

# Kinetic Monte Carlo Simulation of Electron Transfer

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*Collaboratory for Advanced Computing & Simulations*

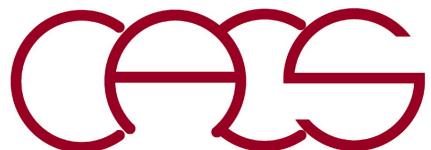
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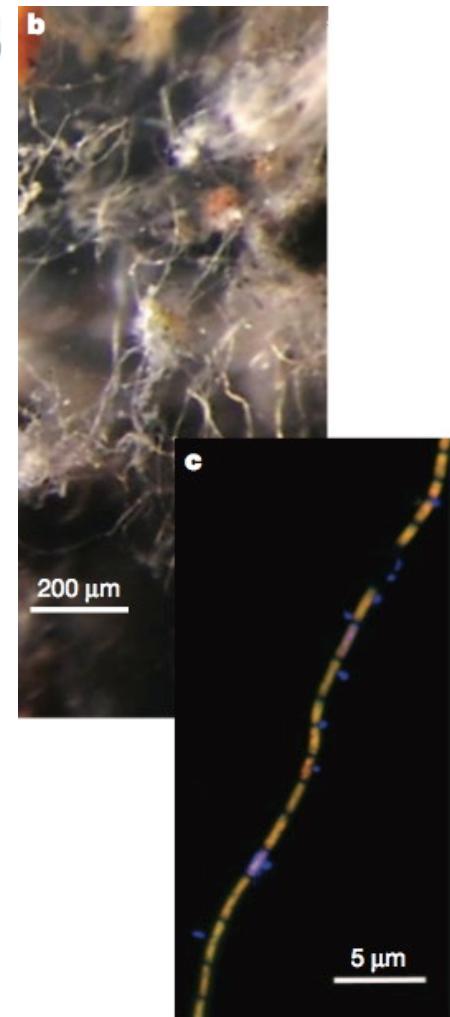
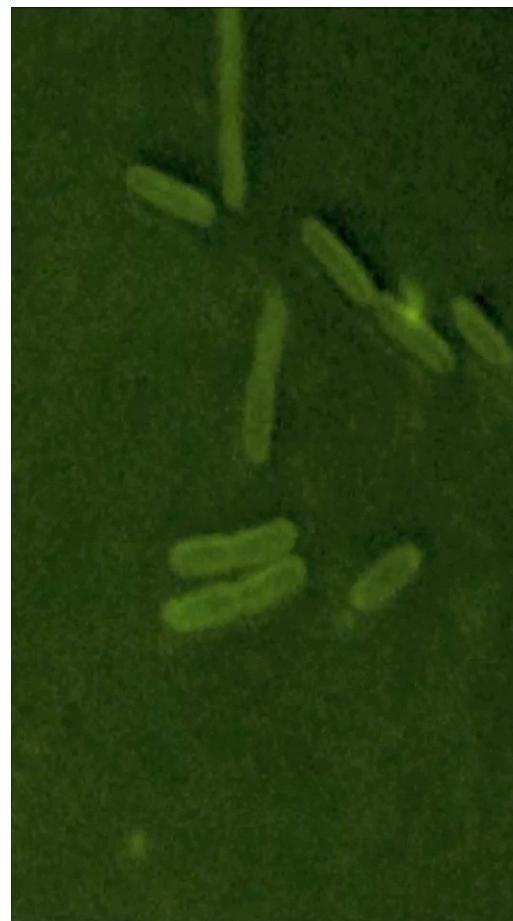
# Biological Electron Transfer

## Filamentous bacteria transport electrons over centimetre distances

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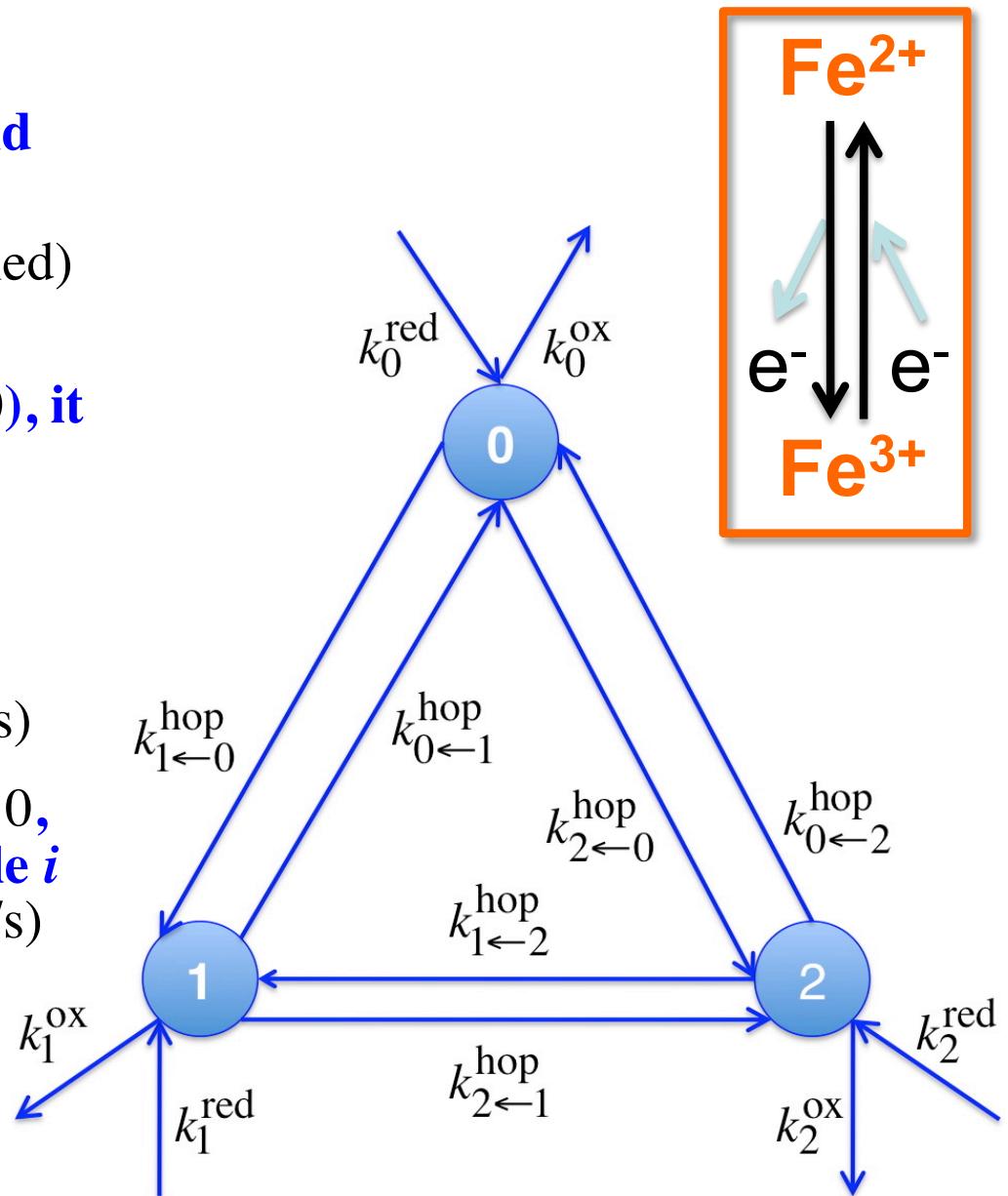
218 | NATURE | VOL 491 | 8 NOVEMBER 2012

Oxygen consumption in marine sediments is often coupled to the oxidation of sulphide generated by degradation of organic matter in deeper, oxygen-free layers. Geochemical observations have shown that this coupling can be mediated by electric currents carried by unidentified electron transporters across centimetre-wide zones. Here we present evidence that the native conductors are long, filamentous bacteria. They abounded in sediment zones with electric currents and along their length they contained strings with distinct properties in accordance with a function as electron transporters. **Living, electrical cables** add a new dimension to the understanding of interactions in nature and may find use in technology development.



