Supporting Information for: A Surface Hopping View of Electrochemistry: Non-Equilibrium Electronic Transport through an Ionic Solution with a Classical Master Equation

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S1 Distribution of the number of charged (B^-) atoms

In Fig. S1 we plot the distribution of the number of charged atoms, i.e. how often does the system have 0, 1, 2,..., 14 charged atoms. Let us denote this distribution $P^{ne}(N_{B^-}, \mu_L, \mu_R)$, where N_{B^-} is the number of charged B^- ions, which varies from 0, 1, 2,..., 14. The histogram in Fig. S1 is the result of averaging over 100000 snapshots of 100 ensembles.

To better understand the distribution $P^{ne}(N_{B^-}, \mu_L, \mu_R)$, let us attempt to reconstruct the low voltage non-equilibrium result from a set of equilibrium simulations. In particular, suppose we calculate the equilibrium probabilities for finding a given number of charged atoms in solution, $P^{eq}(N_{B^-}, \mu, \mu)$. A reasonable approximation for the non-equilibrium result would then be:

$$P^{ne}(N_{B^-}, \mu_L, \mu_R) = \frac{1}{2}\left(P^{eq}(N_{B^-} - \Delta N, \mu_L, \mu_L) + P^{eq}(N_{B^-} + \Delta N, \mu_R, \mu_R)\right) \quad \text{(S1)}$$

where ΔN is defined to be:

$$\Delta N \equiv \frac{\langle N_{B^-}\rangle_R^{eq} - \langle N_{B^-}\rangle_L^{eq}}{2} \quad \text{(S2)}$$

and $\langle N_{B^-}\rangle_L^{eq} \equiv \sum_{N_{B^-}} N_{B^-} P^{eq}(N_{B^-}, \mu_L, \mu_L)$, $\langle N_{B^-}\rangle_R^{eq} \equiv \sum_{N_{B^-}} N_{B^-} P^{eq}(N_{B^-}, \mu_R, \mu_R)$. According to Eq. (S1) and (S2), it is clear that $\langle N_{B^-}\rangle^{ne} = \frac{1}{2}\left(\langle N_{B^-}\rangle_L^{eq} + \langle N_{B^-}\rangle_R^{eq}\right)$.

Fig. S2 plots all of the distributions (equilibrium and non-equilibrium) in Eq. (S1). The non-equilibrium simulation is performed at voltage 0.05V and is the same data

as presented in the blue curve with cross markers from Fig. S1. The two equilibrium simulations have electrochemical potential -3.4eV and -3.45eV, respectively. From Fig. S2, we see that Eq. (S1) is a reasonable estimate, but the agreement is far from perfect. The average number of charged solute atoms as estimated from the equilibrium and non-equilibrium distributions are 2.21 and 2.462, respectively.

