as

$$\Phi_o(\mathbf{R}^N) \equiv \sum_{j=s} \frac{q_j}{r_{jo}} + \phi_w(\mathbf{r}_o), \quad (3)$$

where $\phi_w(\mathbf{r})$ is the potential at position \mathbf{r} due to the presence of the electrodes with a constant potential. Using the Hamil-

tonian described above, one can study the rate of an ET reaction, where a solute will transfer charge Δq to an electrode. The electric potential in the electrode walls is fixed as a constant to simulate the constant potential setup in experiments and simulations.

If the image effect from the electrodes is accounted for, our theoretical formulation can mimic the molecular simulation situation⁹ and captures how the presence of electrodes would affect the energetics of ET. Within our molecular model, an ET event could be characterized by two states, namely, an initial state A and a final state B.

For the initial state A, the solute particle and the electrodes are in their reactant state, and the total energy of the system is

$$H_A = E_t(\mathbf{R}^N, R). \quad (4)$$

For the final state B, the solute particle and the electrodes are in their product state. In molecular simulations the experimental constant potential condition is realized by adjusting the charges of wall particles adiabatically so that all the electrode particles have a fixed potential.⁹ The total energy of the system then reads

$$H_B = E_t(\mathbf{R}^N, P). \quad (5)$$

The energy difference between state A and state B reads

$$\Delta E = H_B - H_A = \Delta q \Phi_o(\mathbf{R}^N) = \Delta q \left(\sum_{j=s} \frac{q_j}{r_{jo}} + \phi_w(\mathbf{r}_o) \right), \quad (6)$$

which can be used as a reaction coordinate just as in the electron transfer reactions in homogeneous fluids.¹⁶

According to the Marcus' picture, the reorganization energy is related to the nuclear motion of the solvent. In the current model, the wall-solute interaction should not affect the reorganization energy when the solute is fixed at a particular position, thus we use

$$X(\mathbf{R}^N) = \Delta q \sum_{j=s} \frac{q_j}{r_{jo}}, \quad (7)$$

the vertical energy gap due to solvent-solute interactions as our reaction coordinate. As one can see, this reaction coordinate X characterizes the solvent effect, which will be zero when the solvent particles are absent. It should be emphasized that even the electrodes do not appear explicitly in the reaction coordinate, but do affect the reorganization energy implicitly by influencing the fluctuations of solvent particles since $\phi_w(\mathbf{r})$ is a nonlinear function of the particle positions due to the image effect of the electrodes.

As noted by Marcus, ET in an electric cell is a thermo-activated process governed by the Frank-Condon (FC) principle, namely, ET happens only if the solvent configurations are such that total energy of the system in the reactant and product state are the same. Using Eq. (6), the transition state is then defined as

$$X(\mathbf{R}^N) = -\delta E_o, \quad (8)$$

where $\delta E_o = \Delta q \phi_w(\mathbf{r}_o)$ is the energy cost for the electron transfer in the absence of a solvent.

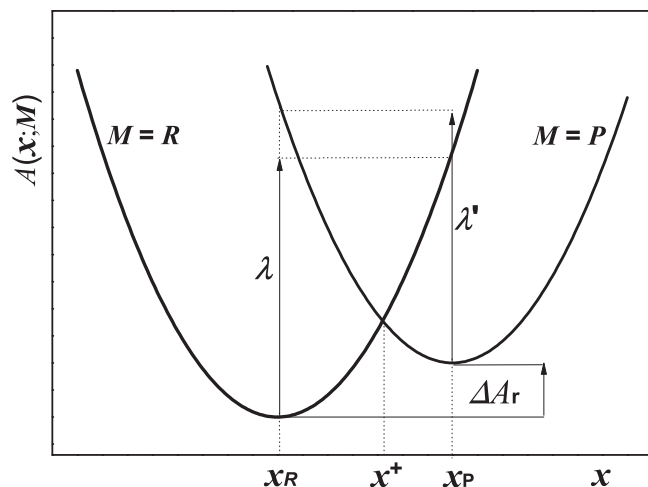


FIG. 2. Schematic free energy curves $A(x; M)$ for a reactant ($M = R$) and a product ($M = P$).

If $p(x; M)$ is defined as the probability distribution function of the reaction coordinate X equal to x in the system with solute charge q_M , then according to the transition rate theory, the reaction rate is proportional to the probability being at the transition state,^{6,15,18}

$$k_{et} = \kappa p(-\delta E_o; R), \quad (9)$$

where $\kappa = 2\pi\gamma^2/\hbar$ for the nonadiabatic case, and γ is the electronic coupling matrix element between the reactant and product state. Therefore the ET rate can be reduced to evaluate the probability distribution of the reaction coordinate X .

In general, the distribution function $p(x; M)$ could be used to construct the free energy curve for the reactant state and product state as shown in Fig. 2, where the intersect point x^+ of two free energy curves defines the transition state. When the linear response approximation or the Gaussian distribution approximation of the reaction coordinate X is used, it is further noted that the reorganization energy could be evaluated from the average information^{14,17-19} as

$$\lambda = \frac{x_R - x_P}{2}, \quad (10)$$

and the free energy difference could be evaluated via

$$\Delta A_r = \delta E_o + \frac{x_R + x_P}{2}, \quad (11)$$

where x_M is the average of X in state M . Furthermore the activation energy for the forward reaction can be evaluated in terms of λ and ΔA_r as

$$\Delta A = A(x^+; R) - A(x_R; R) = \frac{(\lambda + \Delta A_r)^2}{4\lambda}, \quad (12)$$

where $x^+ = \delta E_o$ is used. Using the relationship between λ , A and the probability distribution $p(x; M)$, the reaction rate constant defined by Eq. (9) could be evaluated in a straightforward manner

$$k_{et} = \frac{\kappa}{\sqrt{4\pi\lambda/\beta}} e^{-\beta\Delta A} = \frac{\kappa}{\sqrt{4\pi\lambda/\beta}} e^{-\frac{\beta(\lambda + \Delta A_r)^2}{4\lambda}}, \quad (13)$$

which is the conventional Marcus reaction rate expression.^{5,6} These relations have been used to study homogeneous

electron transfer reactions using molecular simulations extensively^{17,18,20,21} and electron transfer reactions in electrical cells.^{9,11,19}