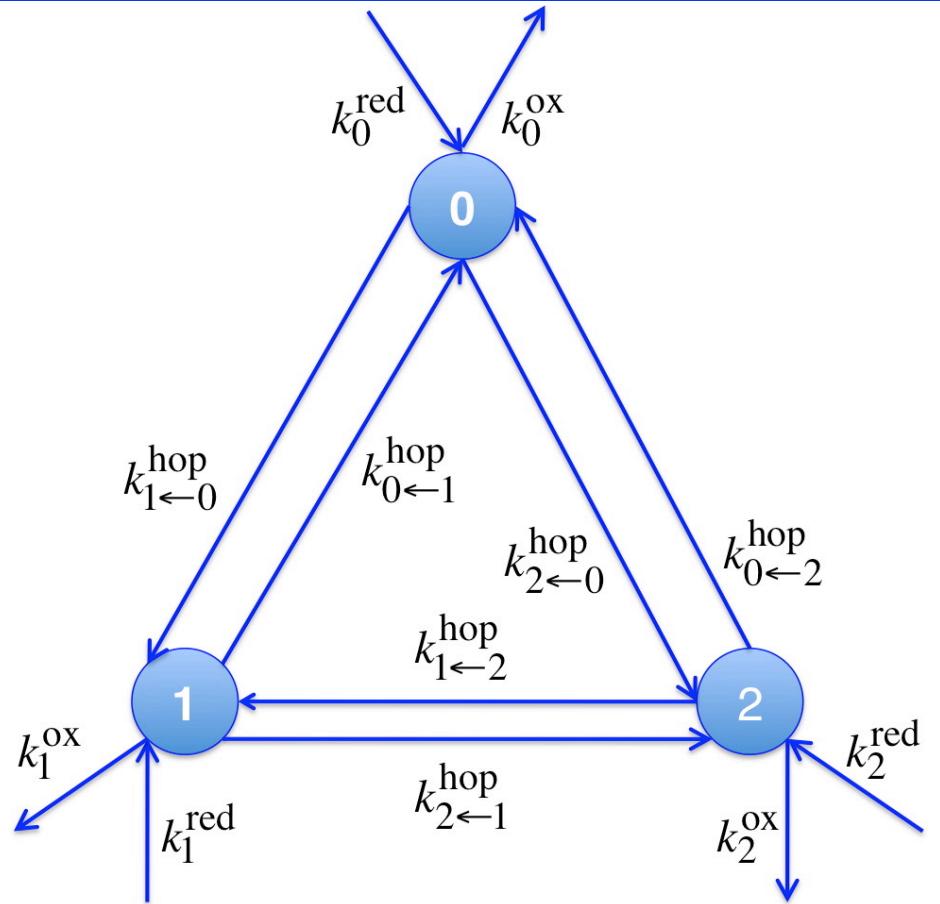
# Model Definition

- A set of  $N$  redox molecules
- Each molecule  $i \in [0, N-1]$  can hold up to one electron:  
 $occ(i) = 1$  (occupied) or  $0$  (unoccupied)
- **Reduction:** If molecule  $i$  is not occupied by an electron ( $occ(i) = 0$ ), it can be reduced (or an electron is injected to it) at a rate of  $k_i^{\text{red}}$  (1/s)
- **Oxidation:** If  $occ(i) = 1$ , molecule  $i$  can be oxidized (or the electron is ejected from it) at a rate of  $k_i^{\text{ox}}$  (1/s)
- **Hopping:** If  $occ(i) = 1$  and  $occ(j) = 0$ , the electron can hop from molecule  $i$  to molecule  $j$  at a rate of  $k_{j \leftarrow i}^{\text{hop}}$  (1/s)



# Molecular Network Topology

- Directed graph consisting of  $N$  nodes (= molecules) and directed edges (= possible hopping from a node to a neighbor node)
- $ngb(i)$ : Number of outgoing edges for molecule  $i$  ( $\text{Max\_ngb}$  = maximum number of outgoing edges per node)
- $lsnbg[N][\text{Max\_ngb}+1]$   
 $lsnbg[i][0] = ngb(i)$   
 $lsnbg[i][k] = \text{molecular ID of the } k\text{-th outgoing neighbor of molecule } i,$   
 $\text{where } k \in [1, ngb(i)]$



Example:  $\text{Max\_ngb} = 2$

$lsnbg[i][k]$	$k = 0$	1	2
$i = 0$	2	1	2
1	2	0	2
2	2	0	1

# Data Structures

- Occupation

$$occ[N] : occ[i] = \begin{cases} 1 & \text{molecule } i \text{ is occupied by an electron} \\ 0 & \text{unoccupied} \end{cases}$$

- Rates (constants)

$$\left\{ \begin{array}{l} rate[N][Max\_ngb + 2] \\ \quad rate[i][0] = k_i^{\text{red}} \\ \quad rate[i][1] = k_i^{\text{ox}} \\ \quad rate[i][k + 1] = k_{lsngh[i][k] \leftarrow i}^{\text{hop}} \end{array} \right.$$

- Occupation-modified rates (dynamic variables)

$$\left\{ \begin{array}{l} rate\_occ[N][Max\_ngb + 2] \\ \quad rate\_occ[i][0] = k_i^{\text{red}} \times (1 - occ[i]) \\ \quad rate\_occ[i][1] = k_i^{\text{ox}} \times occ[i] \\ \quad rate\_occ[i][k + 1] = k_{lsngh[i][k] \leftarrow i}^{\text{hop}} \times (1 - occ[lsngh[i][k]]) \times occ[i] \end{array} \right.$$

Many-body effects

# Algorithm

```

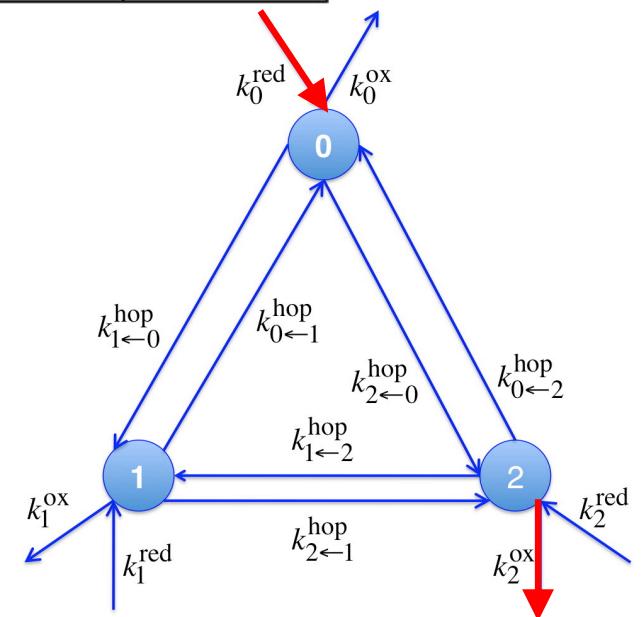
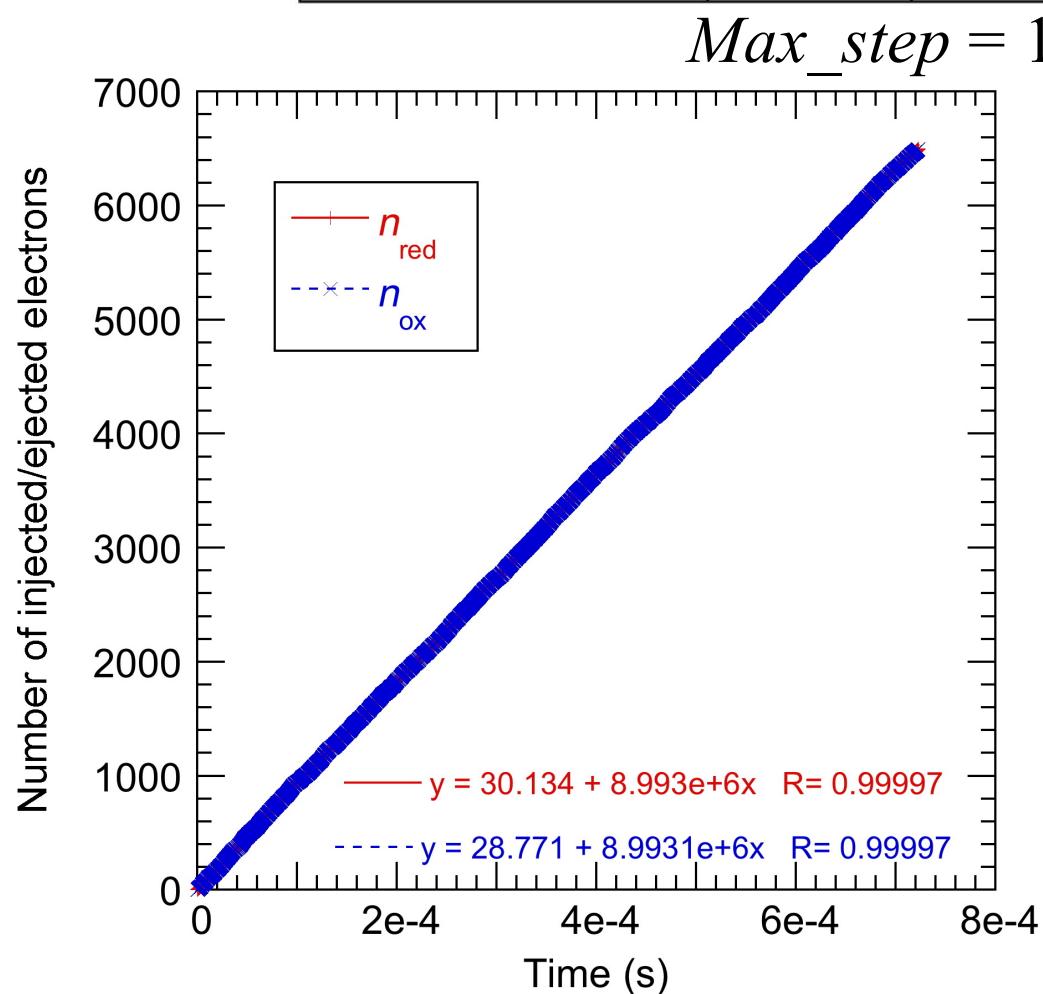
 $occ[i] \leftarrow 0 \text{ } (i = 0 \text{ to } N-1)$ 
 $n_{\text{red}} \leftarrow 0 \text{ } // \text{number of injected electrons}$ 
 $n_{\text{ox}} \leftarrow 0 \text{ } // \text{number of ejected electrons}$ 
 $t \leftarrow 0$ 
for  $step \leftarrow 1$  to  $Max\_step$   $// Max\_step = \text{total number of KMC steps}$ 
     $r \leftarrow 0$ 
    for  $i \leftarrow 0$  to  $N-1$ 
         $r += (rate\_occ[i][0] = rate[i][0] * (1 - occ[i]))$ 
         $r += (rate\_occ[i][1] = rate[i][1] * occ[i])$ 
        for  $k \leftarrow 1$  to  $lsngb[i][0]$ 
             $r += (rate\_occ[i][k+1] = rate[i][k+1] * (1 - occ[lsngb[i][k]]) * occ[i])$ 
         $t = \ln(\text{rand}() / RAND\_MAX) / r$ 
         $r_{\text{th}} \leftarrow r * \text{rand}() / RAND\_MAX$ 
         $r_{\text{acc}} \leftarrow 0$ 
        for  $i \leftarrow 0$  to  $N-1$ 
            if ( $r_{\text{th}} < (r_{\text{acc}} += rate\_occ[i][0])$ )  $// \text{reduction occurs}$ 
                 $occ[i] \leftarrow 1$ ; print  $t, ++n_{\text{red}}, n_{\text{ox}}$ ; break
            else if ( $r_{\text{th}} < (r_{\text{acc}} += rate\_occ[i][1])$ )  $// \text{oxidation occurs}$ 
                 $occ[i] \leftarrow 0$ ; print  $t, n_{\text{red}}, ++n_{\text{ox}}$ ; break
            else
                for  $k \leftarrow 1$  to  $lsngb[i][0]$ 
                    if ( $r_{\text{th}} < (r_{\text{acc}} += rate\_occ[i][k+1])$ )  $// \text{hopping from } i \text{ to } k\text{-th neighbor occurs}$ 
                         $occ[lsngb[i][k]] \leftarrow 1$ ;  $occ[i] \leftarrow 0$ ; break
                if ( $r_{\text{th}} < r_{\text{acc}}$ ) break

