Derivation of the Constitutive Relations

In this supporting information, we derive the constitutive relations under equilibrium condition (Eqs. (9) – (11)) and nonequilibrium condition (Eqs. (15) and (16)). We start by extremizing the effective Hamiltonian $H$ in Eq. (7) with respect to its functional arguments. Under full equilibrium $H$ is extremized with respect to all the field variables $\varphi_S$, $\rho_\text{or}$, $\rho_\text{el}$, $w_\text{or}$, $w_\text{el}$, $w_S$, and $w$, respectively giving rise to the following seven relations:

$$w(\mathbf{r}) = w_S(\mathbf{r}) \quad (S1)$$

$$iw_\text{or}(\mathbf{r}) = \beta \int d\mathbf{r}' \left[ \hat{\rho}_c(\mathbf{r}) + \rho_\text{or}(\mathbf{r}) + \rho_\text{el}(\mathbf{r}) \right] \frac{1}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} \quad (S2)$$

$$iw_\text{el}(\mathbf{r}) = \beta \int d\mathbf{r}' \left[ \hat{\rho}_c(\mathbf{r}) + \rho_\text{or}(\mathbf{r}) + \rho_\text{el}(\mathbf{r}) \right] \frac{1}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} \quad (S3)$$
\[
\rho_{or}(\mathbf{r}) = -i \sum_{S} \frac{e^{\beta \mu_S}}{\eta_S} 4 \pi \mu_S^2 \left( \frac{2 \pi \alpha_S}{\beta} \right)^{\frac{3}{2}} \nabla \cdot \left[ \Gamma(\mathbf{r}) e^{i \omega_S(r) \omega_S - \frac{\alpha_S}{2 \pi} (\nabla w_{el}(\mathbf{r}))^2} \right. \\
\times \left( \cot(\mu_S |\nabla w_{or}(\mathbf{r})|) - \frac{1}{\mu_S |\nabla w_{or}(\mathbf{r})|} \right) \sin(\mu_S |\nabla w_{or}(\mathbf{r})|) \left( \frac{\mu_S |\nabla w_{or}(\mathbf{r})|}{\mu_S |\nabla w_{or}(\mathbf{r})|} \right)^{\frac{3}{2}} \mu_S^2 \nabla w_{or}(\mathbf{r}) \right] \quad (S4)
\]

\[
\rho_{el}(\mathbf{r}) = i \sum_{S} \frac{e^{\beta \mu_S}}{\eta_S} 4 \pi \mu_S^2 \left( \frac{2 \pi \alpha_S}{\beta} \right)^{\frac{3}{2}} \frac{\alpha_S}{\beta} \nabla \cdot \left[ \Gamma(\mathbf{r}) e^{i \omega_S(r) \omega_S - \frac{\alpha_S}{2 \pi} (\nabla w_{el}(\mathbf{r}))^2} \right. \\
\times \left( \frac{\sin(\mu_S |\nabla w_{or}(\mathbf{r})|)}{\mu_S |\nabla w_{or}(\mathbf{r})|} \right) \nabla w_{or}(\mathbf{r}) \right] \quad (S5)
\]

\[
\varphi_S(\mathbf{r}) = \frac{e^{\beta \mu_S}}{\eta_S} 4 \pi \mu_S^2 \left( \frac{2 \pi \alpha_S}{\beta} \right)^{\frac{3}{2}} v_S \Gamma(\mathbf{r}) e^{i \omega_S(r) \omega_S - \frac{\alpha_S}{2 \pi} (\nabla w_{el}(\mathbf{r}))^2} \sin(\mu_S |\nabla w_{or}(\mathbf{r})|) \left( \frac{\mu_S |\nabla w_{or}(\mathbf{r})|}{\mu_S |\nabla w_{or}(\mathbf{r})|} \right)^{\frac{3}{2}} \mu_S^2 \nabla w_{or}(\mathbf{r}) \right] \quad (S6)
\]

\[
\sum_{S} \varphi_S(\mathbf{r}) = 1 \quad (S7)
\]

Under nonequilibrium condition in which \(\rho_{or}\) and \(\varphi_S\) are fixed at their out-of-equilibrium values, \(H\) is extremized with respect to \(\rho_{el}, w_{or}, w_{el}, w_S,\) and \(w\), and therefore, only Eqs. (S3) - (S7) are applicable.