As the probability distribution of X depends on the presence of the electrodes due to image effect implicitly, the reorganization energy evaluation is reduced to evaluate the mean value of x_M or equivalently the electric potential Φ_o at the solute in the presence of the electrodes.

III. MDH APPROACH TO THE REORGANIZATION ENERGY IN AN ELECTRIC CELL

According to Eq. (10), any theory that provides accurate radial distribution functions of an ionic fluid could be used to calculate the reorganization energy of an ET reaction, such as the dressed ion theory^{22,23} and our MDH theory.¹³

The starting point of MDH formulation is the exact Poisson equation in the presence of electrodes with a fixed potential since the external circuit can adjust the potential on the electrode adiabatically in response to the electron transfer near an electrode. Consider a solute o immersed in an ionic fluid between two electrodes, where n_i and q_i are the particle number density and the charge of the i th solvent species, respectively. $x_i = n_i/\sum_i n_i$ is the molar fraction of the i th species. The mean potential $\phi_o(\mathbf{r})$ around the solute o in an ionic fluid satisfies the Poisson equation²⁴

$$\nabla^2 \phi_o(\mathbf{r}) = -\frac{4\pi}{\epsilon_s} [\rho_o^b(\mathbf{r}) + \rho_o^{ind}(\mathbf{r})], \quad (14)$$

where ϵ_s is the dielectric constant in a primitive model level of description of the ionic fluid, $\rho_o^b(\mathbf{r})$ is the bare charge density of the solute, $\rho_o^{ind}(\mathbf{r}) = \sum_j n_j q_j h_{oj}(\mathbf{r})$ is the induced charge density around the solute, with $h_{ij}(\mathbf{r}) = g_{ij}(r) - 1$ the correlation function between i and j species. The fixed potential at the electrodes is treated as a boundary condition of the Poisson equation. The following formulation of the MDH theory is presented with the understanding that the Poisson equation is solved with such a boundary condition, hence the image effect of the electrodes is accounted for.

Suppose that a molecule surface S separates the solute from the solvent, the excluded volume of the solute is Ω_1 and the volume occupied by the solvent is Ω_2 . From the general formulation of the MDH theory, a continuum approach is used to reformulate the Poisson equation.¹³ For simplicity, only the main equations in the MDH theory will be presented in the electric cell situation as the derivation of these results parallels with the derivation in homogeneous ionic fluids.^{13,14} The mean potential is split into a linear combination of Debye modes such that

$$\phi_o(\mathbf{r}) = \sum_l C_l \phi_{ol}(\mathbf{r}), \quad (15)$$

where $\phi_{ol}(\mathbf{r})$ is a Debye mode with parameter k_l defined via

$$\nabla^2 \phi_{ol}(\mathbf{r}) = -\frac{4\pi}{\epsilon_s} \rho_o^b(\mathbf{r}), \quad \mathbf{r} \in \Omega_1, \quad (16)$$

$$\nabla^2 \phi_{ol}(\mathbf{r}) = k_l^2 \phi_{ol}(\mathbf{r}), \quad \mathbf{r} \in \Omega_2.$$

Equation (15) as well as Eq. (16) is a reformulation of Eq. (14), which are the main results of MDH theory in an

electric cell. In this formulation, the solute and the solvent are treated differently, i.e., *the solvent is approximated by a continuum characterized by a set of DH-like modes with Debye parameters $\{k_l\}$ and $\{C_l\}$ which are obtained from the dielectric response function of the solvent, while the solute is treated as a hard object with a suitable molecular shape and charge distribution.* In the current primitive model formulation of Eq. (16), the dielectric constant inside the solute takes the same value as in the solvent, namely, the solvent and solute have the same dielectric constant ϵ_s .

In general, C_l depends on the solute shape and charge distribution. For a primitive model of an ionic fluid, C_l for solvent particles are approximately the same for a given l , i.e., $C_l \approx C_l^s$ for cations and anions¹³ and at the same time both $\{k_l\}$ and $\{C_l^s\}$ could be determined given the dielectric function $\epsilon_l(k)$ of the bulk system.¹³ When the solute size as well as solute charge is not very different from that of the solvent particles, it is noted that $C_l \simeq C_l^s$ is a good approximation for a solute ion. Furthermore, since the dielectric function of the ionic fluid in an electric cell is very similar to the bulk one due to the strong screening as least for the cases studied in the paper, hence the $\{k_l\}$ and $\{C_l\}$ are determined in the same way as presented before.^{13,14}

Therefore, for a solute in an electric cell, the induced mean potential at the center \mathbf{r}_0 of a solute with bare charge q due to the presence of an ionic fluid is

$$\phi_q \equiv \phi_o(\mathbf{r}) - \phi_w(\mathbf{r}_o), \quad (17)$$

and then we have $x_M = q_M \phi_q$, which can be used to evaluate the reorganization energy according to Eq. (10).

In Sec. IV, we will show that our MDH approach leads to accurate reorganization energies when compared with simulation results, while the conventional DH theory breaks down.