```

$r = \sum_{\text{event}} r_{\text{event}}$   
 $\Delta t = -\ln(u_{\text{random}}) / r$

# Example Run

$rate[i][k]$ (1/s)	$k = 0$	1	2	3
$i = 0$	1e7	0	1e9	2e9
1	0	0	3e9	1e7
2	0	2e7	2e7	4e9

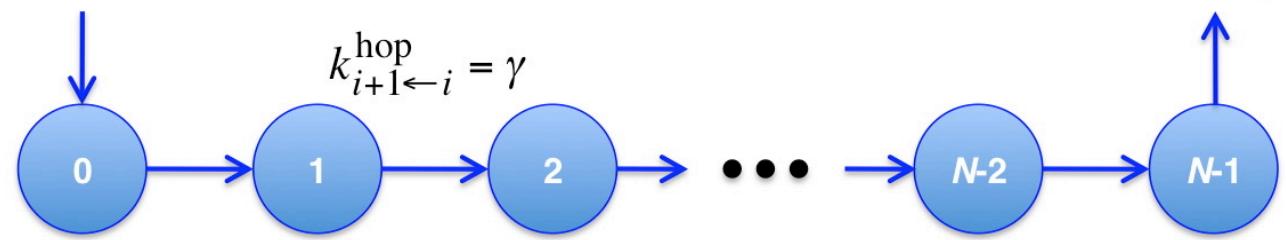


Electric current

$$\begin{aligned}
 & 8.99 \times 10^6 (1/s) \times 1.602 \times 10^{-19} (C) \\
 & = 1.44 \times 10^{-12} (C/s) \\
 & = 1.44 (\text{pA})
 \end{aligned}$$

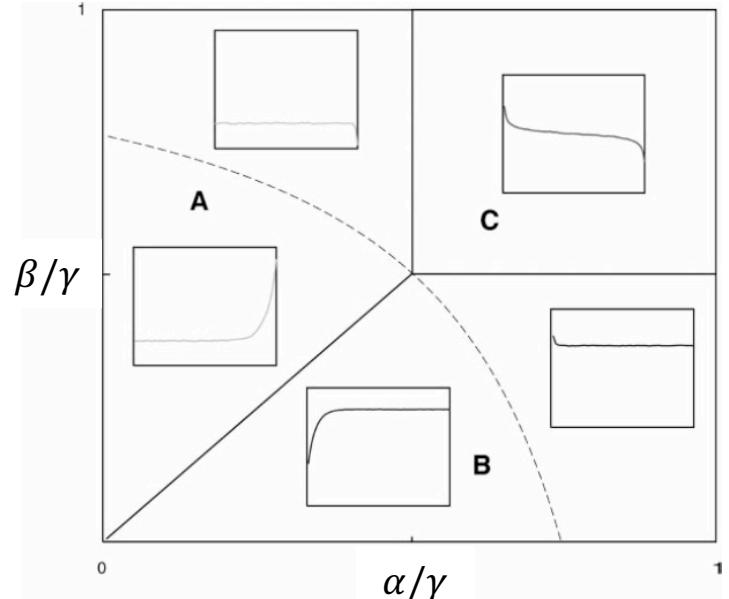
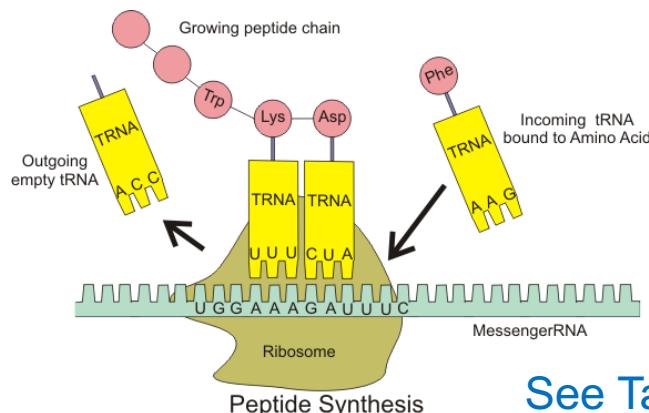
# Asymmetric Simple Exclusion Process

- Linear chain of  $N$  molecules
- *Reduction* can occur only at molecule 0 with  $k^{\text{red}} = \alpha$  (1/s)
- *Oxidation* can occur only at molecule  $N-1$  with  $k^{\text{ox}} = \beta$  (1/s)
- *Hopping* can occur from molecule  $i$  to  $i+1$  ( $i \in [0, N-2]$ ) with  $k_{i+1 \leftarrow i}^{\text{hop}} = \gamma$  (1/s)



**ASEP:**  
“Ising model of  
nonequilibrium  
statistical physics”

- Nonequilibrium phase transition from low-density (LD) to high-density (HD) phase with increasing  $\alpha/\beta$
- Applications in traffic flow and ribosome motion on mRNA during translation



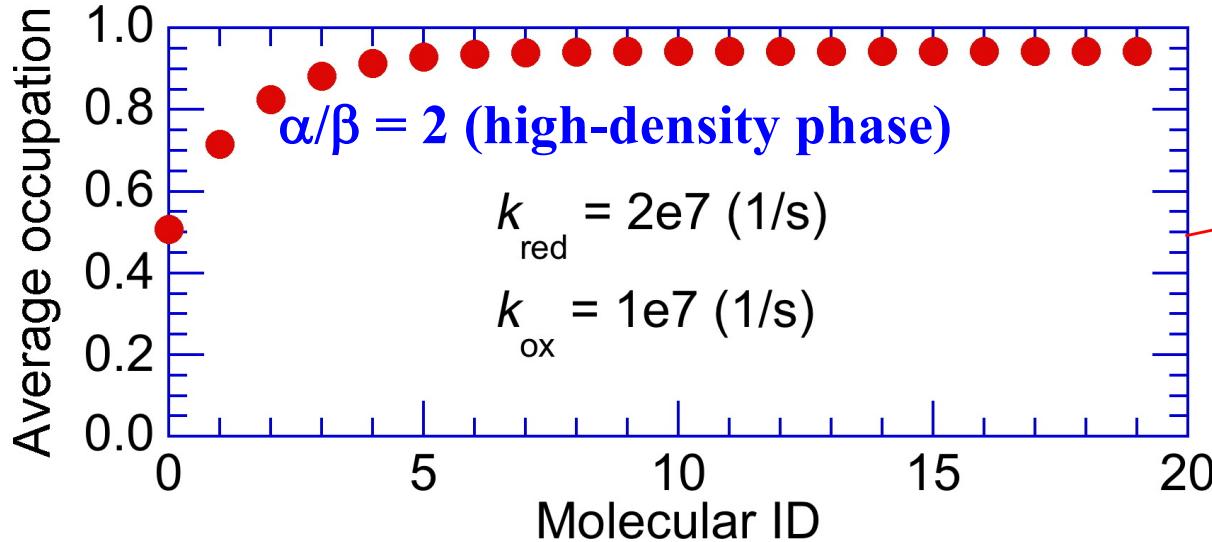
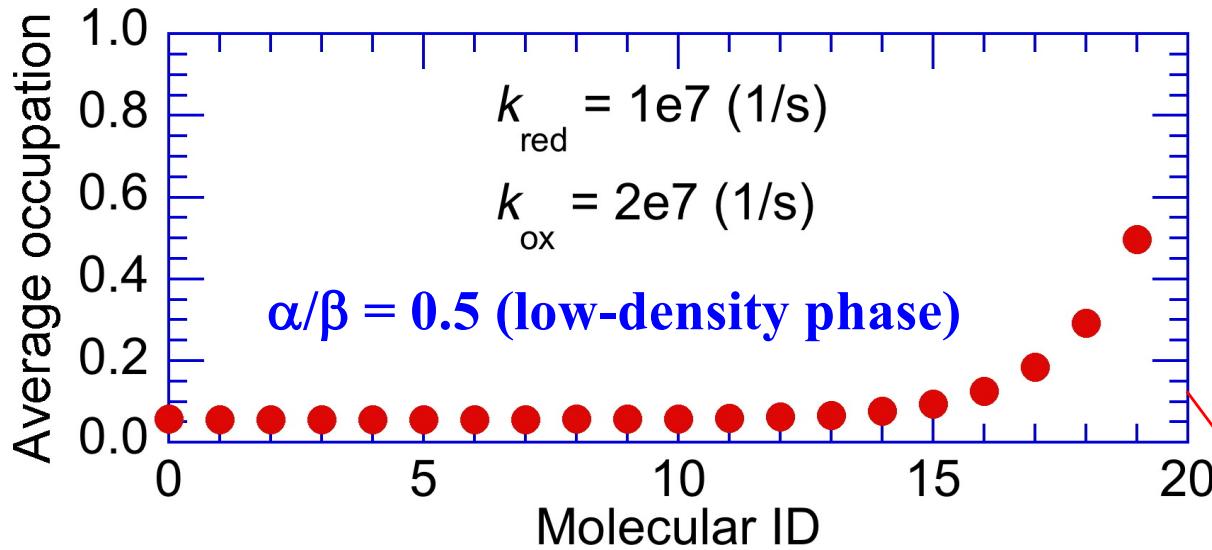
A. Shadschneider, *Physica A* 285, 101 ('00)

