Kinetic Monte Carlo Simulation of Electron Transfer

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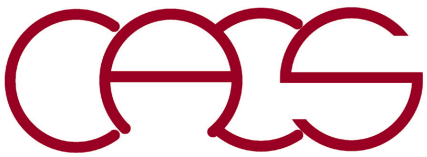

Biological Electron Transfer

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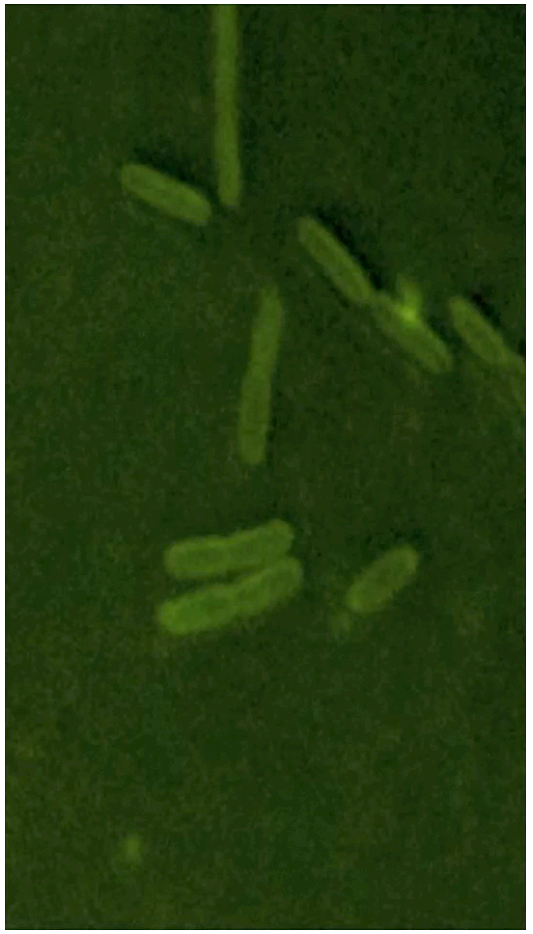
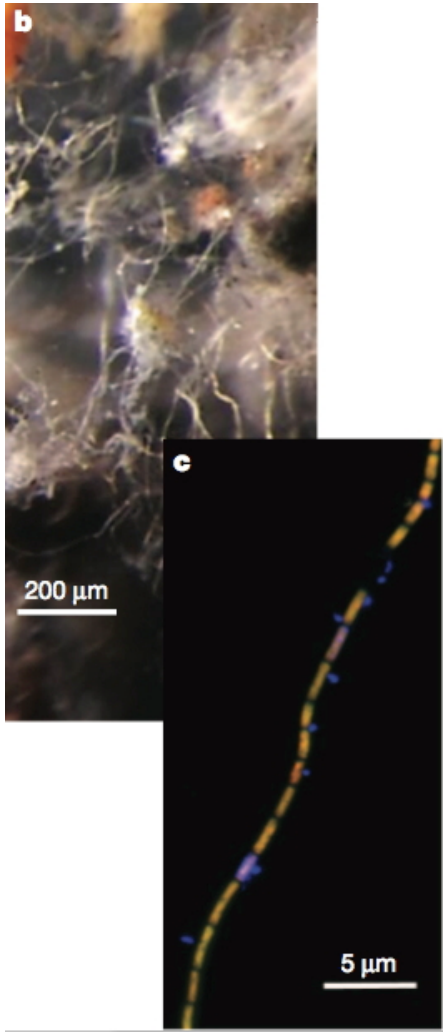
Oxygen consumption in marine sediments is often coupled to the oxidation of sulphide generated by degradation of organic matter in deeper, oxygen-free layers. Geochemical observations have shown that this coupling can be mediated by electric currents carried by unidentified electron transporters across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