To further simplify the equations, we substitute Eq. (S6) into Eqs. (S4) and (S5), and rewrite Eqs. (S4) and (S5) respectively as

\[
\rho_{or}(\mathbf{r}) = -i \nabla \cdot \left[ \sum_{S} \frac{\varphi_S(\mathbf{r})}{v_S} \left( \cot(\mu_S |\nabla w_{or}(\mathbf{r})|) - \frac{1}{\mu_S |\nabla w_{or}(\mathbf{r})|} \right) \nabla \cdot \left( \frac{\mu_S |\nabla w_{or}(\mathbf{r})|}{\mu_S |\nabla w_{or}(\mathbf{r})|} \right)^{\frac{3}{2}} \mu_S^2 \nabla w_{or}(\mathbf{r}) \right] \quad (S8)
\]

and

\[
\rho_{el}(\mathbf{r}) = i \nabla \cdot \left[ \sum_{S} \frac{\alpha_S}{\beta} \frac{\varphi_S(\mathbf{r})}{v_S} \nabla w_{or}(\mathbf{r}) \right] \quad (S9)
\]

Because Eq. (S8) holds under both equilibrium and nonequilibrium conditions, one can show that the conjugate field to the orientational polarization \(w_{or}\) is determined once \(\rho_{or}\) and \(\varphi_S\) are specified. Therefore, when an equilibrium state and a nonequilibrium state have equal
values for $\rho_{or}$ and $\varphi_S$ due to their unchanged nuclear configurations, the two states have the same values for $w_{or}$ as well. To simplify the expressions further, we introduce the the orientational and electronic electric susceptibilities $\chi_{or}(r)$ and $\chi_{el}(r)$, and rewrite Eqs. (S8) and (S9) as

$$\rho_{or}(r) = i \nabla \cdot \left[ \frac{\epsilon_0}{\beta} \chi_{or}(r) \nabla w_{or}(r) \right]$$  \hspace{1cm} (S10)

and

$$\rho_{el}(r) = i \nabla \cdot \left[ \frac{\epsilon_0}{\beta} \chi_{el}(r) \nabla w_{el}(r) \right]$$  \hspace{1cm} (S11)

where $\chi_{or}(r)$ and $\chi_{el}(r)$ are, respectively, given by

$$\chi_{or}(r) = -\frac{\beta}{\epsilon_0} \sum_S \frac{\varphi_S(r)}{v_S} \left( \cot(\mu_S |\nabla w_{or}(r)|) - \frac{1}{\mu_S |\nabla w_{or}(r)|} \right) \frac{1}{\mu_S |\nabla w_{or}(r)|} \mu_S^2$$  \hspace{1cm} (S12)

and

$$\chi_{el}(r) = \frac{\beta}{\epsilon_0} \sum_S \frac{\alpha_S \varphi_S(r)}{v_S}$$  \hspace{1cm} (S13)

Furthermore, upon taking the Laplacian on both sides of Eqs. (S2) and (S3), we can write these equations respectively as

$$-i\frac{\epsilon_0}{\beta} \nabla^2 w_{or}(r) = \hat{\rho}_c(r) + \rho_{or}(r) + \rho_{el}(r)$$  \hspace{1cm} (S14)

$$-i\frac{\epsilon_0}{\beta} \nabla^2 w_{el}(r) = \hat{\rho}_c(r) + \rho_{or}(r) + \rho_{el}(r)$$  \hspace{1cm} (S15)

To make the calculations more convenient, we remove $\rho_{or}$ and $\rho_{el}$ from Eqs. (S14) and (S15) equations using Eqs. (S10) and (S11). The resulting equations are

$$-i\frac{\epsilon_0}{\beta} \nabla \cdot \left[ \nabla \rho_{or}(r) + \chi_{or}(r) \nabla w_{or}(r) + \chi_{el}(r) \nabla w_{el}(r) \right] = \hat{\rho}_c(r)$$  \hspace{1cm} (S16)

$$-i\frac{\epsilon_0}{\beta} \nabla \cdot \left[ \nabla \rho_{el}(r) + \chi_{or}(r) \nabla w_{or}(r) + \chi_{el}(r) \nabla w_{el}(r) \right] = \hat{\rho}_c(r)$$  \hspace{1cm} (S17)

Furthermore, by letting the fields $w_S$, $w_{el}$, and $w_{or}$ go to zero as $|r| \to \infty$ in Eq. (S6), we
may equate the bulk volume fraction $\varphi_S(\infty)$ with the following factor

$$
\varphi_S(\infty) = \frac{e^{\beta \mu_S}}{\eta_S} \frac{4 \pi \alpha_S}{\beta} \left( \frac{2 \pi \alpha_S}{\beta} \right)^{\frac{3}{2}} v_S
$$