See [Taming nonequilibrium statistics & cytoskeletal traffic](#)

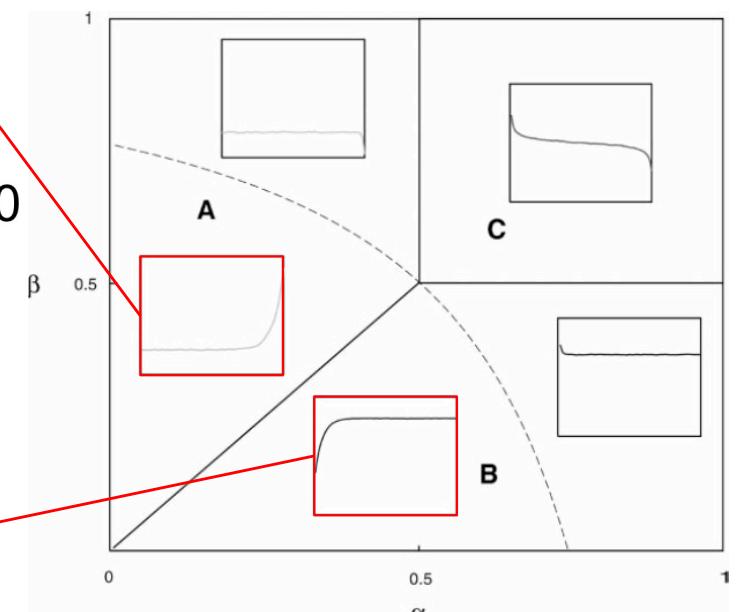
# ASEP Occupation Profile

## KMC simulation results

$N = 20; k_{\text{hop}} = 1\text{e}9 \text{ (1/s)}; \text{Max\_step} = 10^6$



Stationarity:  
 $k_{\text{red}} \times (1 - \text{occ}[0]) = k_{\text{ox}} \times \text{occ}[N-1]$

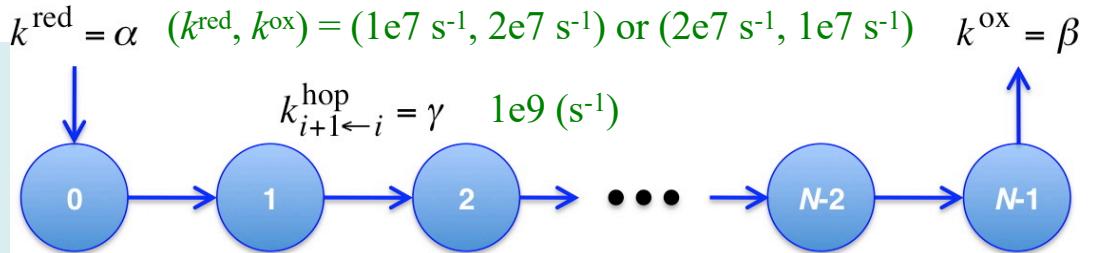


# Algorithm for KMC Simulation of ASEP

```

 $k^{\text{red}} = \alpha$  ( $k^{\text{red}}, k^{\text{ox}}$ ) = (1e7 s-1, 2e7 s-1) or (2e7 s-1, 1e7 s-1)  $k^{\text{ox}} = \beta$ 
occ[i]  $\leftarrow 0$  ( $i = 0$  to  $N-1$ )  $N = 20$ 
nred  $\leftarrow 0$  // number of injected electrons
nox  $\leftarrow 0$  // number of ejected electrons
t  $\leftarrow 0$   $\text{Max\_step} = 10^6$ 

```



```
for step  $\leftarrow 1$  to Max_step // Max_step = total number of KMC steps
```

```
r  $\leftarrow 0$  // Compute total escape rate
```

```
for i  $\leftarrow 0$  to  $N-1$ 
```

```
    r += (rate_occ[i][0] = rate[i][0]*(1-occ[i]))
```

```
    r += (rate_occ[i][1] = rate[i][1]*occ[i])
```

```
    for k  $\leftarrow 1$  to lsngb[i][0]
```

```
        r += (rate_occ[i][k+1] = rate[i][k+1]*(1-occ[lsngb[i][k]])*occ[i]))
```

```
t = ln(rand()/RAND_MAX)/r // Advance time
```

```
rth  $\leftarrow r * \text{rand}() / \text{RAND\_MAX}$  // Pick the next state
```

```
racc  $\leftarrow 0$ 
```

```
for i  $\leftarrow 0$  to  $N-1$ 
```

```
    if (rth < (racc += rate_occ[i][0])) // reduction occurs
```

```
        occ[i]  $\leftarrow 1$ ; print t, ++nred, nox; break
```

```
    else if (rth < (racc += rate_occ[i][1])) // oxidation occurs
```

```
        occ[i]  $\leftarrow 0$ ; print t, nred, ++nox; break
```

```
    else
```

```
        for k  $\leftarrow 1$  to lsngb[i][0]
```

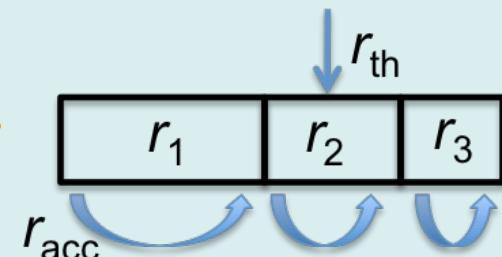
```
            if (rth < (racc += rate_occ[i][k+1])) // hopping from i to k-th neighbor occurs
```

```
                occ[lsngb[i][k]]  $\leftarrow 1$ ; occ[i]  $\leftarrow 0$ ; break
```

```
    if (rth < racc) break
```

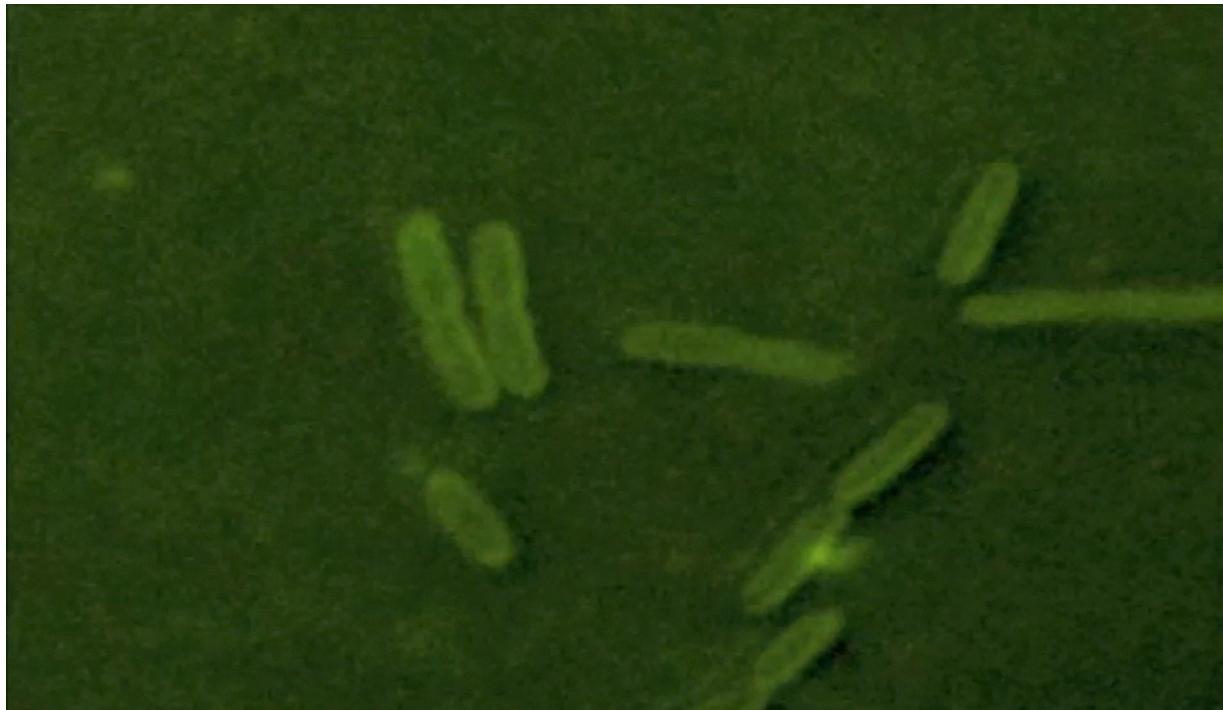
$$r = \sum_{\text{event}} r_{\text{event}}$$

$$\Delta t = -\ln(u_{\text{random}})/r$$



# Application: Bacterial Nanowires

- Electron transfer (ET) governs all known energy-conversion (redox) processes in biology
- A remarkable example is the recent discovery of rapid ET along bacterial nanowires produced by *Shewanella oneidensis* MR-1