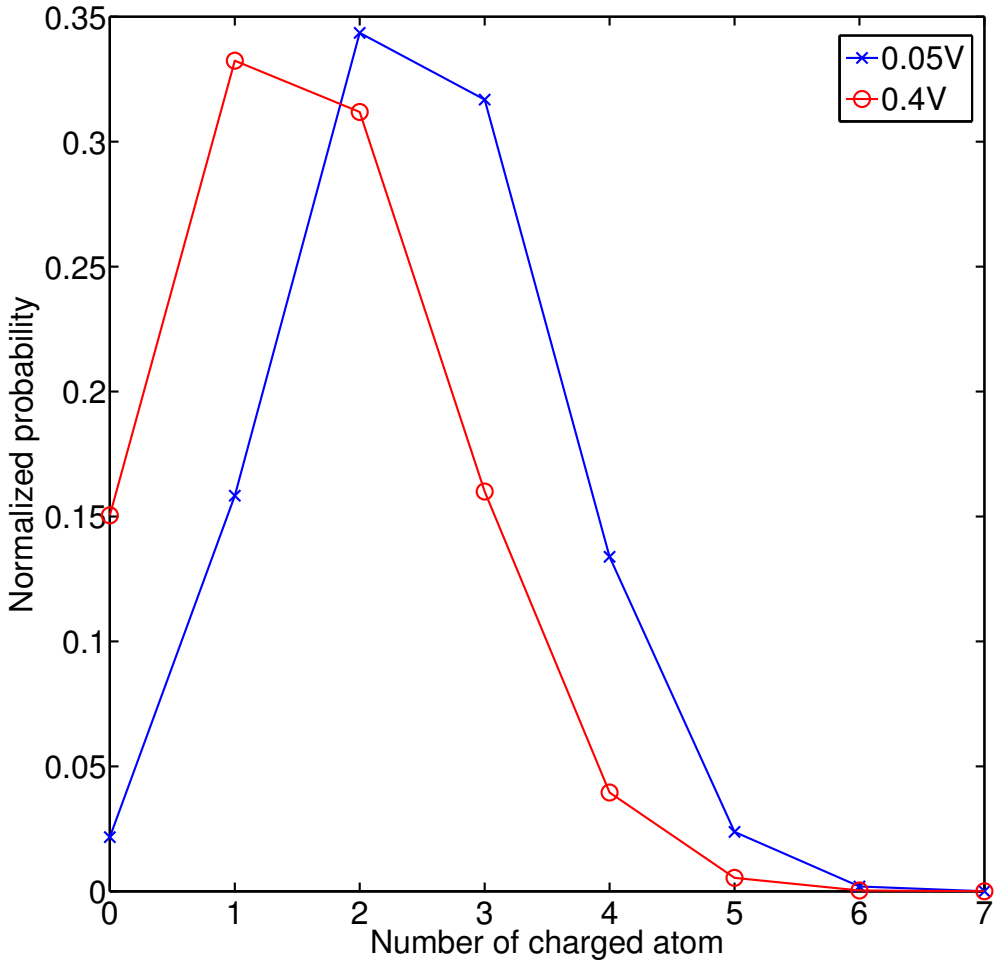

Figure S1: The normalized distributions $P^{ne}(N_{B^-}, \mu_L, \mu_R)$of the number of charged B^- atoms for two different voltages. While the distribution at high voltage is shifted to the left, the overall shapes of these distributions are roughly similar.

