# Kinetic Monte Carlo Simulation of Electron Transfer

**Aiichiro Nakano**

***Collaboratory for Advanced Computing & Simulations***
***Dept. of Computer Science, Dept. of Physics & Astronomy,***
***Dept. of Chemical Engineering & Materials Science***
***Dept. of Biological Sciences***
***University of Southern California***

**Email: anakano@usc.edu**

# Biological Electron Transfer

## Filamentous bacteria transport electrons over centimetre distances

Christian Pfeffer[1], Steffen Larsen[2], Jie Song[3], Mingdong Dong[3], Flemming Besenbacher[3], Rikke Louise Meyer[2,3], Kasper Urup Kjeldsen[1], Lars Schreiber[1], Yuri A. Gorby[4], Mohamed Y. El-Naggar[5], Kar Man Leung[4,5], Andreas Schramm[1,2], Nils Risgaard-Petersen[1] & Lars Peter Nielsen[1,2]

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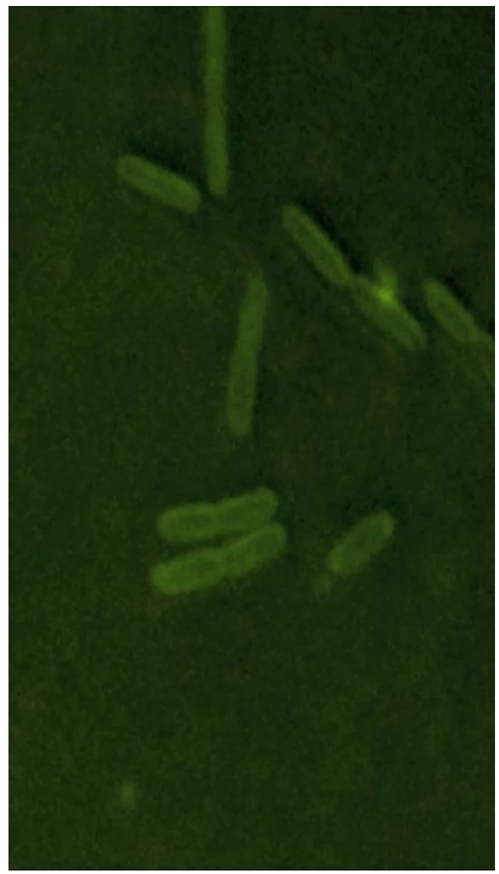
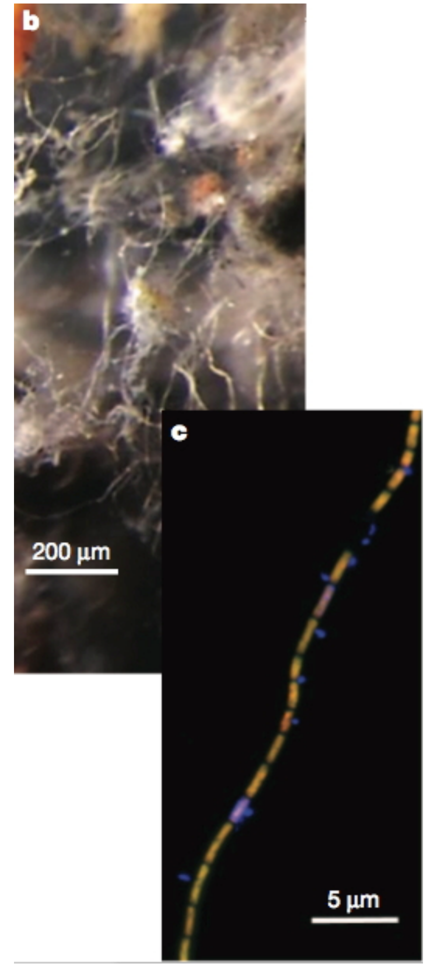
**Oxygen consumption in marine sediments is often coupled to the oxidation of sulphide generated by degradation of organic matter in deeper, oxygen-free layers. Geochemical observations have shown that this coupling can be mediated by electric currents carried by unidentified electron transporters across 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.**

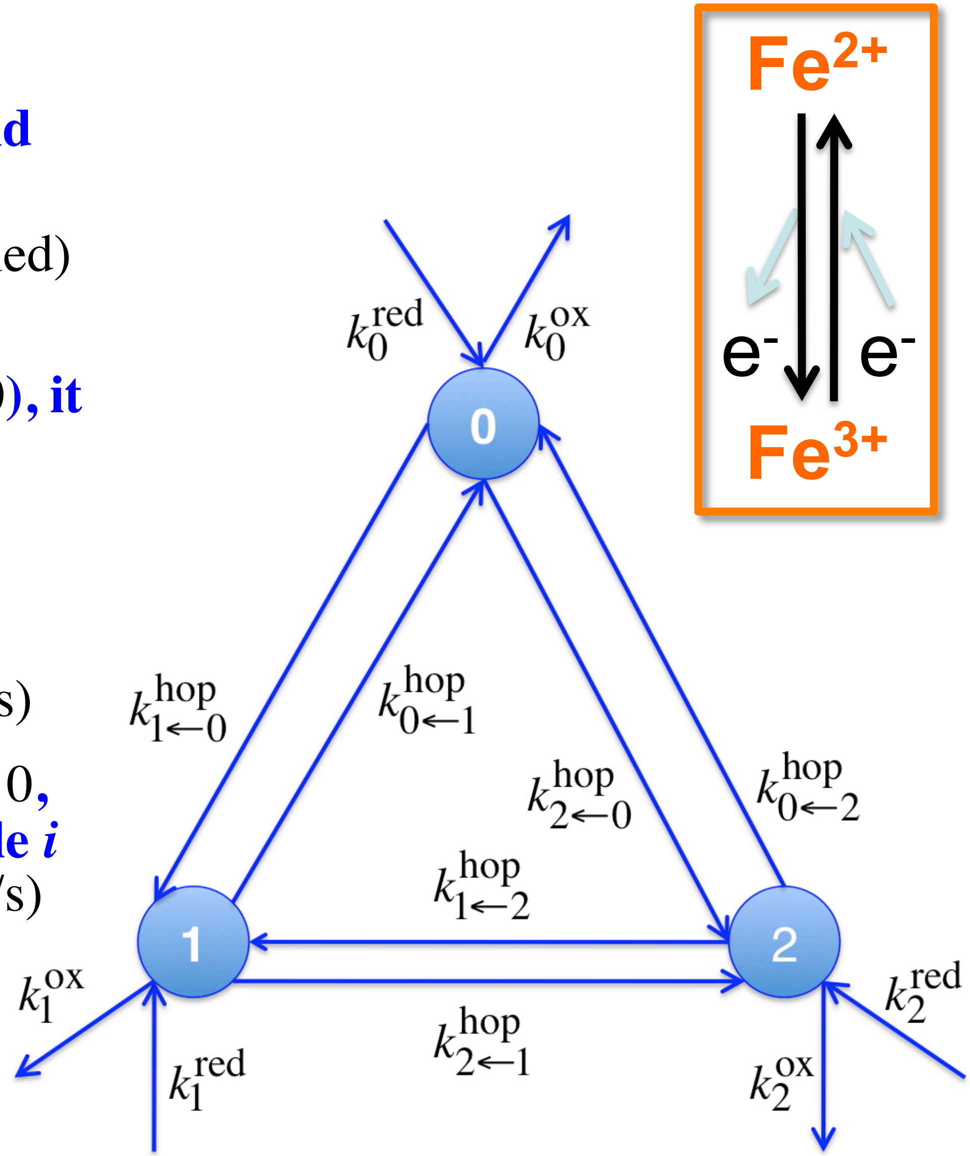




# Model Definition

- **A set of $N$ redox molecules**
- **Each molecule $i \in [0, N\text{-}1]$ 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** $k_i^{\mathrm{red}}$ (1/s)
- ***Oxidation*: If** $occ(i) = 1$**, molecule $i$ can be oxidized (or the electron is ejected from it) at a rate of** $k_i^{\mathrm{ox}}$ (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** $k_{j\leftarrow i}^{\mathrm{hop}}$ (1/s)