IV. APPLICATIONS TO ET NEAR AN ELECTRODE IN MOLTEN SALT SYSTEMS

Consider a molten salt system studied by Madden and co-workers,⁹ which is a mixture of 85% MCl and 15% MCl₂ at temperature $T = 1300$ K, with total particle number density $n_0 \simeq 0.028/\text{\AA}^3$. In this case the conventional inverse Debye length is $k_D \simeq 7.38 \text{\AA}^{-1}$. Molecule dynamics simulations are performed for a homogeneous molten salt system using DL-POLY program²⁵ with the same potential and thermodynamic state as in Ref. 9, and then the pair distribution functions are collected to calculate the dielectric function $\epsilon_l(k)$, which is the input of our MDH theory. The response function $\chi(k) \equiv 1 - \epsilon_s/\epsilon_l(k)$ is fitted to an empirical function,

$$\chi(k) = \frac{a_0 k^2}{k^4 + (a_1 k^2 - a_2) \cos(bk) + a_3 k \sin(bk) + a_2}, \quad (18)$$

with restriction $\chi(0) = 1$ which is equivalent to the perfect screen condition of ionic fluids.²⁶ After the fitting, we could easily find the Debye parameters k_l by solving $\epsilon_l(k = ik_l) = 0$, from which several pairs of k_l can be obtained numerically. As noted in our previous studies,^{13,14} generally the first few (typically 2 or 4) Debye modes are capable of describing the thermodynamics. In this case, the first four Debye parameters are $k_{1,2} = 0.166 \pm 1.680i$, $k_{3,4}$

$= 0.782 \pm 3.604i$. From the Barker-Henderson perturbation theory²⁷ applied to the short ranged interaction of solvent particles, effective hard sphere diameters for those ions are $\sigma_{\text{Cl}^-} = 3.38 \text{\AA}$, $\sigma_{\text{M}^+} = \sigma_{\text{M}^{2+}} = 2.56 \text{\AA}$. Furthermore the molten salt system is mapped to a restrictive primitive model with the same packing fraction, for which the effective size is $\sigma_A = 3.05 \text{\AA}$ to simplify the C_l evaluations. Using the procedure from MDH theory, the first four coefficients for the solvent are found to be $C_{1,2}^s = -0.995 \mp 1.227i$, $C_{3,4}^s = 1.495 \mp 0.684i$, which leads to an excess Coulomb energy $\beta u_{ele}^{ex} = -\frac{\beta \sum_i x_i q_i^2}{2\epsilon_0} \sum_{l=1}^4 \frac{C_l^s k_l}{1+k_l \sigma_A} = -40.2$, that could be compared with the MD results $\beta u_{ele}^{ex} = -43.5$. These $\{C_l\}$ and $\{k_l\}$ are used as the input of MDH approach.

A. MDH approach to the electric double layer structure near an electrode

The electric double layer (EDL) structure is an important property of the electrode-solution system. As a first step of our MDH approach to the properties of an electric cell, the EDL structure near an electrode is studied. In literature, the EDL structure is studied under two kinds of boundary conditions, namely, a constant potential or a constant charge density on the electrode.

From our previous studies^{13,14} we have shown that the MDH input parameter k_l only depends on the electric function of the pure solvent and the C_l dependence on the solute is weak if the solute size is not too different from the solvent size, thus $\{k_l, C_l\}$ can be obtained from pure solvent dielectric function. For the EDL problem, this strategy is not applicable due to the size asymmetry as the electrode can be viewed as an extremely large sphere. On the other hand, if only two Debye modes are used in the EDL structure calculations the two boundary conditions are related to each other as shown in detail in Appendix A. The boundary conditions can lead to a reasonably well description of the EDL structure near an electrode as long as we know the potential given the charge density or vice versa.

The first system is a mixture of MCl and MCl₂ as studied by Madden's group with molecule dynamics (MD) simulations⁹ and is described in the first paragraph of Sec. IV. According to their simulations, the charge density is about $\frac{\sigma_0}{\epsilon_s} = 2.62 \text{ V/\AA}$ for a potential $V_0 = 5.45$ V estimated from the initial slope of Fig. 2 in Ref. 9. With an effective excluded size $d = 2.50 \text{\AA}$ of the wall and the first two Debye parameters $k_{1,2} = 0.166 \pm 1.680i$, one can find that $C_{1,2} = 0.5 \mp 0.406i$, and then the electric potential could be evaluated in a straightforward manner. As shown in Fig. 3, our MDH theory leads to an electric potential profile which is in good agreement with MD results, where the oscillatory behavior of the electric potential is well reproduced, while the conventional DH theory leads to a potential which decays monotonically and is qualitatively wrong.

The second system is an ionic fluid studied by Lamperki and Klos using Monte Carlo simulations.²⁸ The system is a 1:1 restricted primitive model of electrolyte solution with an ionic diameter $a = 4 \text{\AA}$, packing fraction $\eta = 0.35$, and relative dielectric constant $\epsilon_r = 10$ at $T = 1500$ K.

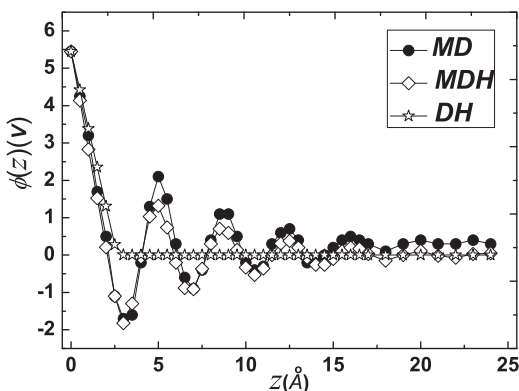


FIG. 3. Electric potential profiles $\phi(z)$ near an electrode with potential $V_E = 5.45$ V, from MD simulations (circle) (from Fig. 2 in Ref. 9), from our MDH approach (diamond) and from DH approach (star). The lines are guides to the eye.