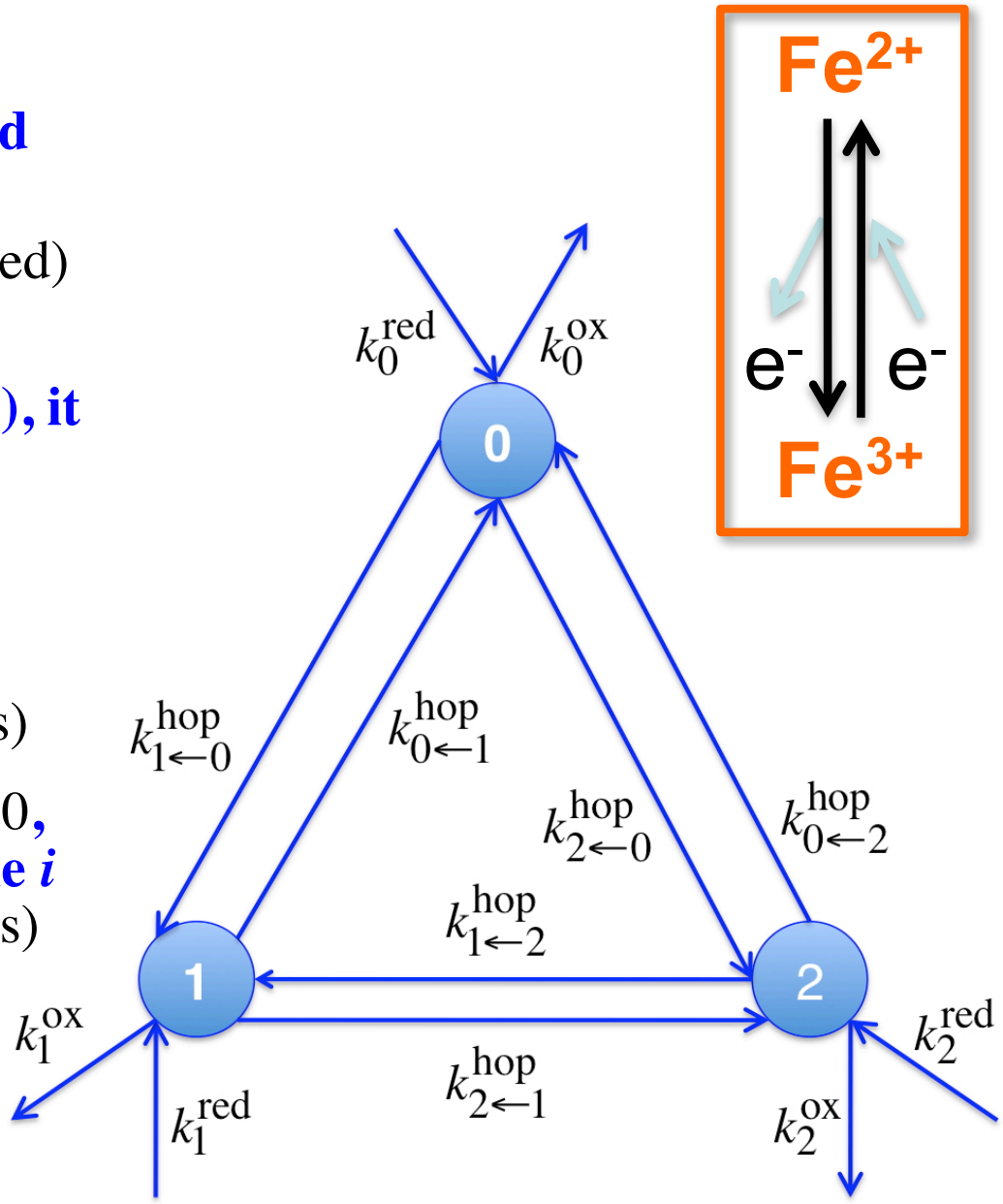




Model Definition

- **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^{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^{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 $k_{j \leftarrow i}^{hop}$ (1/s)**