(S18)

With these simplifications, we summarize the constitutive relations as follows:

$$
w(r) = w_S(r)
$$

(S19)

$$
-i \frac{\epsilon_0}{\beta} \nabla \cdot \left[ \nabla w_{or}(r) + \chi_{or}(r) \nabla w_{or}(r) + \chi_{el}(r) \nabla w_{el}(r) \right] = \hat{\rho}_c(r)
$$

(S20)

$$
-i \frac{\epsilon_0}{\beta} \nabla \cdot \left[ \nabla w_{el}(r) + \chi_{or}(r) \nabla w_{or}(r) + \chi_{el}(r) \nabla w_{el}(r) \right] = \hat{\rho}_e(r)
$$

(S21)

$$
\varphi_S(r) = \Gamma(r) \varphi_S(\infty) e^{iw_S(r) v_S - \frac{\alpha_S}{\beta} (\nabla w_{el}(r))^2 \sin(\bar{\mu}_S |\nabla w_{or}(r)|)} \frac{1}{\bar{\mu}_S |\nabla w_{or}(r)|} \mu_S^2
$$

(S22)

$$
\sum_S \varphi_S(r) = 1
$$

(S23)

where

$$
\chi_{or}(r) = -\frac{\beta}{\epsilon_0} \sum_S \varphi_S(r) \left( \cot(\bar{\mu}_S |\nabla w_{or}(r)|) - \frac{1}{\bar{\mu}_S |\nabla w_{or}(r)|} \right) \frac{1}{\bar{\mu}_S |\nabla w_{or}(r)|} \mu_S^2
$$

(S24)

and

$$
\chi_{el}(r) = \frac{\beta}{\epsilon_0} \sum_S \frac{\alpha_S \varphi_S(r)}{\bar{\mu}_S |\nabla w_{or}(r)| \mu_S^2}
$$

(S25)

The saddle-point condition yields purely imaginary values for the fields $w_{or}$, $w_{el}$, $w$, and $w_S$. In order to work with real quantities and for the convenience of relating our theory to classical electrostatics, we make a change of variables $w_{or} = -i \beta \phi_{or}$, $w_{el} = -i \beta \phi_{el}$, $w = i \beta u$, and $w_S = i \beta u_S$ in Eqs. (S19) – (S23). This results in Eq. (9) – (11) in main text. The nonequilibrium constitutive relations in Eqs. (15) and (16) correspond to Eqs. (S21) – (S23).
Comparison between the DSCFT prediction and Molecular Dynamics Simulation for the Activation Energy

Here we present a comparison between the DSCFT prediction and molecular dynamics (MD) simulation for the activation energies for the ferrous/ferric exchange reaction in water/methanol mixture. The MD simulations are performed by us, using the nonpolarizable SPC/E model for water and the H1 model for methanol (as used in Ref. S1). The forcefield parameters for the Fe ions are the same as that in Ref. S2. The activation is sampled with the umbrella sampling method, following the method in Ref. S3. The distance between the centers of the donor and the acceptor is kept at $d = 5.5 \, \text{Å}$, the same as that in the DSCFT calculations. The simulations are carried out with a Langevin integrator at temperature 300 K with friction coefficient 1 ps$^{-1}$ and step size 2 fs. The system is first equilibrated for 8000 ps, followed by sampling a frame per 0.2 ps for 32000 ps.

The comparison between the activation energies calculated from the DSCFT and from the MD simulation are presented in Figure S1. We see that the qualitative trend in the MD simulation result is well captured by the DSCFT. We note that the water and methanol molecules in the MD simulation are nonpolarizable and the simulation is subject to system size effects and statistical errors. However, the MD results took months to obtain on a GPU computer cluster, while the DSCFT results were obtained within an hour on a personal computer.

In the three solvent mixtures considered in our paper, only the water/methanol mixture can be reasonably approximated by nonpolarizable solvent models. For the other two cases, polarizability of the solvents is important to their physical behavior. Since the comparison is only available for one scenario considered in our manuscript, and the comparison is not a direct one (DSCFT uses polarizable solvent while MD uses nonpolarizable solvent), we present the comparisons here in the supplementary information rather than in the manuscript.
Figure S1: The activation energies for ferrous/ferric exchange reaction in water/methanol mixture calculated from the DSCFT (red line) and from the MD simulation (blue scattered points).

References