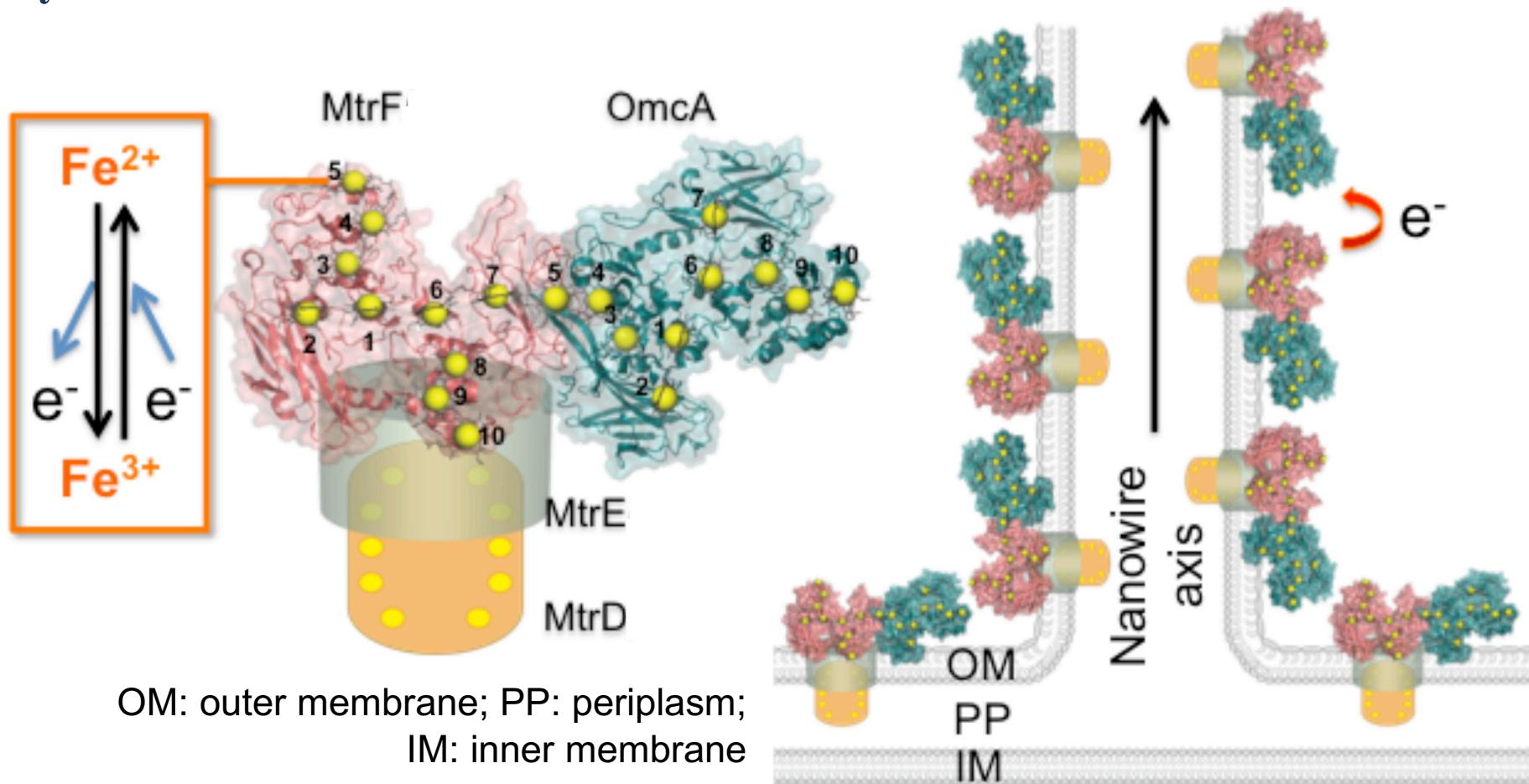
*Shewanella* emitting electrically conducting nanowires



S. Pirbadian *et al.*, PNAS 111, 12883 ('14)

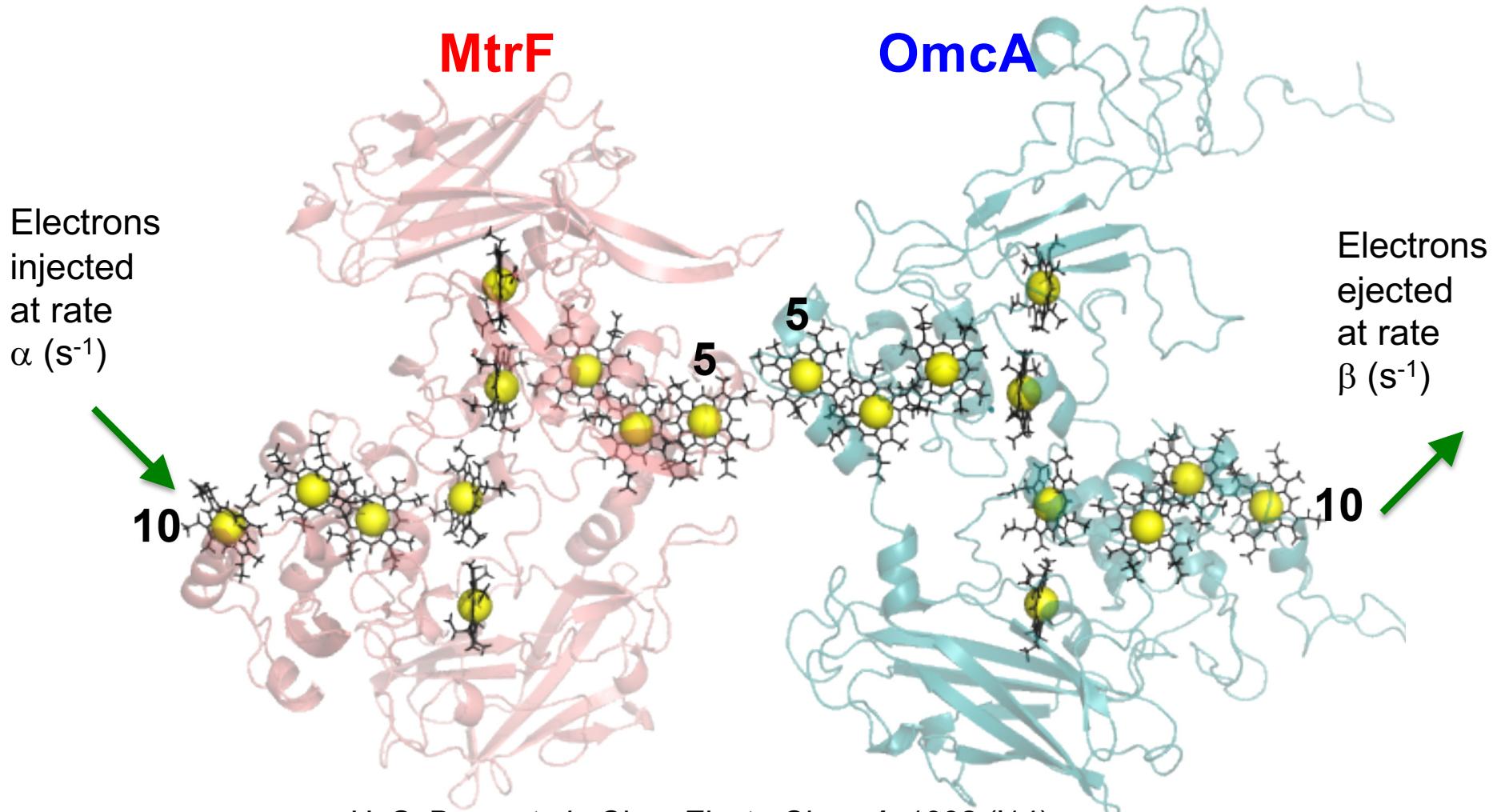
# Scientific Problem & Research Goal

- Outer-membrane cytochromes, MtrF & OmcA, are hypothesized media for ET, but how they are assembled into a conducting complex remains a mystery
- **Goal:** Determine the structure of MtrF-OmcA complex & visualize ET dynamics in it to understand electric conduction mechanisms