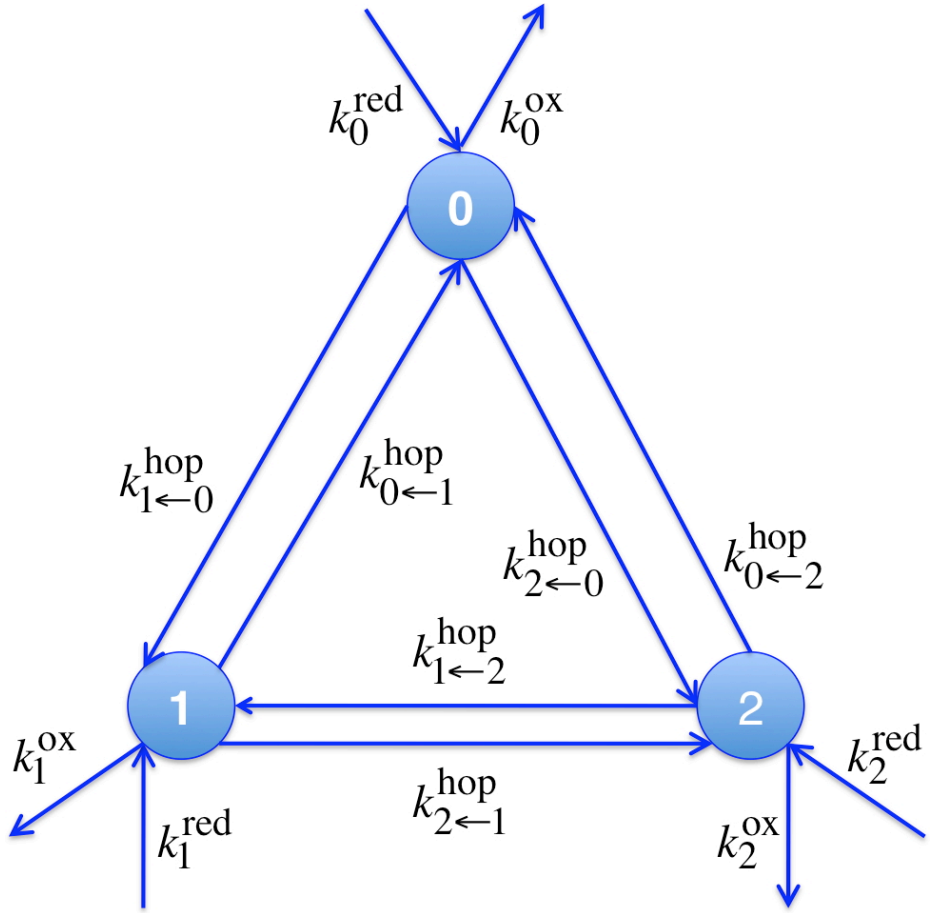


Molecular Network Topology

- **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)**

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

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

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

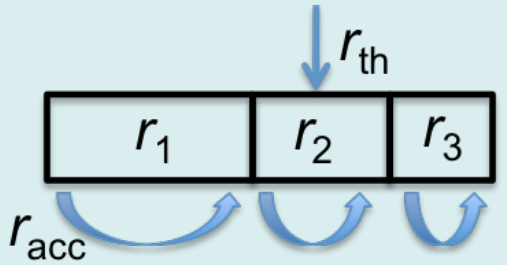
Many-body effects

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
```

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