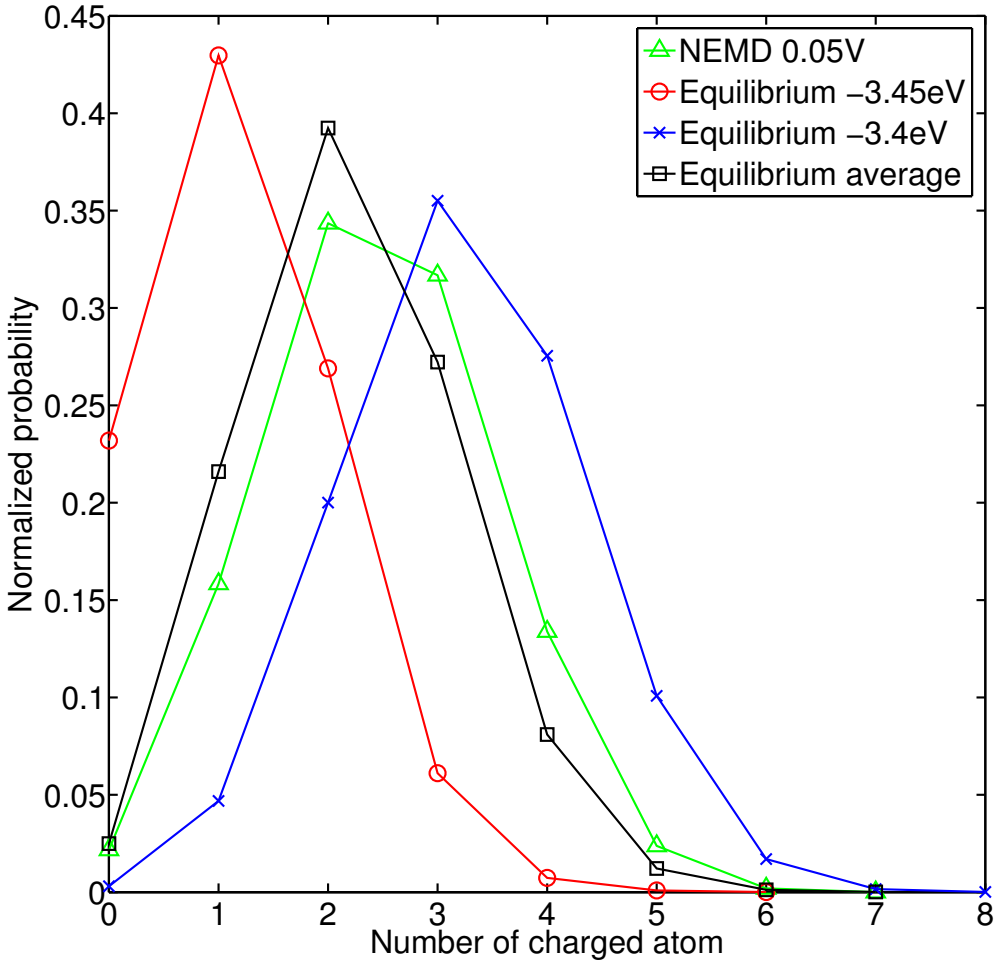

Figure S2: A comparison of the distributions of number of charged B^- atoms from non-equilibrium versus from equilibrium simulations. The non-equilibrium simulation has voltage 0.05V and $\mu_L = -3.45$eV and $\mu_R = -3.4$eV. In the two equilibrium simulations, the electrochemical potential of two electrodes are $\mu_L = \mu_R = -3.45$eV or $\mu_L = \mu_R = -3.4$eV. The average of the two equilibrium simulations results in a reasonable approximation of the non-equilibrium histogram but the agreement is not perfect. The green curve here is identical to the blue curve in Fig. S1.

S2 Resonant charge transfer

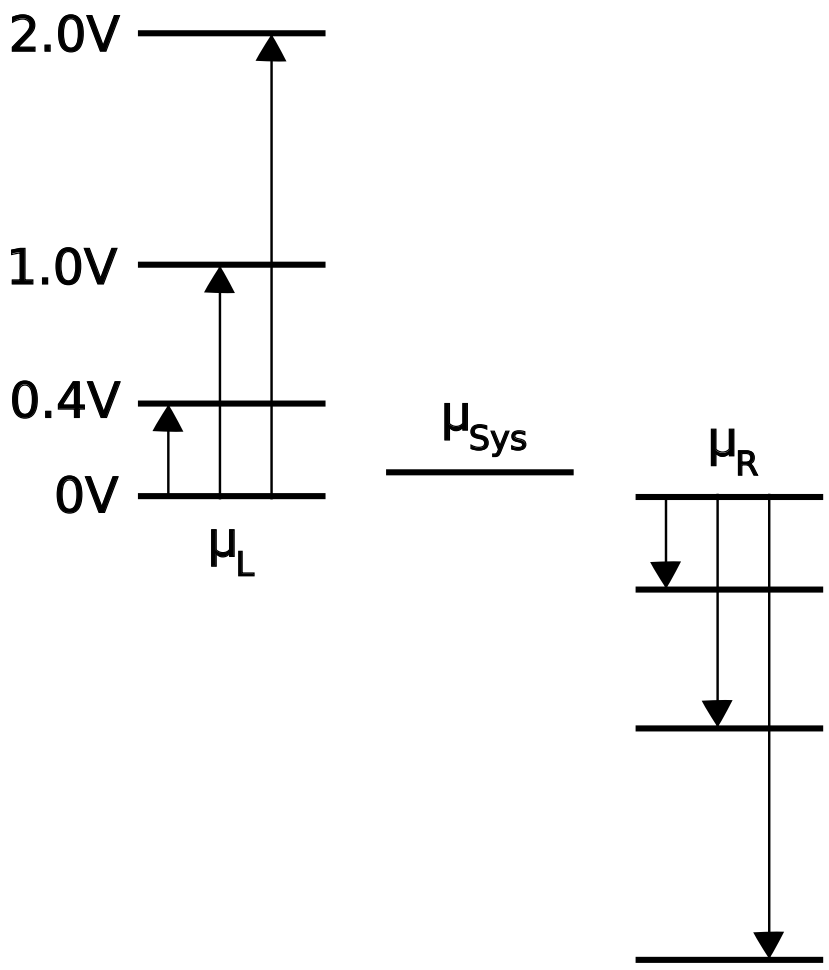

Figure S3: The schematic figure showing how the applied voltage is change in a resonant system.