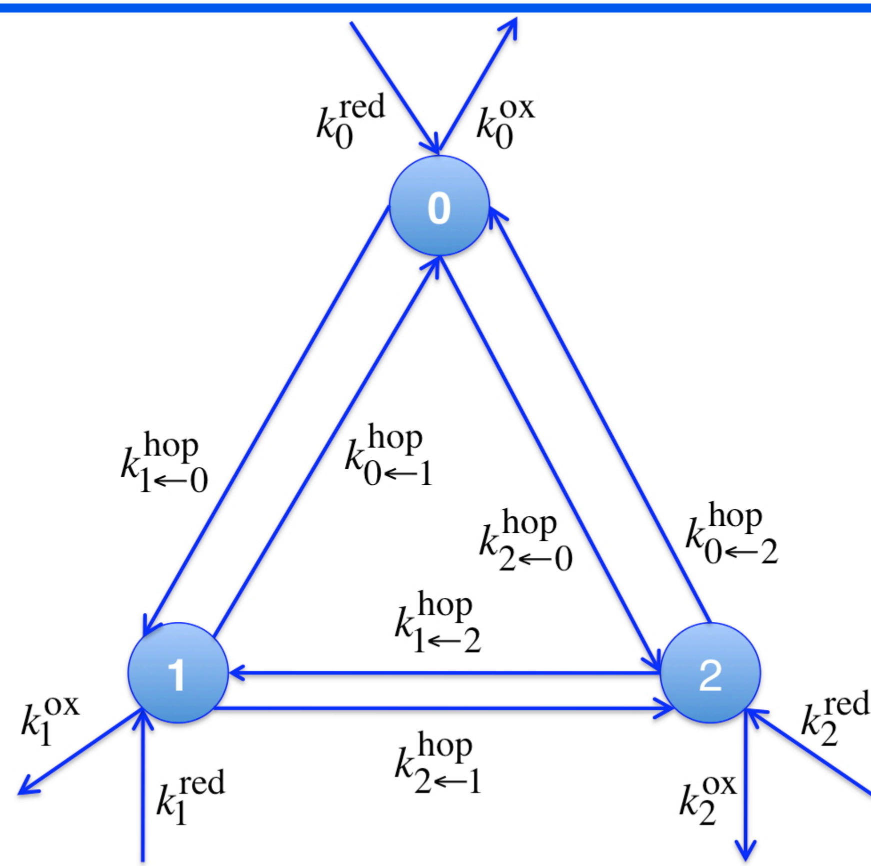


# Molecular Network Topology

- **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 $i$ ($Max\_ngb$ = maximum number of outgoing edges per node)**
- $lsngb[N][Max\_ngb+1]$

  $lsngb[i][0] = ngb(i)$

  $lsngb[i][k]$ = molecular ID of the $k$-th outgoing neighbor of molecule $i$, where $k \in [1, ngb(i)]$




Example: $Max\_ngb = 2$

| $lsngb[i][k]$ | $k = 0$ | 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)**

$$rate[N][Max\_ngb+2]$$
$$\begin{cases} rate[i][0] = k_i^{\text{red}} \\ rate[i][1] = k_i^{\text{ox}} \\ rate[i][k+1] = k_{lsngb[i][k] \leftarrow i}^{\text{hop}} \end{cases}$$

- **Occupation-modified rates (dynamic variables)**

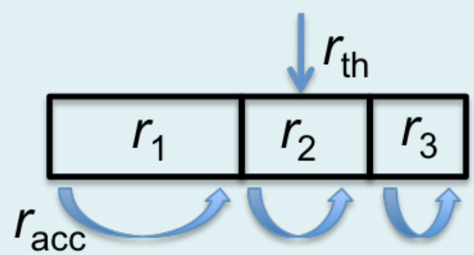
$$rate\_occ[N][Max\_ngb+2]$$
$$\begin{cases} rate\_occ[i][0] = k_i^{\text{red}} \times (1 - occ[i]) \\ rate\_occ[i][1] = k_i^{\text{ox}} \times occ[i] \\ rate\_occ[i][k+1] = k_{lsngb[i][k] \leftarrow i}^{\text{hop}} \times (1 - occ[lsngb[i][k]]) \times occ[i] \end{cases}$$

# Algorithm

```
occ[i] ← 0 (i = 0 to N-1)
n_red ← 0  // number of injected electrons
n_ox ← 0  // number of ejected electrons
t ← 0
for step ← 1 to Max_step  // Max_step = total number of KMC steps
  r ← 0
  for i ← 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 ← 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
  r_th ← r*rand()/RAND_MAX
  r_acc ← 0
  for i ← 0 to N-1
    if (r_th < (r_acc += rate_occ[i][0]) // reduction occurs
        occ[i] ← 1; print t, ++n_red, n_ox; break
    else if (r_th < (r_acc += rate_occ[i][1]) // oxidation occurs
        occ[i] ← 0; print t, n_red, ++n_ox; break
    else
      for k ← 1 to lsngb[i][0]
        if (r_th < (r_acc += rate_occ[i][k+1]) // hopping from i to k-th neighbor occurs
          occ[lsngb[i][k]] ← 1; occ[i] ← 0; break
    if (r_th < r_acc) break
```

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

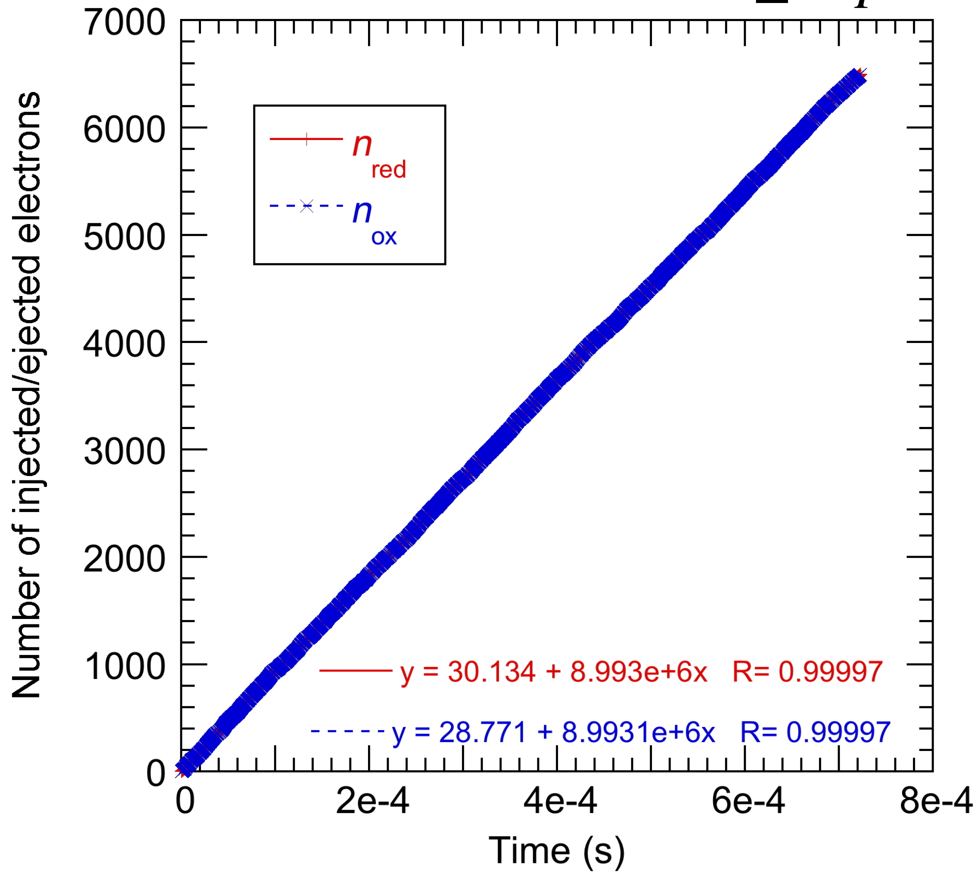
$$\Delta t = -\ln(u_{\mathrm{random}})/r$$