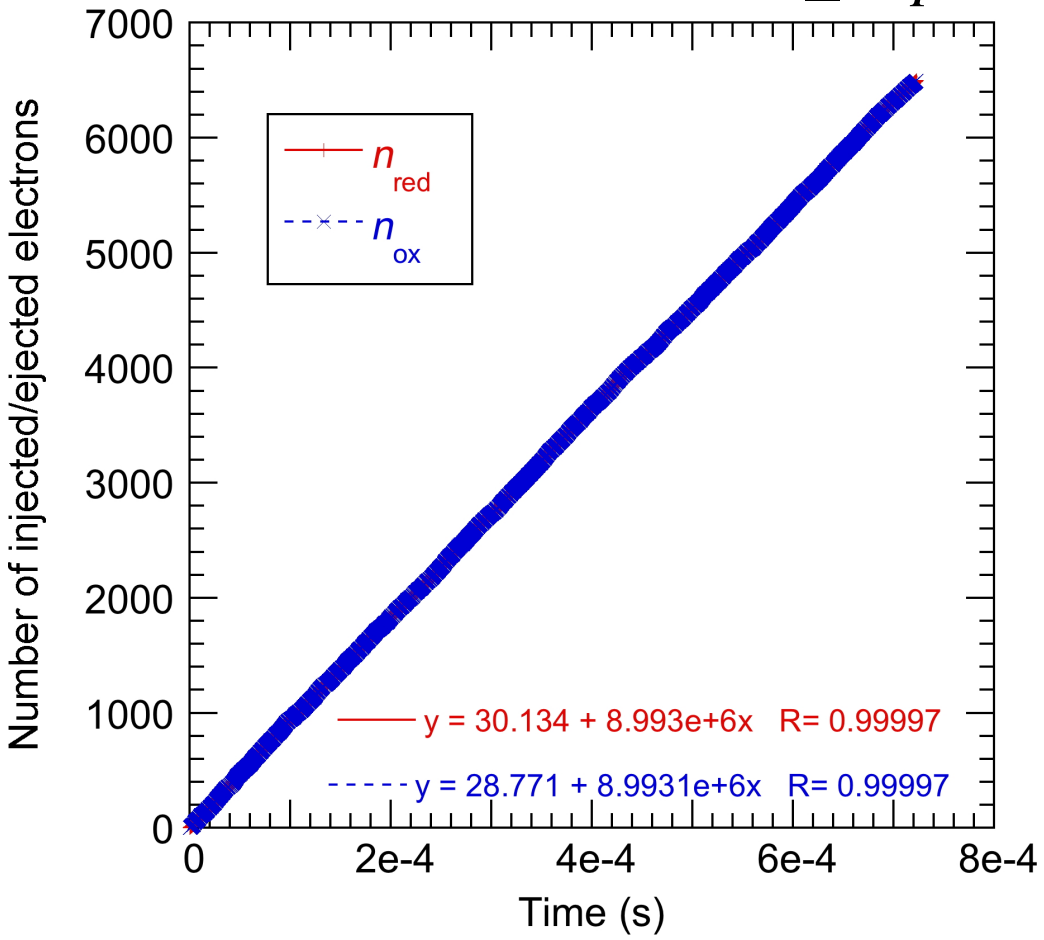
$$\Delta t = -\ln(u_{\text{random}}) / r$$

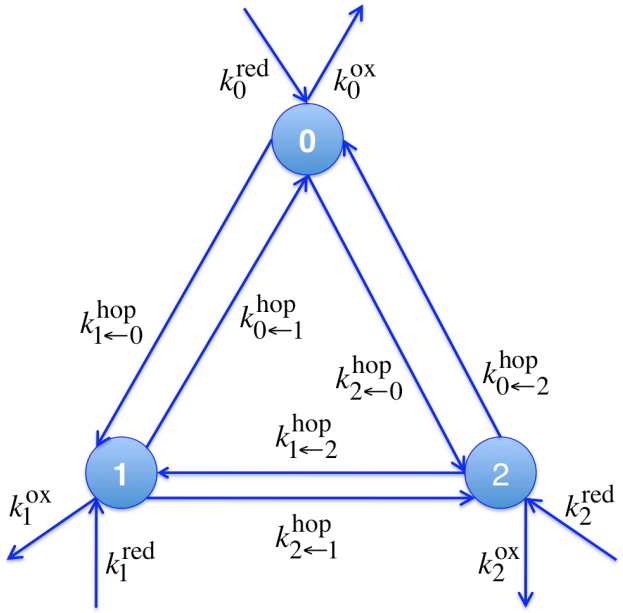


Example Run

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

$Max\_step = 10^6$



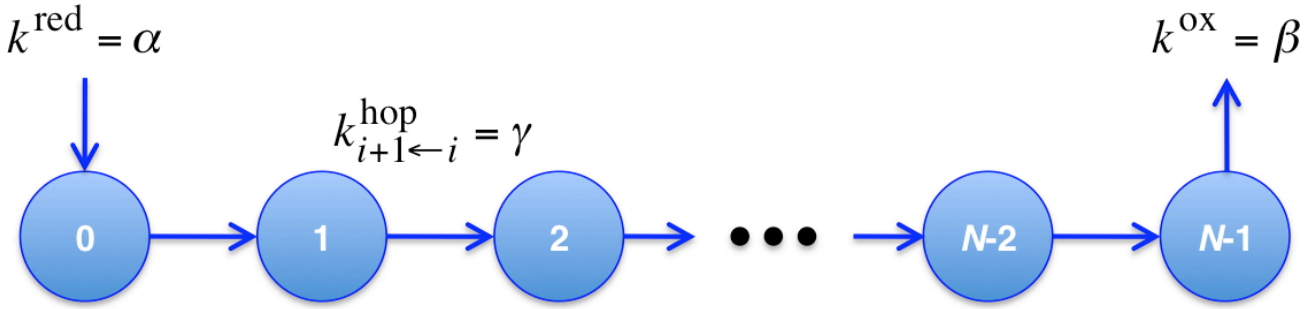


Electric current

$$8.99\times10^{6}\,(1/s)\times1.602\times10^{-19}\,(C)$$
$$=1.44\times10^{-12}\,(C/s)$$
$$=1.44\,(pA)$$

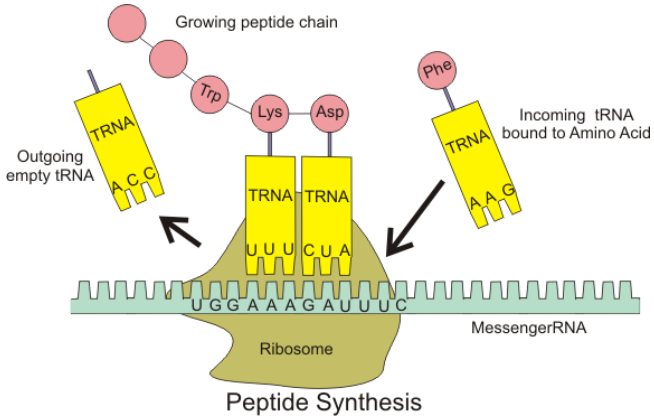
Asymmetric Simple Exclusion Process