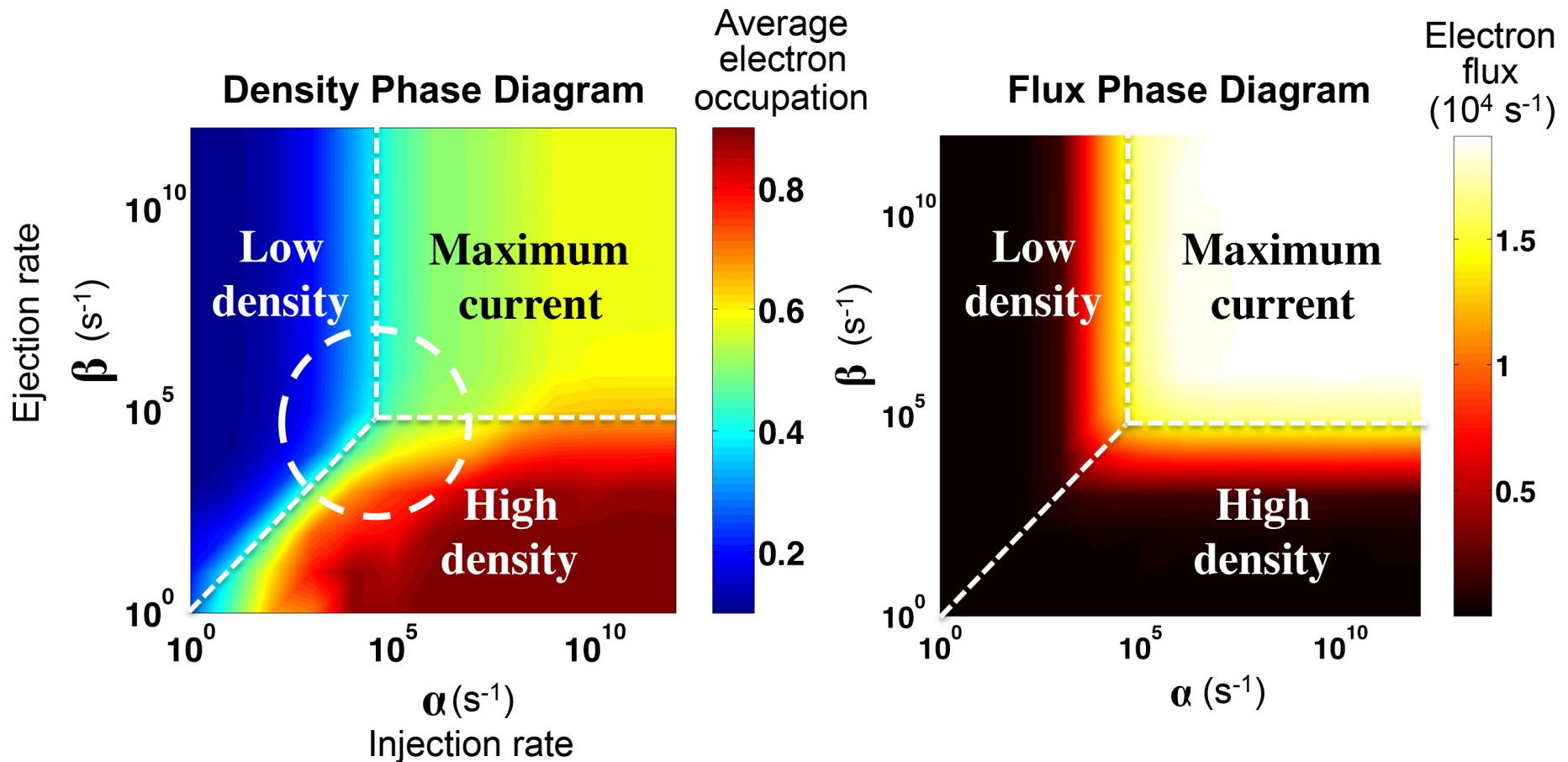
# Result: Complex Structure

## Top-ranked MtrF-OmcA complex structure



- H. S. Byun *et al.*, *ChemElectroChem* **1**, 1932 ('14)  
C. M. Nakano *et al.*, *Comput. Phys. Commun.* **193**, 1 ('15)  
C. M. Nakano *et al.*, *J. Mol. Graph. Model.* **65**, 94 ('16)  
T. Wei *et al.*, *J. Phys. Chem. Lett.* **7**, 929 ('16)  
H. Byun *et al.*, *Comput. Phys. Commun.* **219**, 246 ('17)

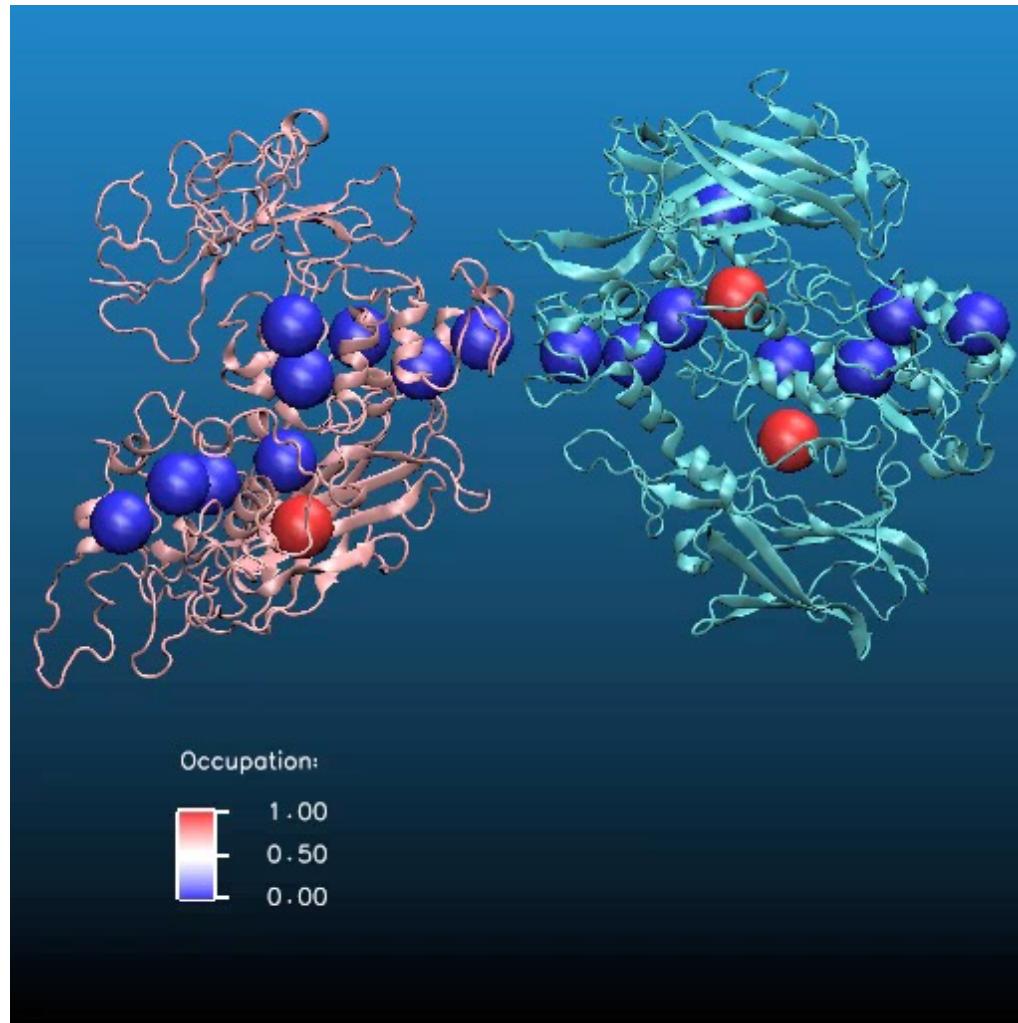
# Result: ET Phase Diagram



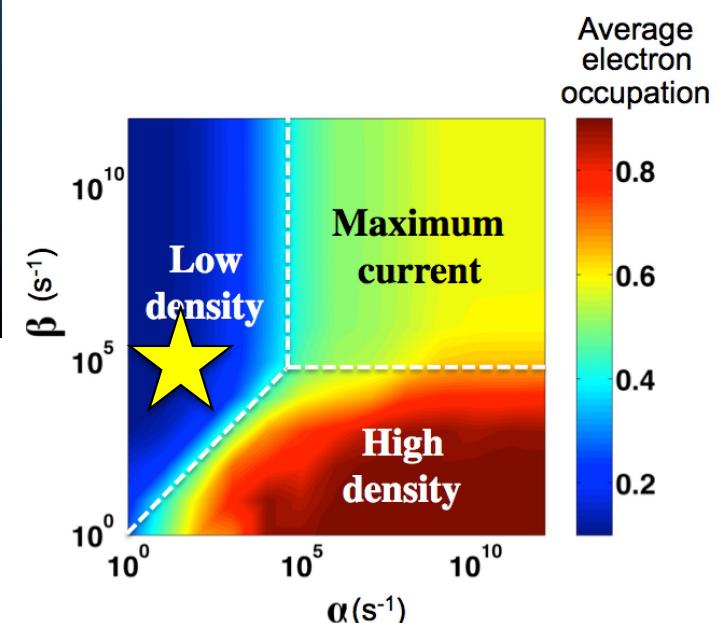
- KMC results exhibit a nonequilibrium phase transition from low-density to high-density phases for increased ratio of electron injection rate ( $\alpha$ ) to ejection rate ( $\beta$ )
- When both  $\alpha$  &  $\beta$  exceed the smallest  $k_{ij}$ , another transition to the maximum-current phase was found
- Observed respiration rates ( $10^3\text{-}10^4 \text{ s}^{-1}$ ) indicate that “life operates around the triple phase junction,” thus a small change in the electrochemical environment effectively triggers a large electric response