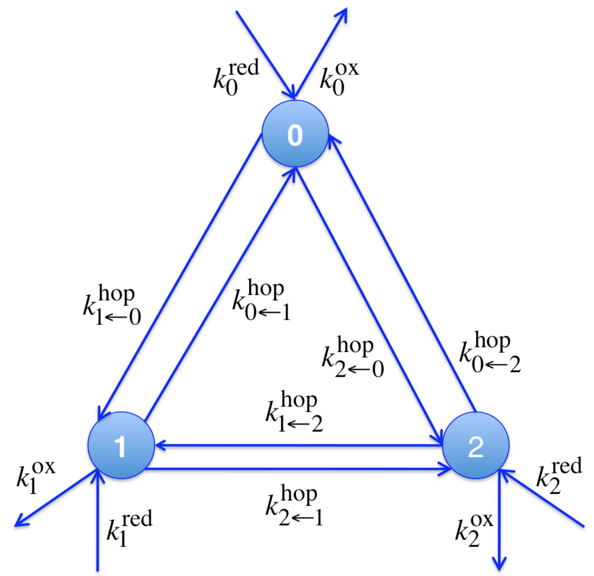


# Example Run

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

$Max\_step = 10^6$



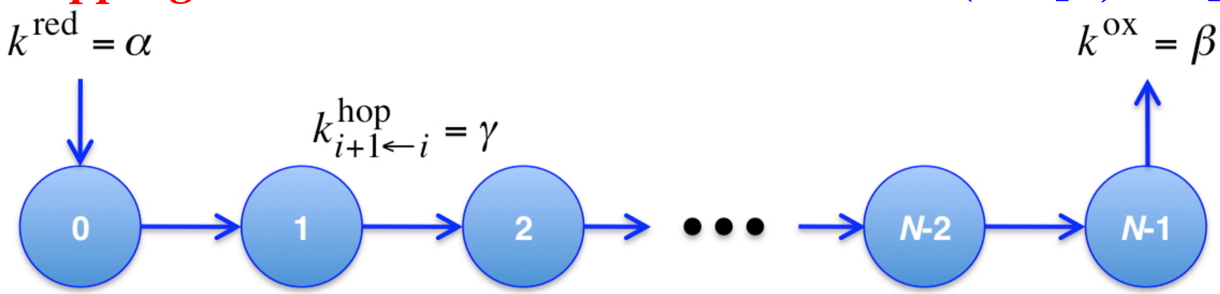




## Electric current

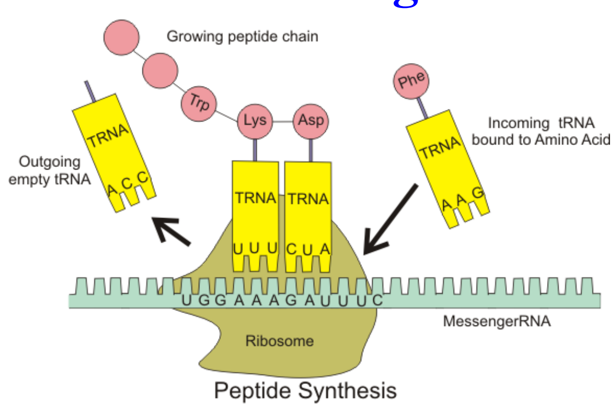
$$8.99 \times 10^6 (1/s) \times 1.602 \times 10^{-19} (C)$$
$$= 1.44 \times 10^{-12} (C/s)$$
$$= 1.44 (pA)$$

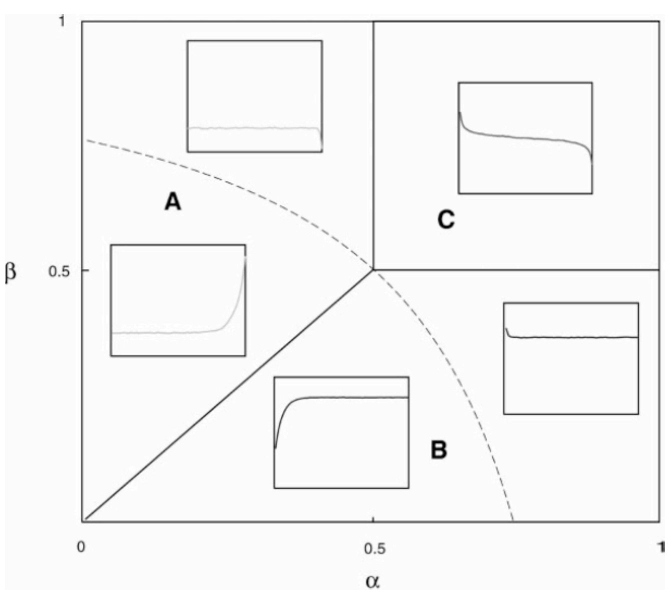
# Asymmetric Simple Exclusion Process

- **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 ($i \in [0, N\text{-}2]$) with $k_{i+1\leftarrow i}^{\text{hop}} = \gamma$ (1/s)**




- **Nonequilibrium phase transition from low-density (LD) to high-density (HD) phase with increasing α/β**
- **Applications in traffic flow and ribosome motion on mRNA during translation**