We use hyper-netted-Chain (HNC) integral equations to compute the pair distribution functions of the pure solvent system, which could be further used to compute the dielectric function $\epsilon_l(k)$, from which the parameters of the first two Debye modes for the pure solvent are $k_{1,2} = 0.340 \pm 0.879i$ and $C_{1,2}^s = 0.5 \mp 0.526i$. For the wall-fluid system, the excluded length of the hard wall is $d = a/2$, and the charge density σ of the wall is kept as constant. In this case, the contact value V_E of the electric potential at the wall from Monte Carlo simulations is used to evaluate $C_{1,2}$ at a given charge density, from which we have $C_{1,2} = 0.5 \mp 0.603i, 0.5 \mp 0.562i, 0.5 \mp 0.450i$ for the charge density $\sigma = 0.025, 0.15, 0.4$ C/m² respectively. As shown in Fig. 4, our MDH theory again could reproduce the simulation results reasonably well.

B. MDH approach to the reorganization energy

As the electric potential satisfies the superposition principle, the potential V_E in the electrode will not affect the induced potential contributed from the solvent particles, so the quantity $x_R - x_P$ is independent of the potential in the electrode, and hence could be evaluated for a system with zero potential in the electrode.

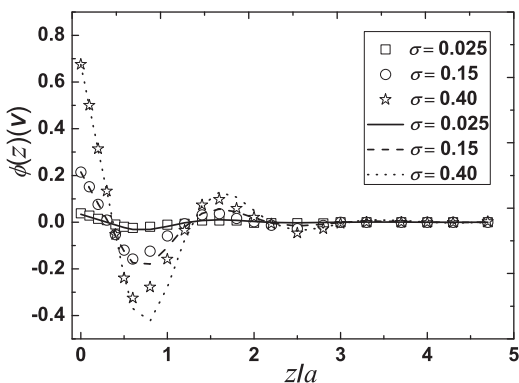


FIG. 4. Electric potential profiles $\phi(z)$ near an electrode with charge density $\sigma = 0.025, 0.15, 0.4$ C/m² from Monte Carlo simulations (from Fig. 6 in Ref. 28) (symbol), and from our MDH theory (line).

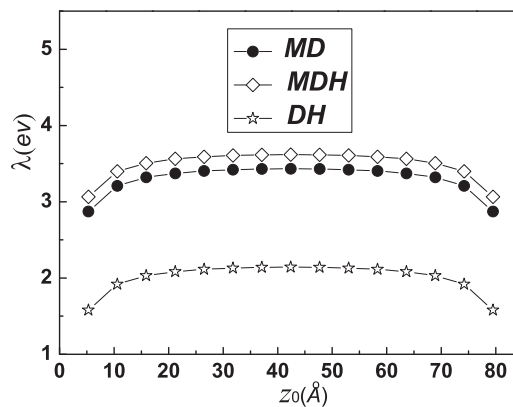


FIG. 5. Dependence of reorganization energy λ on the ion-electrode distance z_0 , from MD simulation experiments (circle) where the reorganization energy is recalculated via $\lambda = \frac{x_R - x_P}{2}$ and $x_M = \Delta q(\phi_q - \phi_w)$ with $\phi_q (q = 1, 2)$ depicted from Fig. 11 in Ref. 9, our MDH approximation (diamond), and DH theory (star). The lines are guides to the eye.

The free energy contribution from Coulomb interactions could be modeled as an electrostatic problem. As illustrated in Fig. 7, the system is separated into three regions. Region I (denoted by $\Omega_{1,4}$) is the exclude volume of the electrode atoms, and region II (denoted by Ω_2) is the solvent continuum described by multiple-Debye modes, while region III (denoted by Ω_3) is the exclude volume of the solute. From our MDH approach, the electric potential could be found by solving the linearized Poisson-Boltzmann equation with suitable boundary conditions. Applying the boundary condition leads to a set of linear equations, which generally needs to be solved numerically. As shown in Appendixes A and B, an analytical solution of this problem could also be found given if the excluded volume of the electrodes and that of the solute have no overlap. The reorganization energy can be evaluated from the MDH theory with 4 Debye modes when the coefficients $\{C_l\}$ are approximated by $\{C_l^s\}$ of the bulk system. The reorganization energy λ for ET in the molten salt system of MCl and MCl₂ as a function of the solute position z_0 is shown in Fig. 5. The reorganization energy is calculated via $\lambda = \frac{x_R - x_P}{2}$, with $x_M = \Delta q(\phi_q - \phi_w)$, and ϕ_w is calculated from the image charge method²⁹ as shown in Eq. (B12). To test the validity of our approach, the MD simulation data from Madden's group had been used for comparison, i.e., the average potential $\phi_q (q = 1, 2)$ presented in Fig. 11 of Ref. 9 is used to recalculate the reorganization energy.³⁰ ϕ_q from our MDH theory as well as the conventional DH theory is also used for the calculation. As one can see, the reorganization energy λ has a distinct dependence on the position z_0 of the solute ion inside the electric cell. Our MDH theory leads to reorganization energy which is in good agreement with MD simulations, where the average difference is smaller than 7%. The reorganization energy calculated from DH theory is also presented, which underestimates the reorganization energy by about 40%, and hence is not suitable for the rate calculation of ET processes in an electric cell.