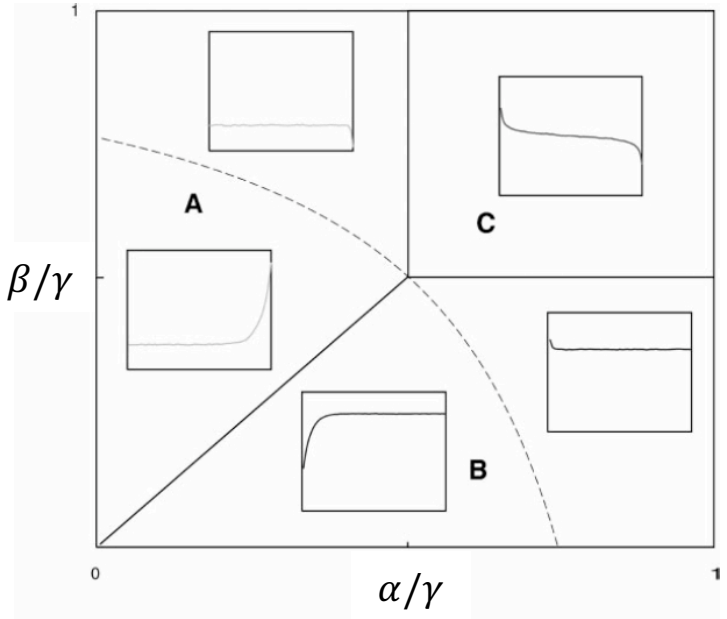
- **Linear chain of *N* molecules**
- ***Reduction* can occur only at molecule 0 with $k^{\text{red}} = \alpha$ (1/s)**
- ***Oxidation* can occur only at molecule *N*-1 with $k^{\text{ox}} = \beta$ (1/s)**
- ***Hopping* can occur from molecule *i* to *i*+1 ($i \in [0, N\text{-}2]$) with $k^{\text{hop}}_{i+1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



ASEP: "Ising model of nonequilibrium statistical physics"