# Animation: Low-Density Phase

Electron  
injection  
rate:  
 $\alpha = 10^2 \text{ s}^{-1}$



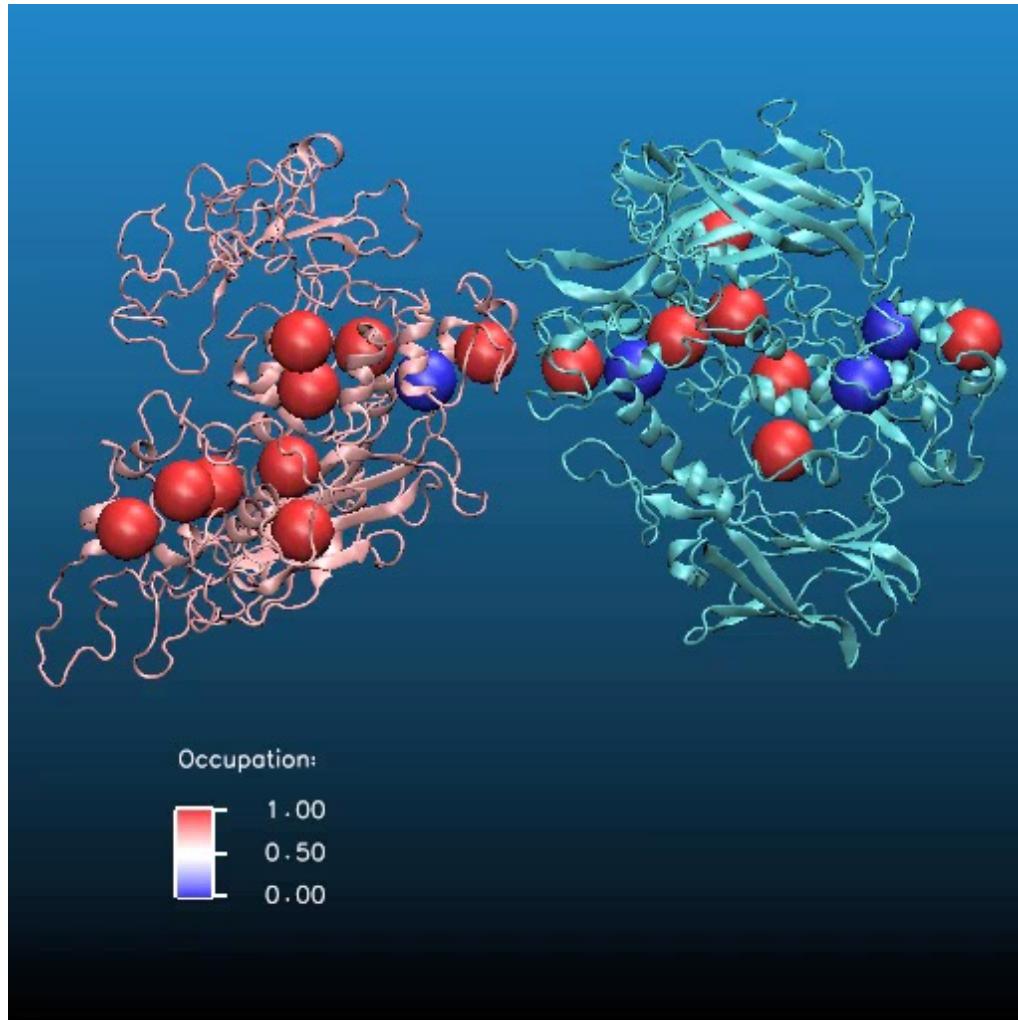
Electron  
ejection  
rate:  
 $\beta = 10^5 \text{ s}^{-1}$



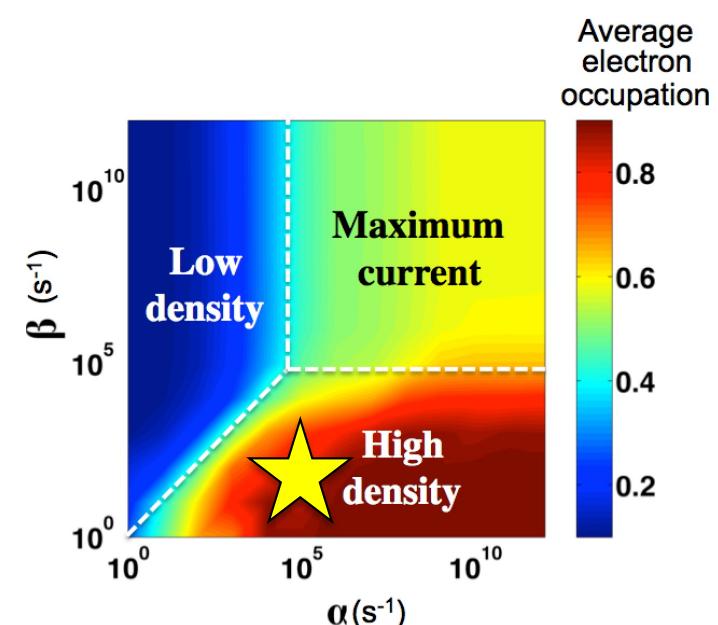
- Electron flow is limited by the small number of electrons

# Animation: High-Density Phase

Electron  
injection  
rate:  
 $\alpha = 10^5 \text{ s}^{-1}$



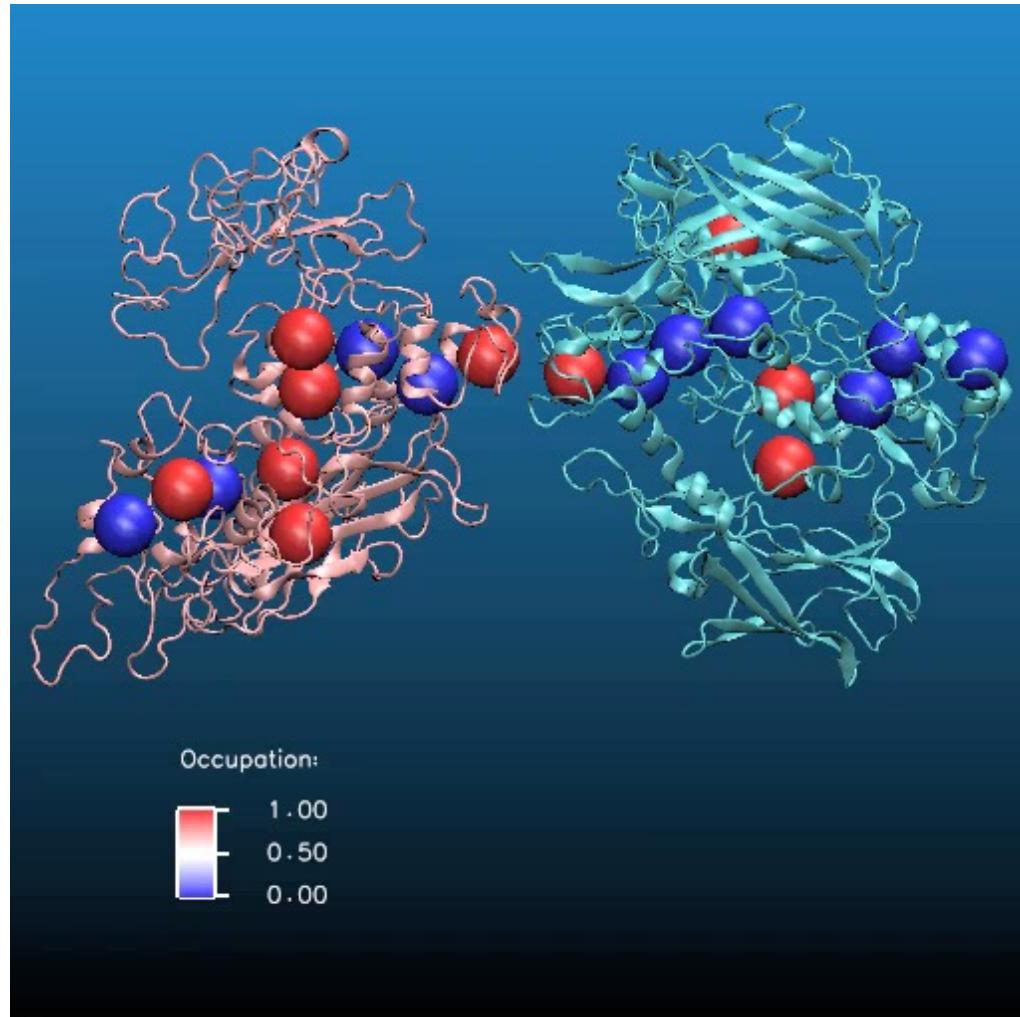
Electron  
ejection  
rate:  
 $\beta = 10^2 \text{ s}^{-1}$



- Electron flow is limited by the congestion of electrons

# Animation: Maximum-Current Phase

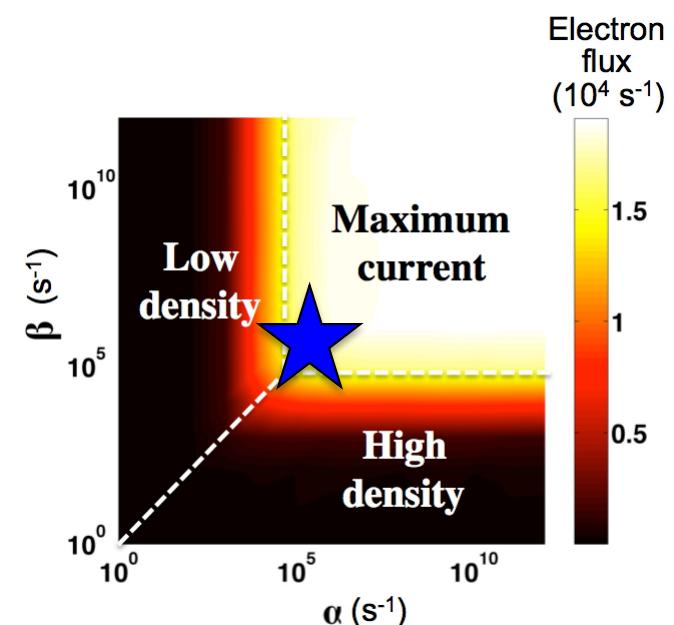
Electron  
injection  
rate:  
 $\alpha = 10^5 \text{ s}^{-1}$