It would be of interest to understand the nonlinear dependence of the reorganization energy λ on the solute position z_0 . As one can see, such kind of dependence is related to the

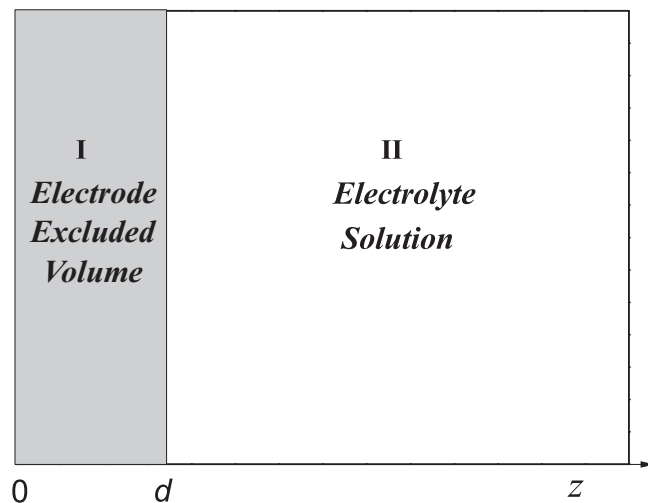


FIG. 6. A schematic interface diagram between an electrode and an electrolyte solution. Due to the finite size of the particles in the electrode and the electrolyte solution an excluded region $0 < z < d$ always exists in the interfacial region. The fixed potential or charge density of an electrode is the values at $z = 0$. It is assumed that the excluded region and the electrolyte solution have the same dielectric constant ϵ_s if a primitive model of the electrolyte solution is adopted.

electrostatic response of the solvent particles and the image effect of the electrodes. For the molten salt system which has very strong electrostatic screening, ϕ_q would converge to its bulk value even if the solute is not too far away from the electrodes, and hence is almost a constant through the cell, which had been verified from MD simulations⁹ and from our MDH calculation. However, ϕ_w comes from the image effect of the electrodes, which has a much pronounced dependence on the solute position z_0 . Hence the dependence of reorganization energy on z_0 would be very similar to that of the electrode-solute interaction energy on z_0 , which could explain the non-linear behavior of λ . As one can imagine, such kind of dependence should be universal for strong coupling system such as molten salts, room temperature ionic liquids or even in polar fluids with large dielectric constant.

V. CONCLUDING REMARKS

In conclusion, a general and accurate theoretical estimate of the reorganization energy of an ET near an electrode is presented using the recent developed MDH approach. Applications to ET near an electrode in molten salts show that our theory could reproduce the reorganization energy from MD simulations reasonably well. The major factor that impacts the accuracy of our theoretical estimate of the reorganization energy is the accuracy of the C_l coefficients. Currently, some methodologies to improve the calculations of C_l are under way.

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APPENDIX A: ELECTRIC DOUBLE LAYER STRUCTURE NEAR AN ELECTRODE

Consider an electrode immersed in an ionic fluid as shown in Fig. 6, when the surface charge density of the electrode is fixed at σ_0 , MDH theory¹³ suggests that the potential near the electrode could be written as a linear combination of Debye modes:

$$\phi(z) = \sum_l C_l \phi_l(z). \quad (\text{A1})$$

For each Debye mode there is a corresponding linearized Poisson-Boltzmann equation:

$$\begin{aligned} \frac{d^2}{dz^2} \phi_l(z) &= 0, \quad 0 < z < d, \\ \frac{d^2}{dz^2} \phi_l(z) &= k_l^2 \phi_l(z), \quad d < z. \end{aligned} \quad (\text{A2})$$

In general, C_l will be a function of the charge density.

At equilibrium, an electrode will have a unique electric potential V_0 for a given charge density σ_0 , and vice versa. Solutions for the above linearized Poisson-Boltzmann equation with a fixed charge density σ_0 can be found to be

$$\begin{aligned} \phi(z) &= V_0 - \frac{\sigma_0}{\epsilon_s} z, \quad 0 < z < d, \\ \phi(z) &= \sum_l C_l \phi_l(z) = \frac{\sigma_0}{\epsilon_s} \sum_l \frac{C_l}{k_l} e^{-k_l(z-d)}, \quad d < z. \end{aligned} \quad (\text{A3})$$

Continuous conditions for the electric potential and the electric field at $z = d$ lead to

$$V_0 = \frac{\sigma_0}{\epsilon_s} \left(\sum_l \frac{C_l}{k_l} + d \right) \quad \text{and} \quad \sum_l C_l = 1, \quad (\text{A4})$$

which relates the potential and the charge density.

When an electric potential V_0 rather than a charge density σ_0 is fixed, one can introduce a set of renormalized linear coefficient \tilde{C}_l so that the relationship Eq. (A4) between the potential and the charge density is fulfilled

$$\begin{aligned} \phi(z) &= V_0 - \frac{\sigma_0}{\epsilon_s} z, \quad 0 < z < d, \\ \phi(z) &= \sum_l \tilde{C}_l \phi_l(z) = V_0 \sum_l \frac{\tilde{C}_l}{1 + k_l d} e^{-k_l(z-d)}, \quad d < z, \end{aligned} \quad (\text{A5})$$

where $\tilde{C}_l = C_l(\frac{1}{k_l} + d) / \sum_l C_l(\frac{1}{k_l} + d)$ is a weighted average of C_l if the normalization condition $\sum_l C_l = 1$ is used.

When two Debye modes are used, there is a unique solution for C_1 and C_2 if the capacitance ($C = V_0/\sigma_0$) of the interface is known. If four modes are considered, we suggest a half-empirical method to evaluate C_l , namely, we assume that the ratios $\gamma_{31} = \frac{C_3}{C_1}$ and $\gamma_{42} = \frac{C_4}{C_2}$ are insensitive to the solute size and charge, and hence γ_{31} and γ_{42} for the solvent species

evaluated from our MDH theory could be used as constraints for the electrode problem, and then one can solve Eq. (A4) to find $C_{1,2,3,4}$ given the capacitance is known.