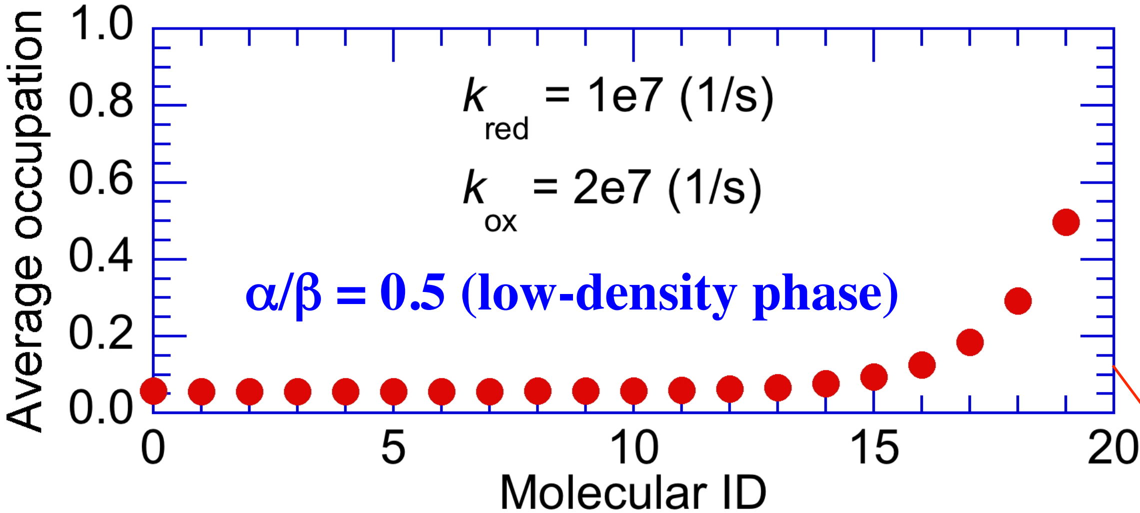



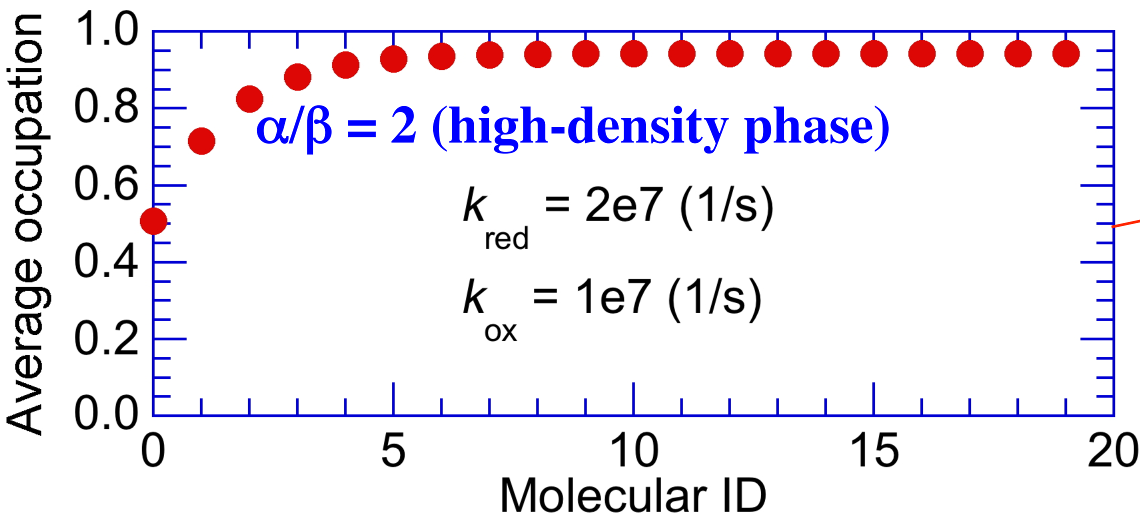

A. Shadschneider, *Physica A* **285**, 101 ('00)

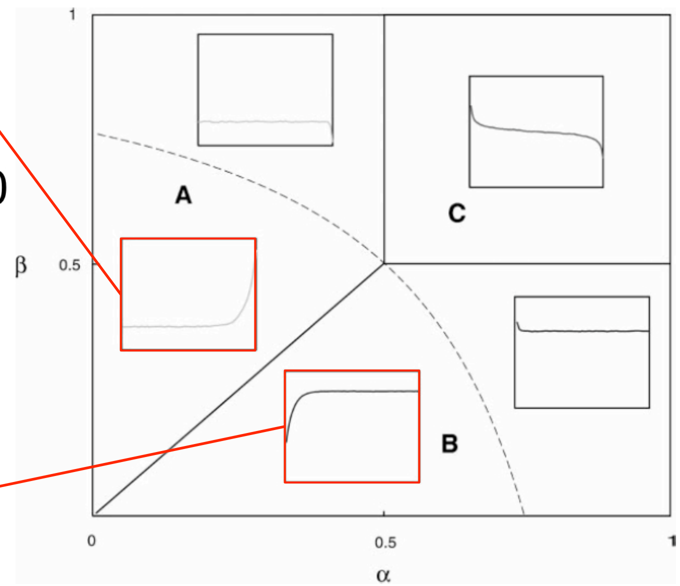
# ASEP Occupation Profile

**KMC simulation results**

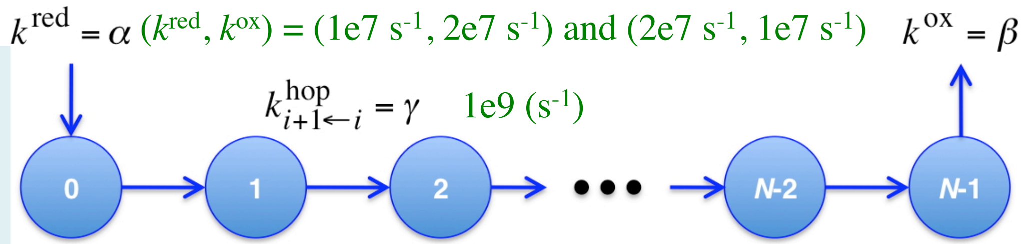
$N = 20$; $k_{hop} = 1e9$ (1/s); $Max\_step = 10^6$



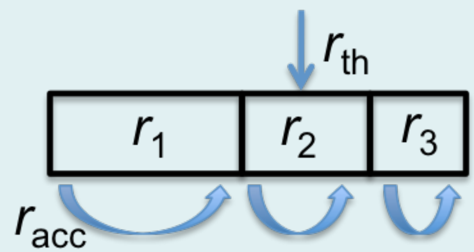
# Algorithm for KMC Simulation of ASEP




```
occ[i] ← 0 (i = 0 to N-1)   N = 20
n_red ← 0  // number of injected electrons
n_ox ← 0  // number of ejected electrons
t ← 0                Max_step = 10^6
for step ← 1 to Max_step  // Max_step = total number of KMC steps
   r ← 0
   for i ← 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 ← 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
   r_th ← r*rand()/RAND_MAX
   r_acc ← 0
   for i ← 0 to N-1
      if (r_th < (r_acc += rate_occ[i][0]) // reduction occurs
         occ[i] ← 1; print t, ++n_red, n_ox; break
      else if (r_th < (r_acc += rate_occ[i][1]) // oxidation occurs
         occ[i] ← 0; print t, n_red, ++n_ox; break
      else
         for k ← 1 to lsngb[i][0]
            if (r_th < (r_acc += rate_occ[i][k+1]) // hopping from i to k-th neighbor occurs
               occ[lsngb[i][k]] ← 1; occ[i] ← 0; break
      if (r_th < r_acc) break
```