- **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**



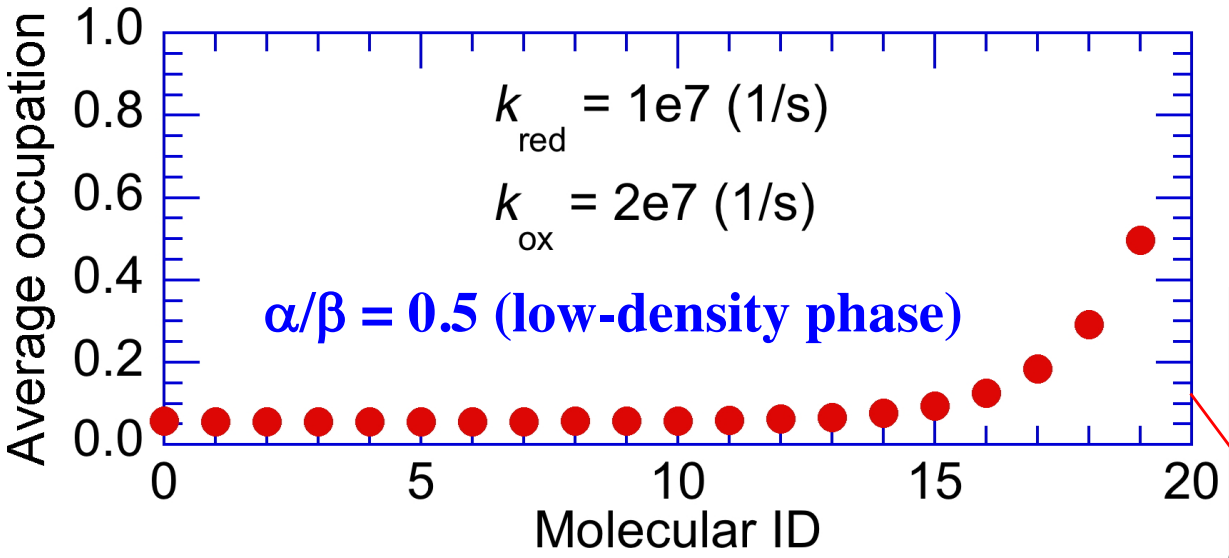


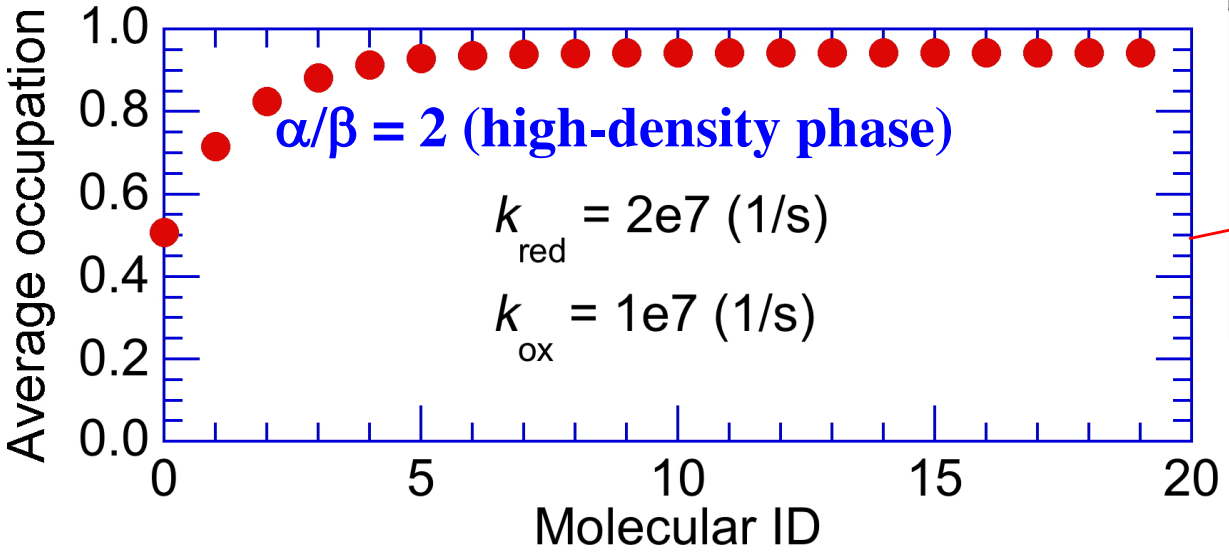
A. Shadschneider, *Physica A* **285**, 101 ('00)

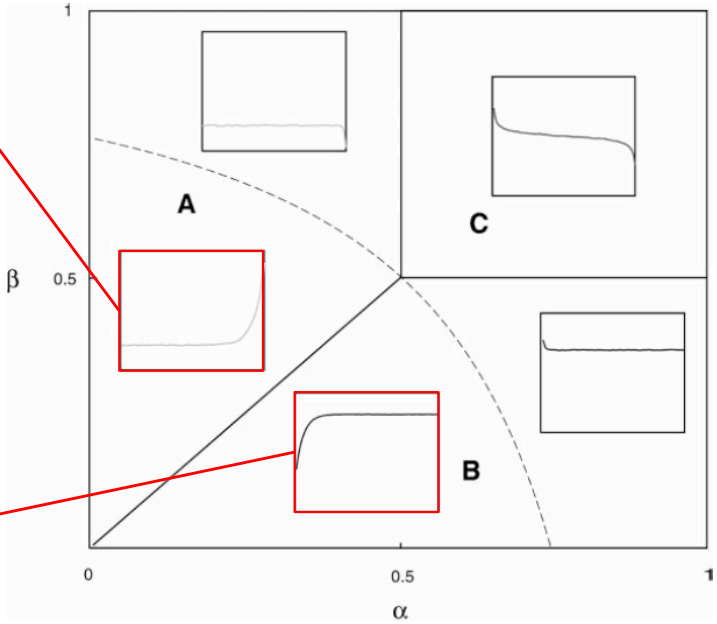
ASEP Occupation Profile

KMC simulation results

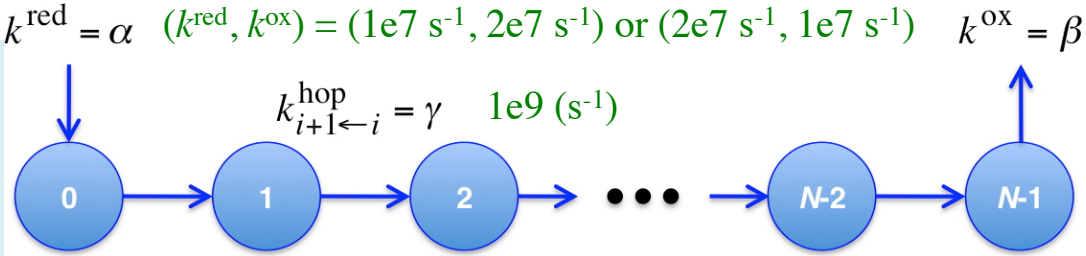
$N = 20$; k_{hop} = 1e9 (1/s); $Max\_step = 10^6$







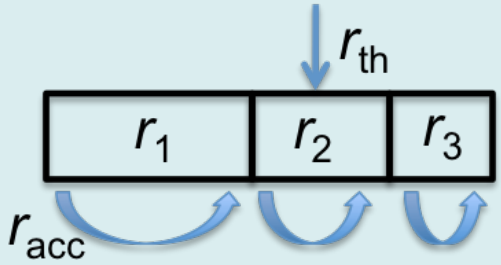
Algorithm for KMC Simulation of ASEP