Electron  
ejection  
rate:  
 $\beta = 10^5 \text{ s}^{-1}$

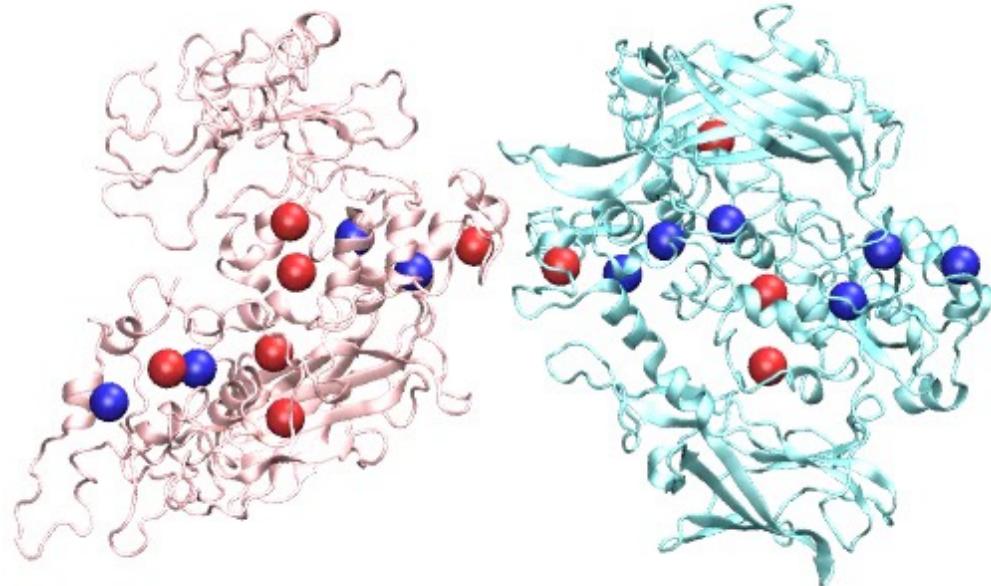


- Large electric current is facilitated by balanced electron injections & ejections
- Life operates around the triple junction

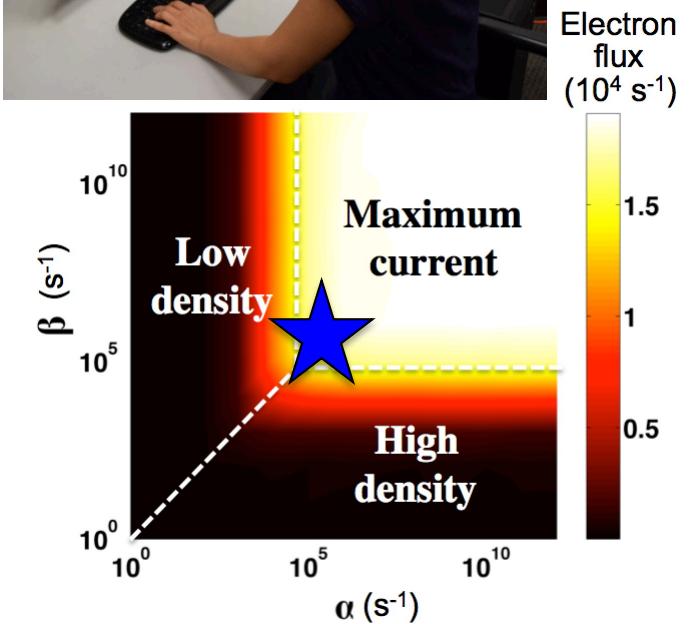
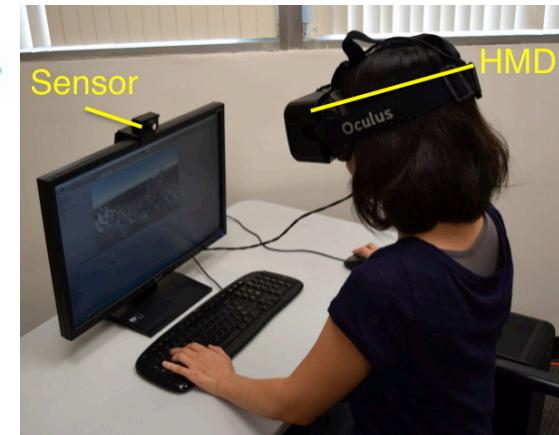


# Animation: Maximum-Current Phase

Electron  
injection  
rate:  
 $\alpha = 10^5 \text{ s}^{-1}$



Electron  
ejection  
rate:  
 $\beta = 10^5 \text{ s}^{-1}$



- Each electron-transfer event is represented by a directed edge

# Navigation in Virtual Reality

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C. M. Nakano *et al.*, *J. Mol. Graph. Model.* **65**, 94 ('16)

# GEARS

**GEARS (Game-engine-assisted research platform for scientific computing)**  
allows users to develop & perform immersive & interactive simulations within  
commodity virtual reality (VR) platforms



Oculus Rift + Leap Motion



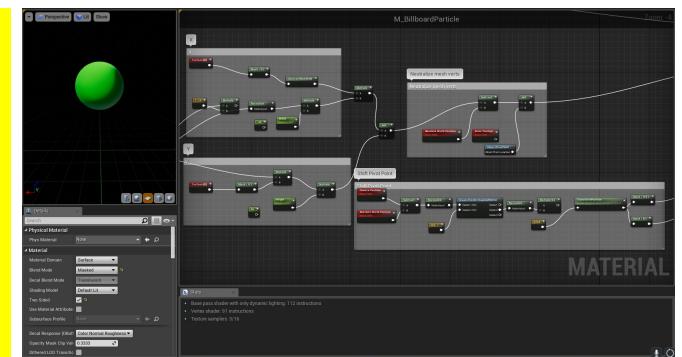
HTC Vive



Photoexcitation in MoSe<sub>2</sub>

## Accomplishments:

- Implemented simulation workflows in VR-capable Unity & Unreal game engines
- Enhanced interaction utilities, *e.g.*, virtual confocal microscopy
- Developed an interface with community MD software, LAMMPS, & demonstrated immersive & interactive 250K-atom simulations on desktop

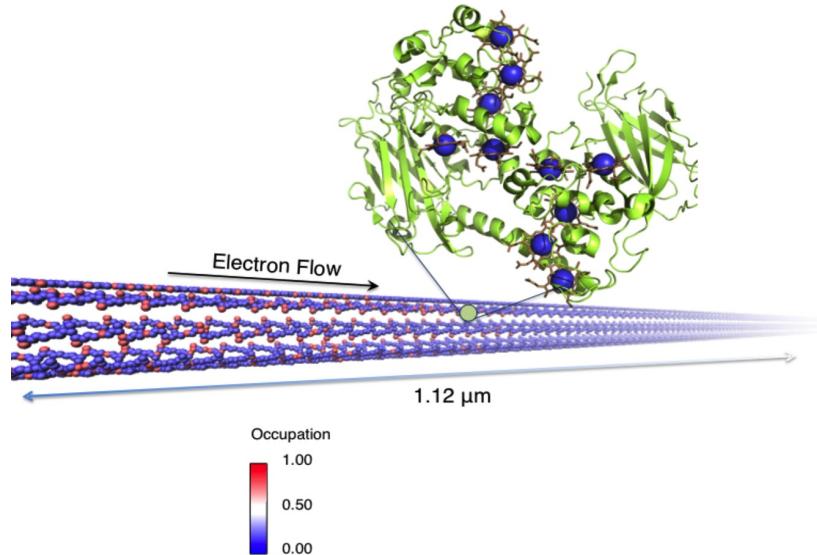


LammpsVR editor

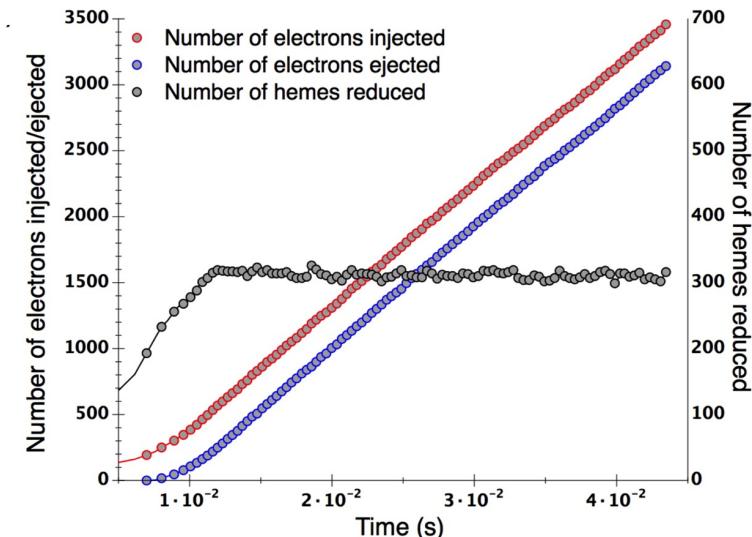


# Scalable Parallel KMC

- 93.5% of perfect speedup for a 4.2 billion-heme system on 1,024 Intel Xeon processors at USC Center for High Performance Computing



Computer Physics Communications 219 (2017) 246–254

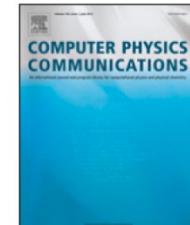


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A derivation and scalable implementation of the synchronous parallel kinetic Monte Carlo method for simulating long-time dynamics



CrossMark

Hye Suk Byun <sup>a</sup>, Mohamed Y. El-Naggar <sup>a,b,c</sup>, Rajiv K. Kalia <sup>a,d,e,f</sup>, Aiichiro Nakano <sup>a,b,d,e,f,\*</sup>,  
Priya Vashishta <sup>a,d,e,f</sup>