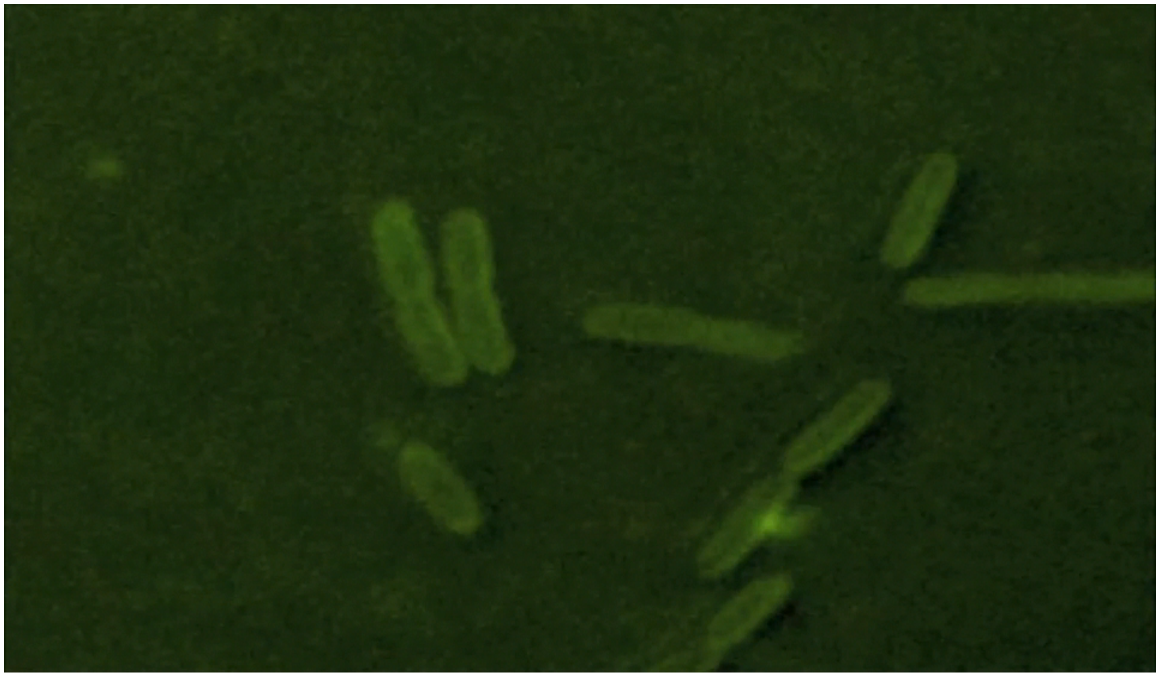
$$r = \sum_{event} r_{event}$$

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



# Motivation: 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**

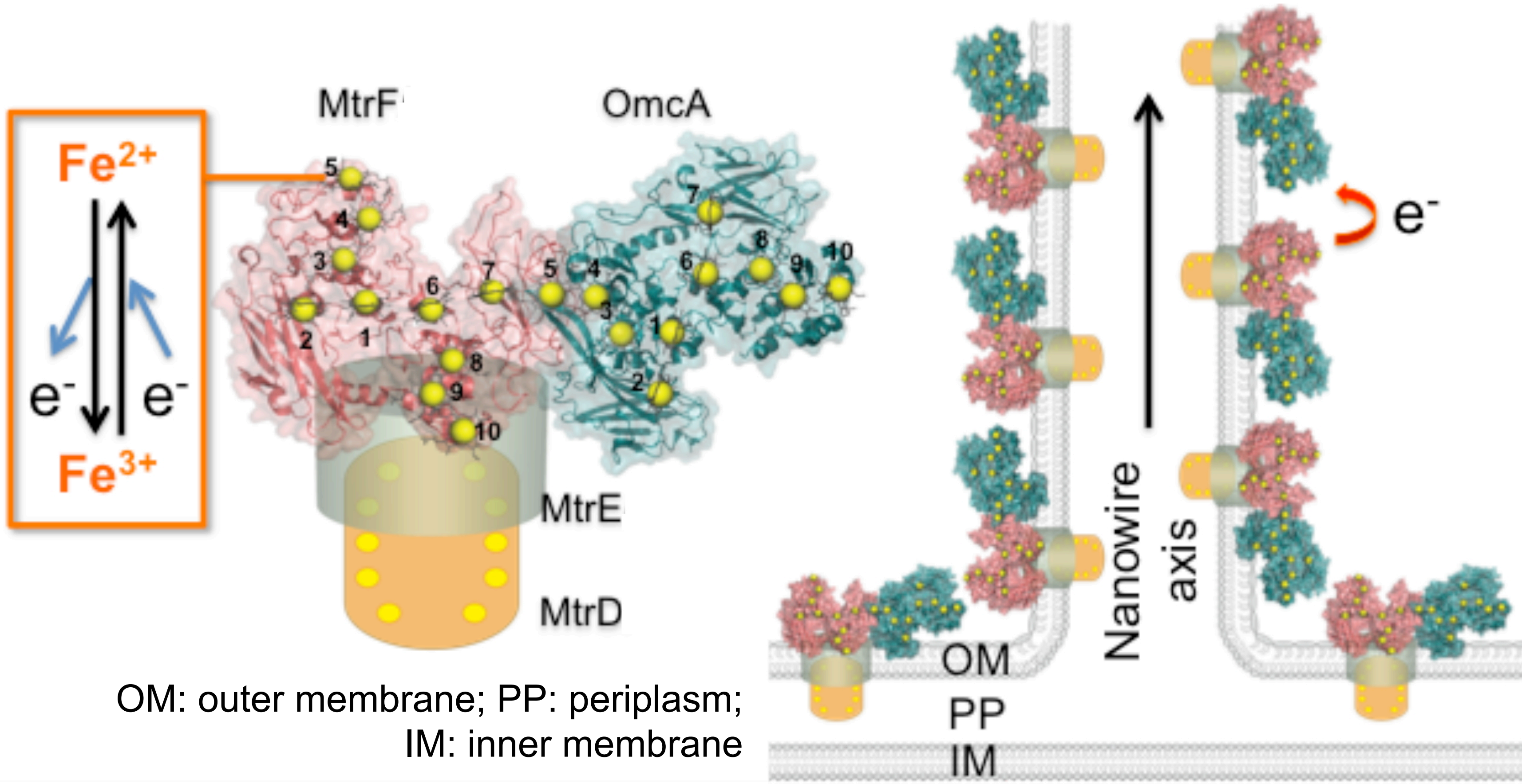


*Shewanella* emitting electrically conducting nanowires


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

# Scientific Problem & Research Goal

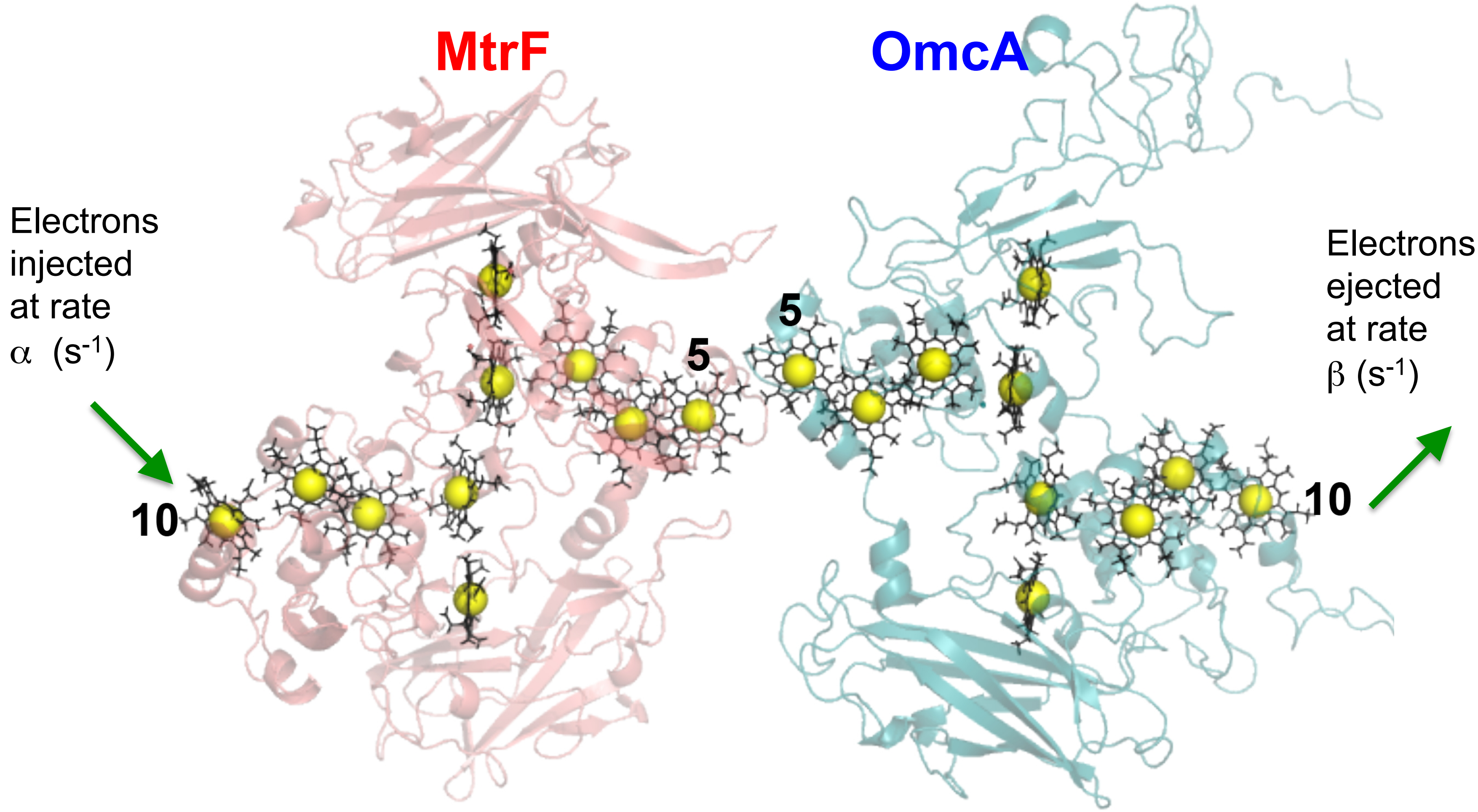
- **Outer-membrane cytochromes, MtrF & OmcA, are hypothesized media for ET, but how they are assembled into a conducting complex remains a mystery**
- ***Goal*: Determine the structure of MtrF-OmcA complex & visualize ET dynamics in it to understand electric conduction mechanisms**