```
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   // Compute total escape rate
    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   // Advance time
    r_th ← r*rand()/RAND_MAX   // Pick the next state
    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
```

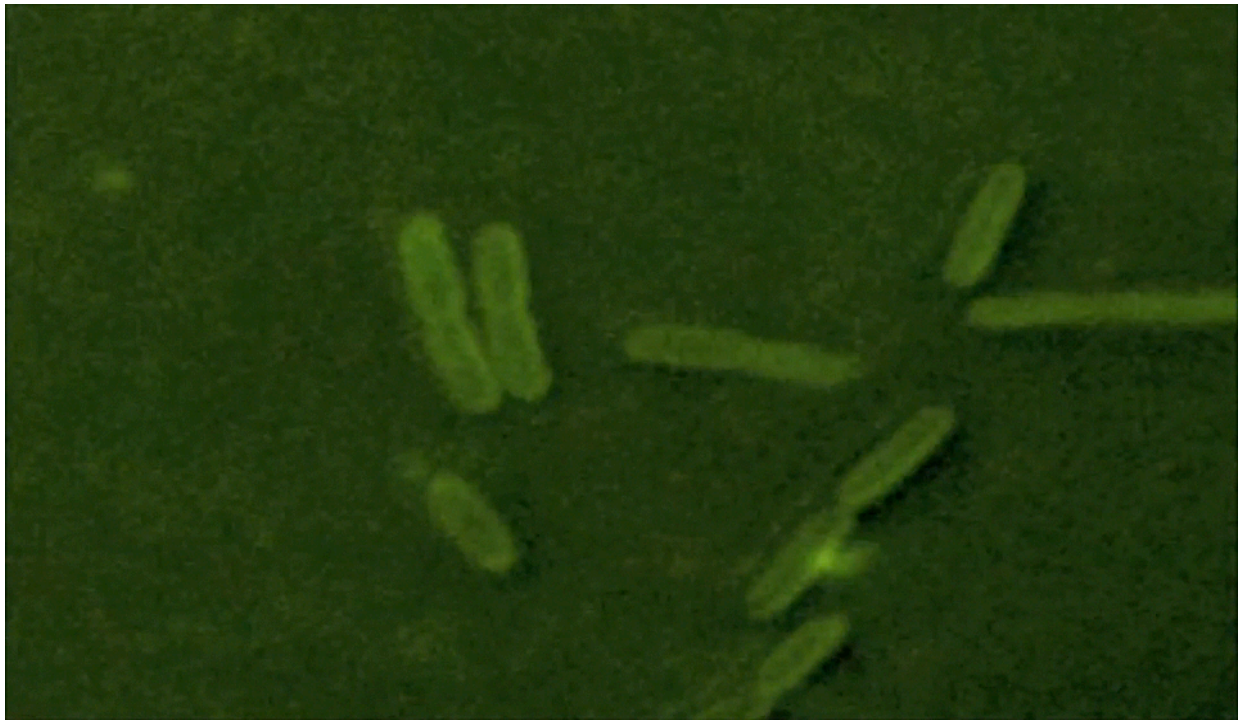
$$r = \sum_{event} r_{event}$$