APPENDIX B: SOLVATION ENERGY OF AN ION IN AN IONIC FLUID BETWEEN TWO ELECTRODES

Consider the electrostatic problem for an ion immersed in an ionic fluid between two parallel electrodes. In general an ionic fluid could be described as a mixture of polar species and ionic species. Since the purpose of this section is to study solvation in an ionic fluid, a primitive model of an ionic fluid is adopted, namely, the polar species dielectric response is characterized by a dielectric constant ϵ_1 and the screening effect of ionic species is captured by a Debye screening length κ_D as in the conventional Debye-Hückel theory.

In order to find the potential at the center of the solute ion, a similar strategy as in Ref. 31 for the linearized Poisson-Boltzmann equation will be used. Due to the excluded volume effect, the space for $z > 0$ will be divided into four subspaces. As shown in Fig. 7, the solute ion is treated as a hard sphere with radius a and has a charge q at the center. The electrodes also have an excluded region characterized by a width d to account for the molecular sizes of the electrode particles and the solvent particles. If the distance between two electrodes is L , the electric potentials are given by the following linearized Poisson-Boltzmann equations:

$$\begin{aligned} \nabla^2 \phi_i(\mathbf{r}) &= 0, & \mathbf{r} \in \Omega_i (i = 1, 4), \\ \nabla^2 \phi_2(\mathbf{r}) &= \kappa_D^2 \phi_2(\mathbf{r}), & \mathbf{r} \in \Omega_2, \\ \nabla^2 \phi_3(\mathbf{r}) &= -\frac{4\pi}{\epsilon_0} q \delta(\mathbf{r} - \mathbf{r}_0), & \mathbf{r} \in \Omega_3, \end{aligned} \quad (\text{B1})$$

ϵ_0 is the dielectric constant for the solute ion and the electrode excluded volumes, while ϵ_1 is the dielectric constant of the solvent background for the ionic fluid, hence one can define a relative dielectric constant $\epsilon_r = \epsilon_1/\epsilon_0$. Due to the cylindrical symmetry of the system, two coordinates (ρ, z) are used to describe the potential. It would be useful to introduce a local polar coordinate (r_2, θ) via $r_2 = \sqrt{\rho^2 + (z - z_0)^2}$ and $x = \cos \theta = (z - z_0)/r_2$ relative to the center of the solute ion.

For the case where $a + d < z_0 < L - d - a$ such that the ion has no overlap with either electrode, the general solution for the above system reads

$$\begin{aligned} \phi_1(\mathbf{r}) &= \int_0^\infty [g_1(k)e^{-kz} + h_1(k)e^{k(z-d)}]J_0(k\rho)dk, \\ \phi_2(\mathbf{r}) &= \sum_{n=0}^\infty B_n k_n(\kappa_D r_2) P_n(\cos \theta) \\ &\quad + \int_0^\infty [f_1(k)e^{-\gamma(k)(z-d)} + f_2(k)e^{\gamma(k)(z-L+d)}]J_0(k\rho)dk, \quad (\text{B2}) \\ \phi_3(\mathbf{r}) &= \frac{q}{\epsilon_0 r_2} + \sum_{n=0}^\infty A_n r_2^n P_n(\cos \theta), \\ \phi_4(\mathbf{r}) &= \int_0^\infty [g_2(k)e^{-k(z-L+d)} + h_2(k)e^{k(z-L)}]J_0(k\rho)dk, \end{aligned}$$

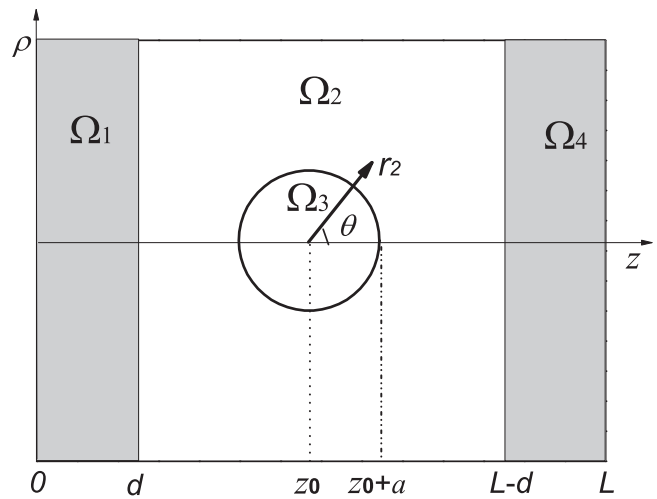


FIG. 7. A schematic diagram for the model of an ion in an electric cell treated as an electrostatic problem.

with $\gamma(k) = \sqrt{\kappa_D^2 + k^2}$. $J_n(x)$ is the n th Bessel function, $k_n(x)$ is the n th modified Bessel function of the third kind, and $P_n(x)$ is the n th Legendre polynomial.³²