OM: outer membrane; PP: periplasm;
IM: inner membrane

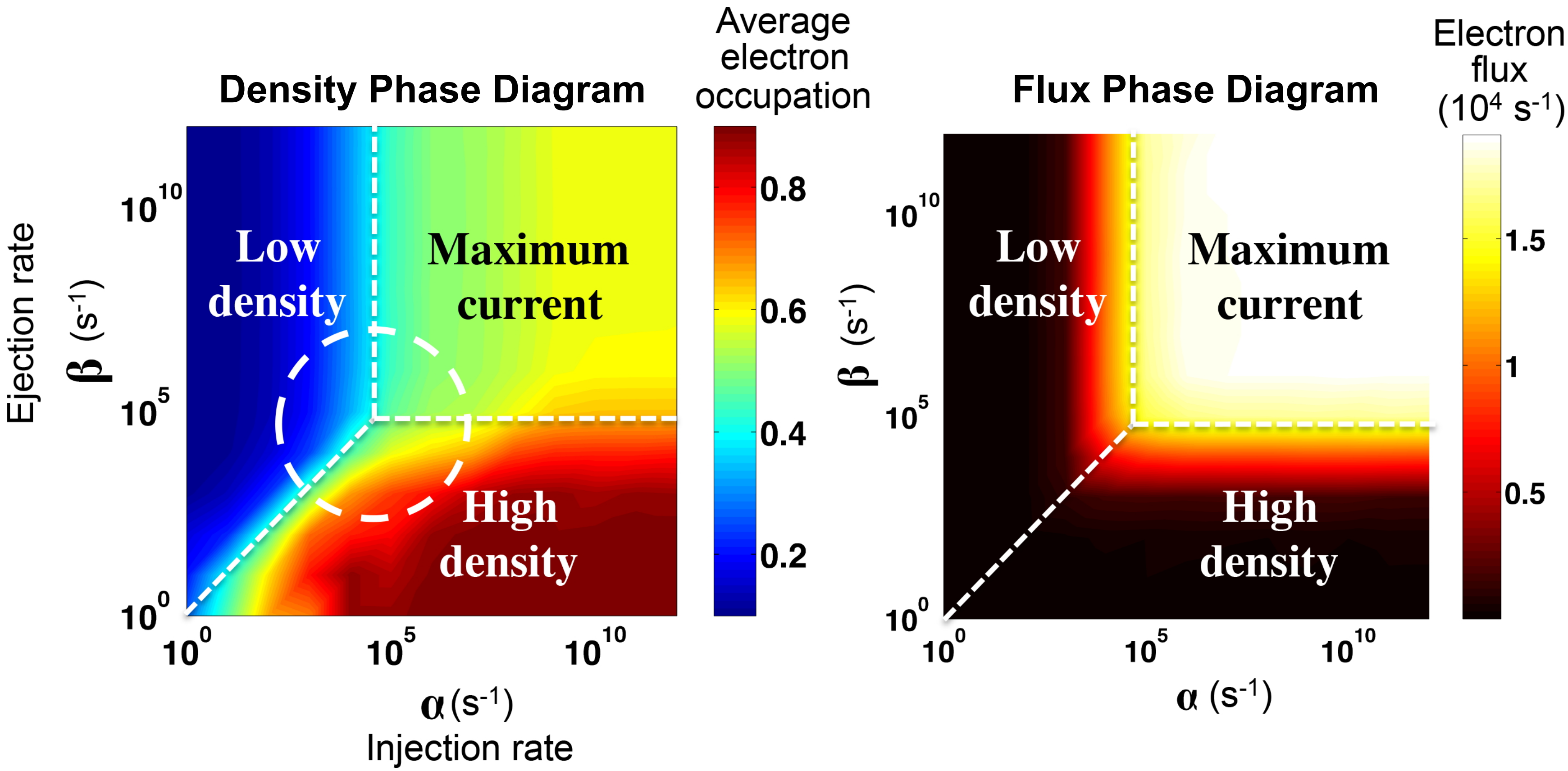
# Result: Complex Structure

## 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)

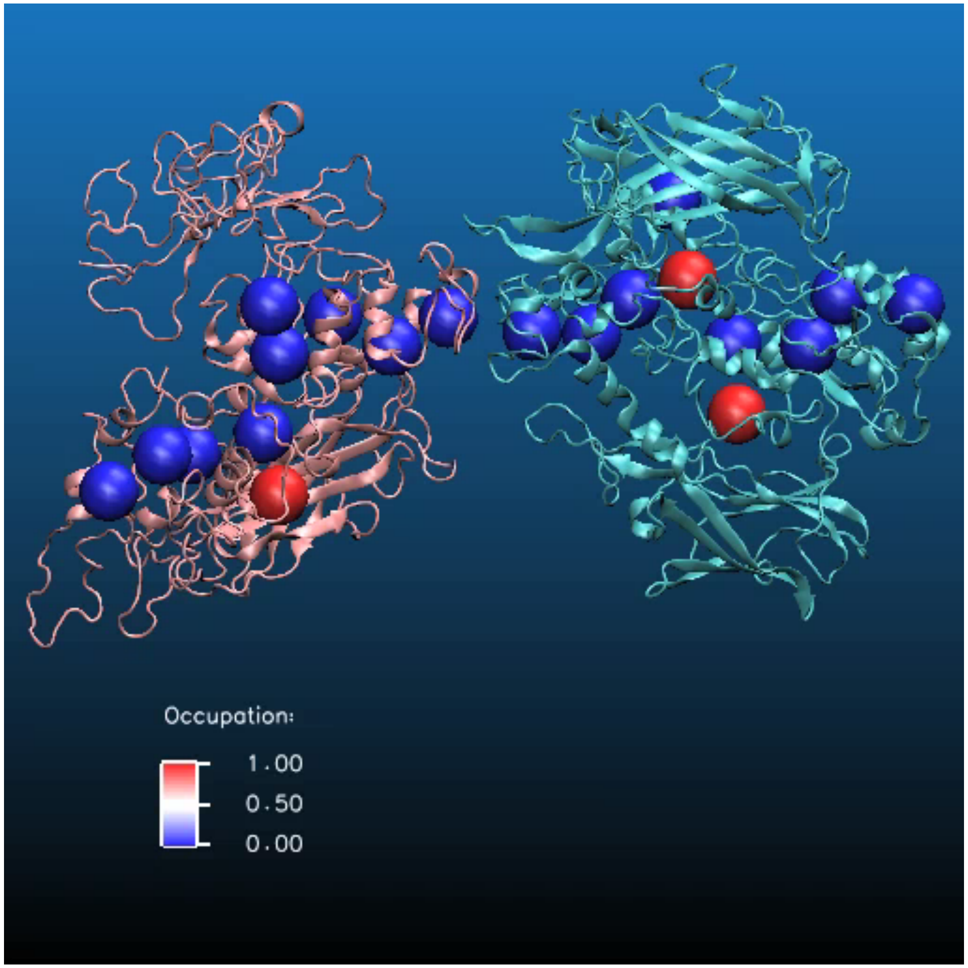
# Result: ET Phase Diagram




- KMC results exhibit a nonequilibrium phase transition from low-density to high-density phases for increased ratio of electron injection rate (α) to ejection rate (β)
- When both α & β exceed the smallest $k_{ij}$, another transition to the maximum-current phase was found
- Observed respiration rates ($10^3$-$10^4$ 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

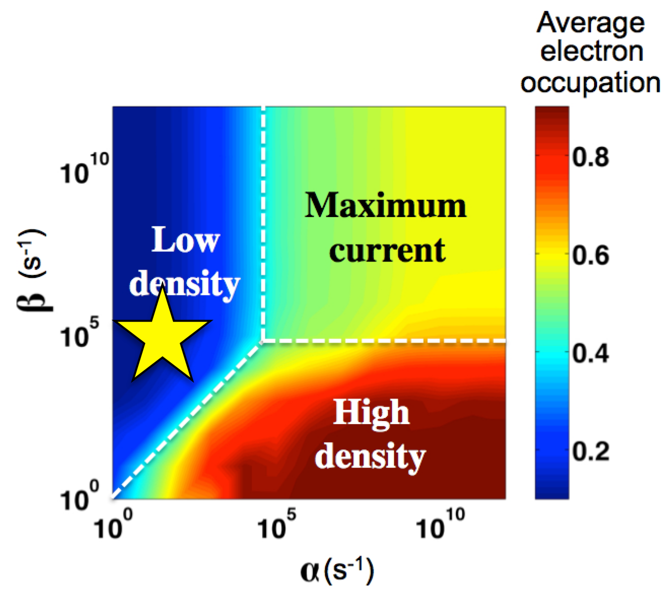
# Animation: Low-Density Phase

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



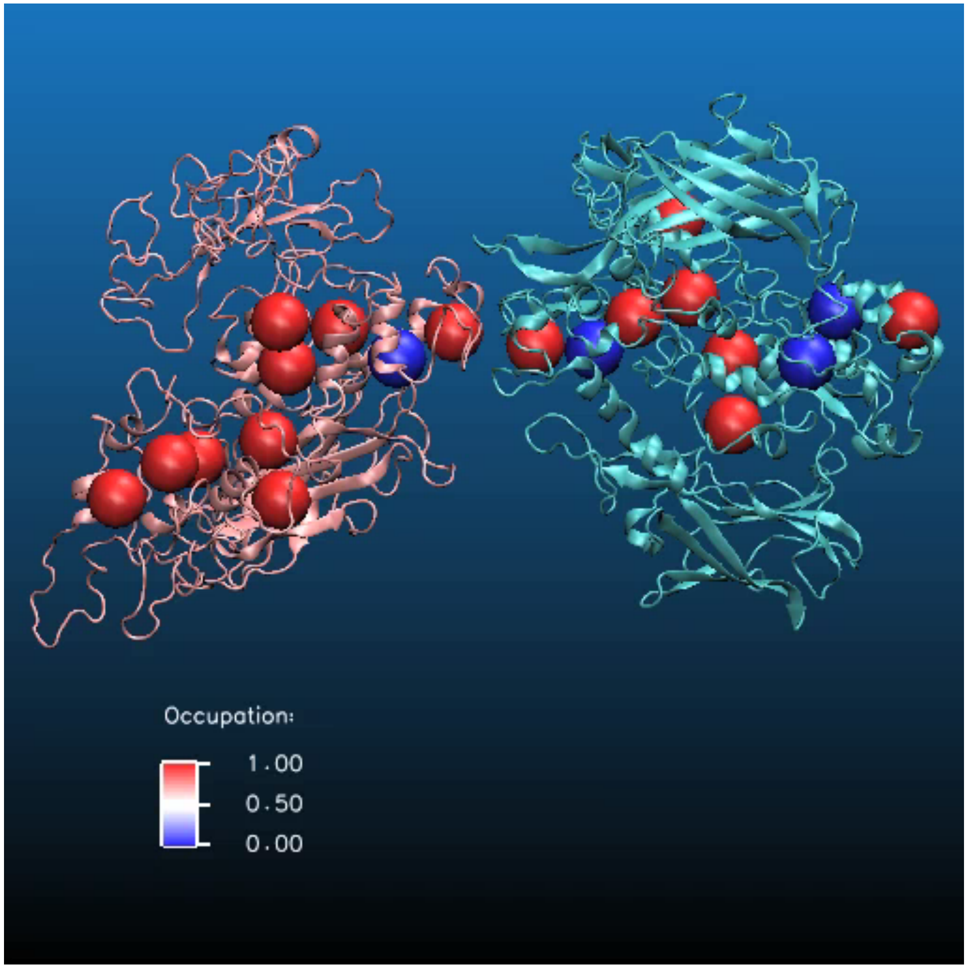

Electron ejection rate: $\beta = 10^5\ s^{-1}$

- Electron flow is limited by the small number of electrons



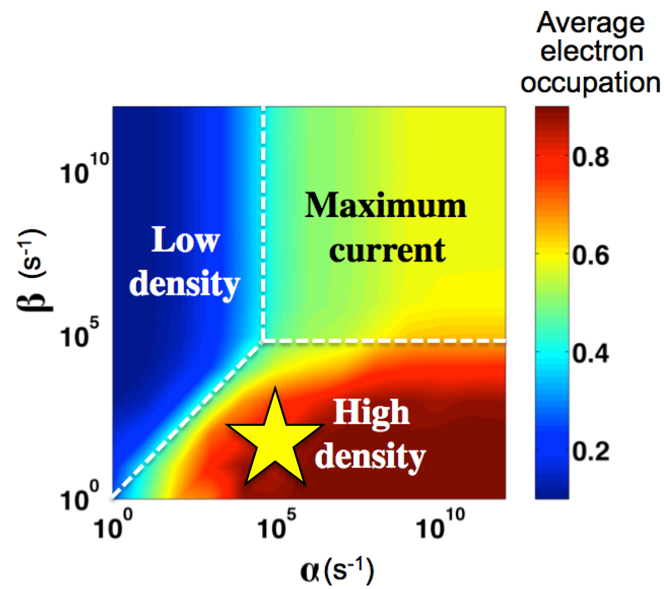
# Animation: High-Density Phase

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



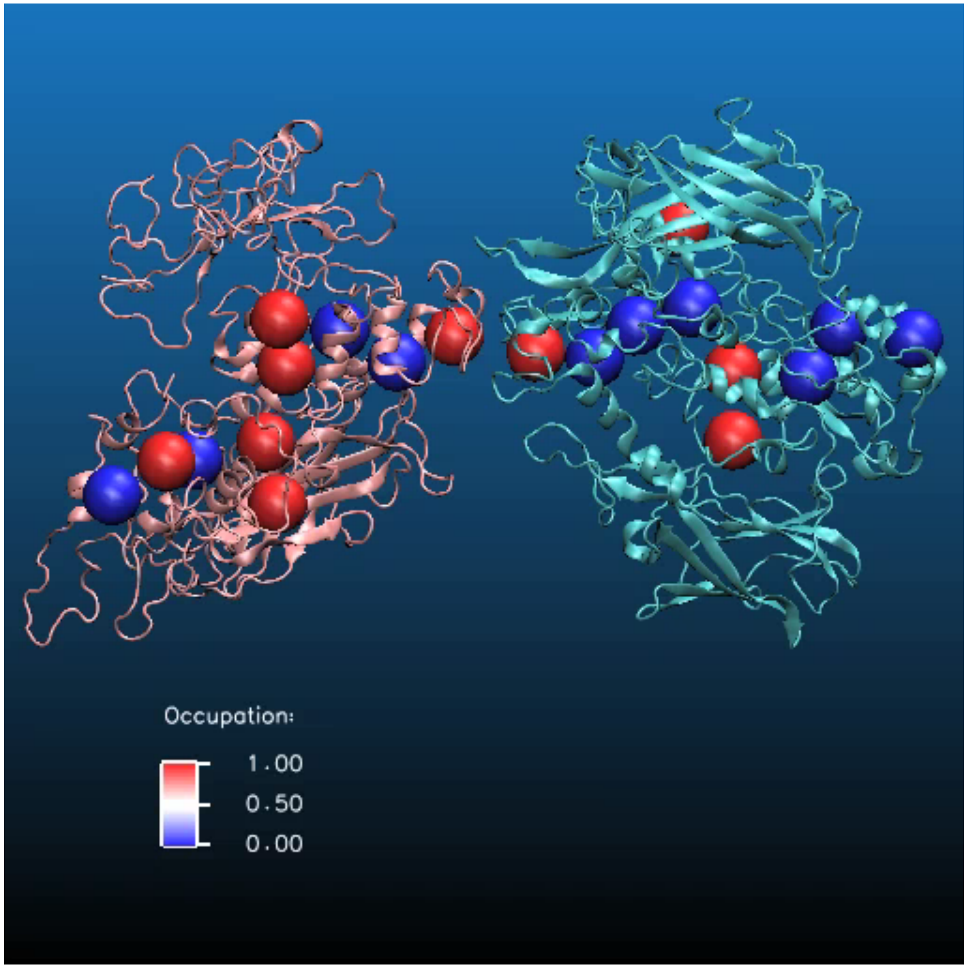

Electron ejection rate:
$\beta = 10^2\ s^{-1}$