The unknown coefficients $A_n, B_n, f(k), g(k), h(k)$ can be determined by applying the boundary conditions of the potential on the electrode with $z = 0, d, L - d, L$ and on the surface of the sphere at $r_2 = a$, which reads

$$\begin{aligned} \phi_1|_{z=0} &= 0, \\ \phi_1|_{z=d} &= \phi_2|_{z=d}, \\ \epsilon_0 \frac{\partial \phi_1}{\partial z}|_{z=d} &= \epsilon_1 \frac{\partial \phi_2}{\partial z}|_{z=d}, \\ \phi_4|_{z=L} &= 0, \\ \phi_4|_{z=L-d} &= \phi_2|_{z=L-d}, \quad (\text{B3}) \\ \epsilon_0 \frac{\partial \phi_4}{\partial z}|_{z=L-d} &= \epsilon_1 \frac{\partial \phi_2}{\partial z}|_{z=L-d}, \\ \phi_3|_{r_2=a} &= \phi_2|_{r_2=a}, \\ \epsilon_0 \frac{\partial \phi_3}{\partial r_2}|_{r_2=a} &= \epsilon_1 \frac{\partial \phi_2}{\partial r_2}|_{r_2=a}. \end{aligned}$$

Just as in the traditional treatment of the electric boundary problem,³² the orthogonal conditions $\int_{-1}^1 P_n(x)P_m(x)dx = \frac{2}{2n+1}\delta_{mn}$ and $\int_0^\infty x J_0(kx)J_0(k'x)dx = \frac{1}{k}\delta(k - k')$ could be applied to simplify the equations derived from the boundary conditions. Note that A_n and B_n with larger indices generally have smaller contribution as $A_0 \gg A_1 \gg A_2 \gg \dots$ and $B_0 \gg B_1 \gg B_2 \gg \dots$, one can truncate it to a system with a few unknowns, which leads to a perturbative solution to the original problem. To the lowest order, one can take $A_n = 0$ and $B_n = 0$ for $n \geq 1$ and only keep the zero index coefficient A_0, B_0 , from which the zeroth

order equation reads

$$\begin{aligned}
 g_1(k) + h_1(k)e^{-kd} &= 0, \\
 g_1(k)e^{-kd} + h_1(k) &= f_1(k) \\
 &+ f_2(k)e^{\gamma(k)(2d-L)} + B_0U_{10}(k), \\
 -g_1(k)ke^{-kd} + h_1(k)k &= -\epsilon_r\gamma(k)[f_1(k) \\
 &- f_2(k)e^{\gamma(k)(2d-L)}] + B_0U_{20}(k), \\
 g_2(k)e^{-kd} + h_2(k) &= 0, \\
 g_2(k) + h_2(k)e^{-kd} &= f_1(k)e^{\gamma(k)(2d-L)} \\
 &+ f_2(k) + B_0U_{30}(k), \\
 -g_2(k)k + h_2(k)ke^{-kd} &= -\epsilon_r\gamma(k)[f_1(k)e^{\gamma(k)(2d-L)} \\
 &- f_2(k)] + B_0U_{40}(k), \\
 \frac{q}{\epsilon_0 a} + A_0 &= B_0k_0(\kappa_D a) + \int_0^\infty [f_1(k)V_{10}(k) \\
 &+ f_2(k)V_{30}(k)]dk, \\
 -\frac{q}{\epsilon_0 a^2} &= \epsilon_r B_0\kappa_D k'_0(\kappa_D a) \\
 &+ \int_0^\infty [f_1(k)V_{20}(k) + f_2(k)V_{40}(k)]dk,
 \end{aligned} \tag{B4}$$

with

$$\begin{aligned}
 U_{10}(k) &= \frac{\pi}{2} \frac{k}{\kappa_D \gamma(k)} e^{-\gamma(k)(z_0-d)}, \\
 U_{20}(k) &= \epsilon_r \frac{\partial U_{10}}{\partial d} = \frac{\pi}{2} \frac{k\epsilon_r}{\kappa_D} e^{-\gamma(k)(z_0-d)}, \\
 U_{30}(k) &= \frac{\pi}{2} \frac{k}{\kappa_D \gamma(k)} e^{-\gamma(k)(L-z_0-d)}, \\
 U_{40}(k) &= -\epsilon_r \frac{\partial U_{30}}{\partial d} = -\frac{\pi}{2} \frac{k\epsilon_r}{\kappa_D} e^{-\gamma(k)(L-z_0-d)}, \\
 V_{10}(k) &= i_0(\kappa_D a) e^{-\gamma(k)(z_0-d)}, \\
 V_{20}(k) &= \epsilon_r \frac{\partial V_{10}}{\partial a} = -\epsilon_r \kappa_D i_1(\kappa_D a) e^{-\gamma(k)(z_0-d)}, \\
 V_{30}(k) &= i_0(\kappa_D a) e^{-\gamma(k)(L-z_0-d)}, \\
 V_{40}(k) &= \epsilon_r \frac{\partial V_{30}}{\partial a} = -\epsilon_r \kappa_D i_1(\kappa_D a) e^{-\gamma(k)(L-z_0-d)},
 \end{aligned} \tag{B5}$$

and $i_n(x)$ is the n th modified Bessel function of the first kind. The above equation could be solved analytically. With the first six equations in Eq. (B4), $f_i(k)$, $g_i(k)$, $h_i(k)$ could be found as a linear function of B_0 . Specifically, we have

$$f_i(k) \equiv B_0 \Lambda_i(k), \quad (i = 1, 2), \tag{B6}$$

where $\Lambda_i(k)$ is defined as

$$\begin{aligned}
 \Lambda_1(k) &= [E_1(k)C_1(k) + E_2(k)C_2(k)]/[E_1(k)^2 - E_2(k)^2], \\
 \Lambda_2(k) &= [E_1(k)C_2(k) + E_2(k)C_1(k)]/[E_2(k)^2 - E_1(k)^2],
 \end{aligned} \tag{B7}$$

and

$$\begin{aligned}
 w(k) &= k \frac{1 + e^{-2kd}}{1 - e^{-2kd}}, \\
 E_1(k) &= w(k) + \epsilon_r \gamma(k), \\
 E_2(k) &= [w(k) - \epsilon_r \gamma(k)]e^{\gamma(k)(2d-L)}, \\
 C_1(k) &= U_{20}(k) - w(k)U_{10}(k), \\
 C_2(k) &= U_{40}(k) + w(k)U_{30}(k).
 \end{aligned} \tag{B8}$$

Note that $k'_0(x) = -k_1(x)$, the seventh and eighth equation in Eq. (B4) could be further simplified as

$$\begin{aligned}
 A_0 - B_0k_0(\kappa_D a) &= -\frac{q}{\epsilon_0 a} + B_0\alpha, \\
 \epsilon_r B_0\kappa_D k_1(\kappa_D a) &= \frac{q}{\epsilon_0 a^2} + B_0\beta,
 \end{aligned} \tag{B9}$$

with

$$\begin{aligned}
 \alpha &\equiv \int_0^\infty [\Lambda_1(k)V_{10}(k) + \Lambda_2(k)V_{30}(k)]dk, \\
 \beta &\equiv \int_0^\infty [\Lambda_1(k)V_{20}(k) + \Lambda_2(k)V_{40}(k)]dk,
 \end{aligned} \tag{B10}$$

and finally we have

$$\begin{aligned}
 A_0 &= -\frac{q}{\epsilon_0 a} + \frac{q[k_0(\kappa_D a) + \alpha]}{\epsilon_0 a^2[\epsilon_r \kappa_D k_1(\kappa_D a) - \beta]}, \\
 B_0 &= \frac{q}{\epsilon_0 a^2[\epsilon_r \kappa_D k_1(\kappa_D a) - \beta]}.
 \end{aligned} \tag{B11}$$

The coefficient A_0 is of special interest since it is the potential at the center of the solute induced by the solvent and the electrodes. Then the mean electric potential x_M could be evaluated via $x_M = q_M(A_0 - \phi_w)$, and hence the reorganization energy λ according to Eq. (10). The potential ϕ_w is due to the presence of two electrodes, and could be evaluated as a summation of electric potential of infinite image charges²⁹ or the method here without the presence of the solvent. After a lengthy manipulation one can find the final result from the image method as

$$\phi_w = -\frac{q}{2\epsilon_0 z_0} \left[1 + \sum_{m=1}^{\infty} \frac{2}{(K^2 m^2 - 1)mK} \right], \tag{B12}$$

with $K = L/z_0$. Naturally, in the absence of the solvent, A_0 should reduce to ϕ_w as $\lim_{\kappa_D \rightarrow 0, \epsilon_r \rightarrow 1} A_0 = \phi_w$, which serves as a test for the validity of the analytical solution Eq. (B11). For the particular model of an electron transfer reaction with $q = e$ and $\Delta q = e$, the reorganization energy is

$$\begin{aligned}
 \lambda &= \frac{e^2}{2\epsilon_0} \left[\frac{-k_0(\kappa_D a) - \alpha}{a^2[\epsilon_r \kappa_D k_1(\kappa_D a) - \beta]} + \frac{1}{a} \right. \\
 &\quad \left. - \frac{1}{2z_0} \left(1 + \sum_{m=1}^{\infty} \frac{2}{(K^2 m^2 - 1)mK} \right) \right].
 \end{aligned} \tag{B13}$$

According to Eq. (B13), one can find the corresponding reorganization energy λ_l for one Debye mode with Debye parameter κ_l . When we apply the MDH approach to the electron transfer near an electrode, the total reorganization energy

could be evaluated by a linear combination of individual Debye modes, i.e., $\lambda = \sum_l C_l \lambda_l$.

It is also worthwhile to check some of the limits of Eq. (B13). For a single wall limit with $K = L/z_0 \rightarrow \infty$ and $d \rightarrow 0$, it is noted that $\phi_w = \frac{-q}{2\epsilon_0 z_0}$, $\alpha = -k_0(\kappa_D R) i_0(\kappa_D a)$ and $\beta = \epsilon_r \kappa_D k_0(\kappa_D R) i_1(\kappa_D a)$. Let $R = 2z_0$, the reorganization energy in this case reads

$$\lambda = \frac{e^2}{2\epsilon_0} \left[\frac{-k_0(\kappa_D a) + k_0(\kappa_D R) i_0(\kappa_D a)}{\epsilon_r \kappa_D a^2 [k_1(\kappa_D a) - k_0(\kappa_D R) i_1(\kappa_D a)]} + \frac{1}{a} - \frac{1}{R} \right], \quad (\text{B14})$$

which is half of the reorganization energy of an electron transfer reaction between two spheres with opposite charge as it should be (see Eq. (B.9) in Ref. 14). Furthermore, if there is not free ions such that $\kappa_D \rightarrow 0$, then Eq. (B14) leads to the familiar Marcus result $\lambda = \frac{e^2}{2\epsilon_0} (\frac{1}{\epsilon_r} - \frac{1}{\epsilon_r}) (\frac{1}{a} - \frac{1}{R})$, which is the reorganization energy for an electron transfer reaction near an electrode in the presence of a dipole fluid.⁸ When the continuum solvent background is absent, i.e., $\epsilon_r = 1$, then Eq. (B14) leads to $\lambda = \frac{e^2}{2\epsilon_0} [\frac{\kappa_D}{1+\kappa_D a} + \frac{1}{R} \frac{e^{-\kappa_D(R-a)}}{1+\kappa_D a} - \frac{1}{R}]$ as long as $\kappa_D a \ll 1$, which coincides with Eq. (91) in the paper of Marcus⁸ to the order of $\kappa_D a$.

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