- Electron flow is limited by the congestion of electrons



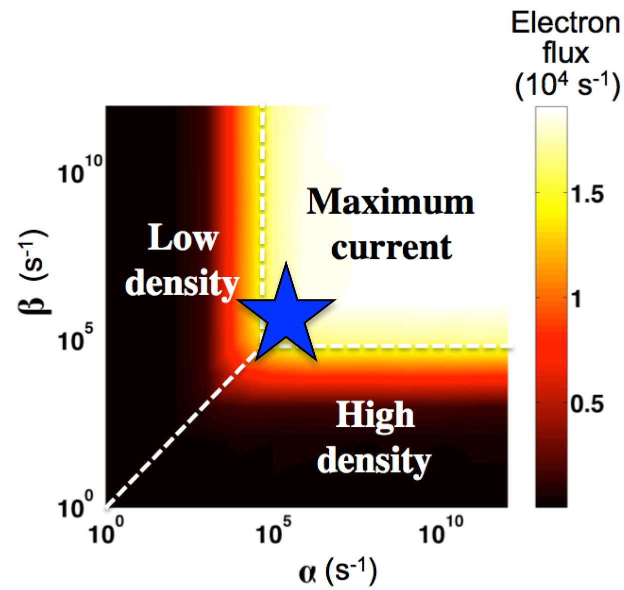
# Animation: Maximum-Current Phase

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



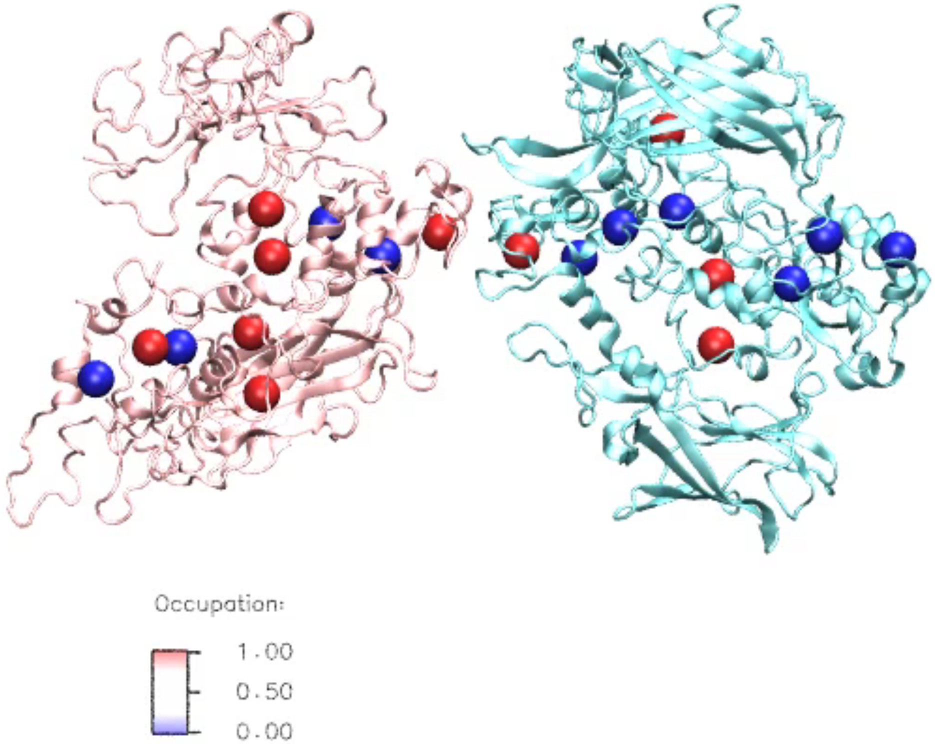

Electron ejection rate: $\beta = 10^5\ s^{-1}$

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



# Animation: Maximum-Current Phase

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




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

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