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

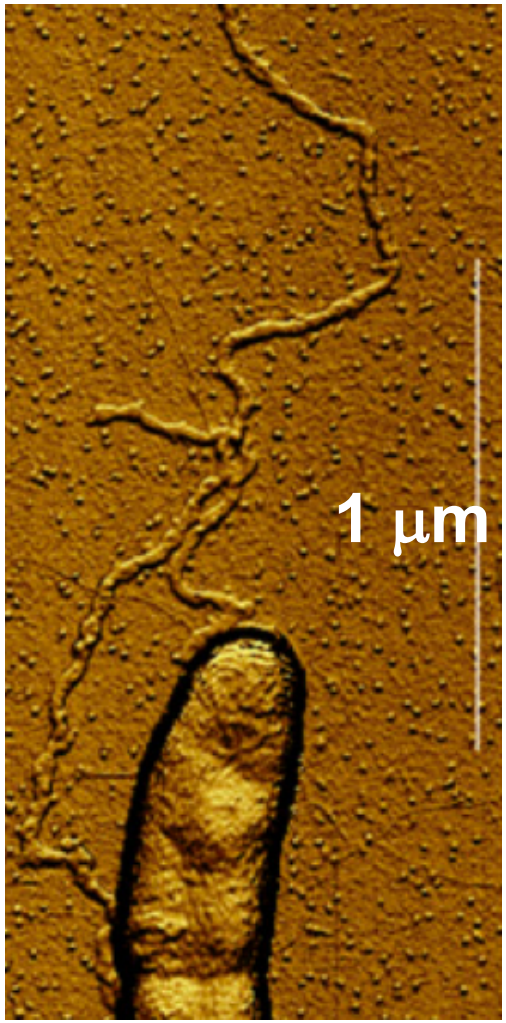


Application: Bacterial Nanowires

- **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**



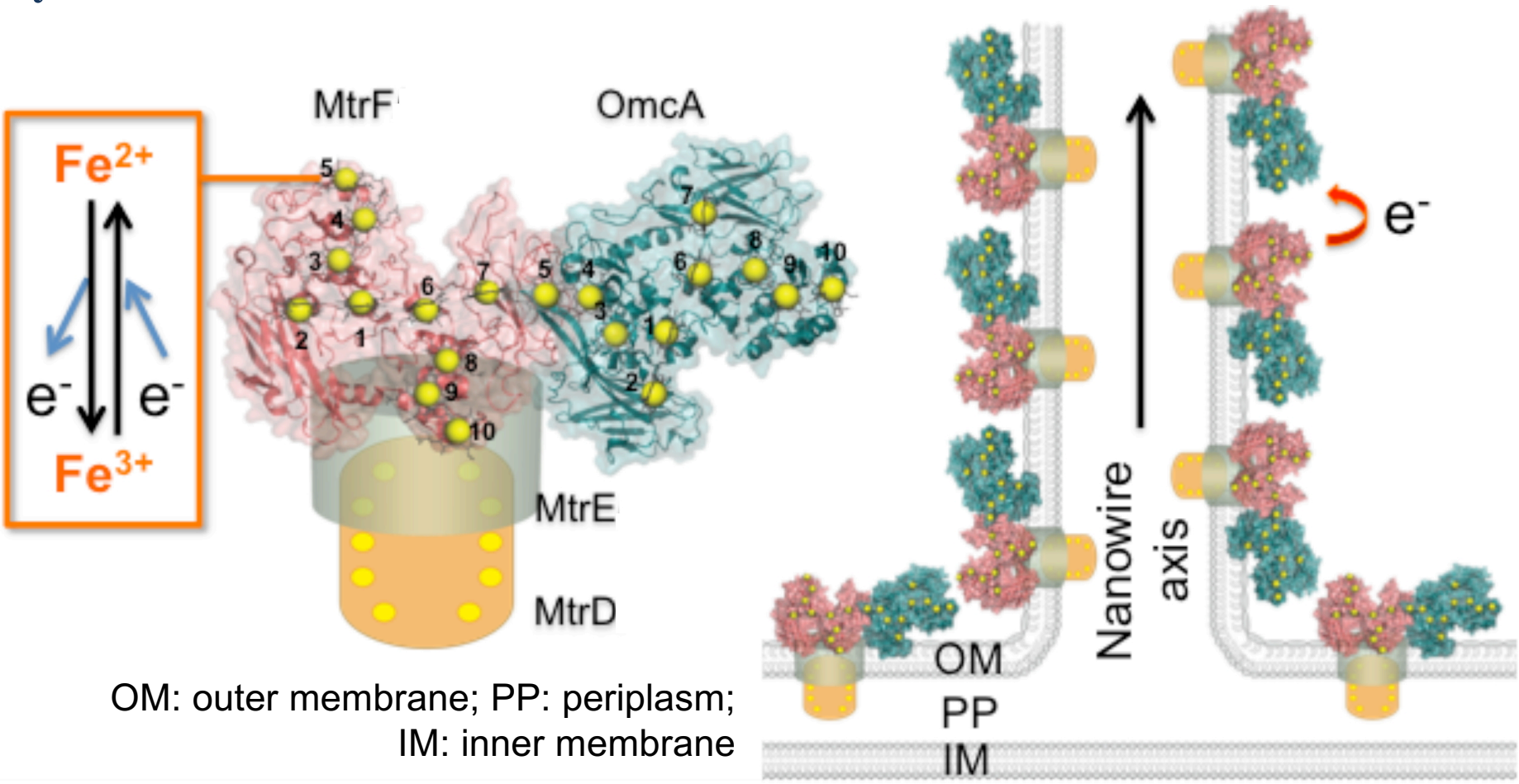
Shewanella emitting electrically conducting nanowires



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

Scientific Problem & Research Goal

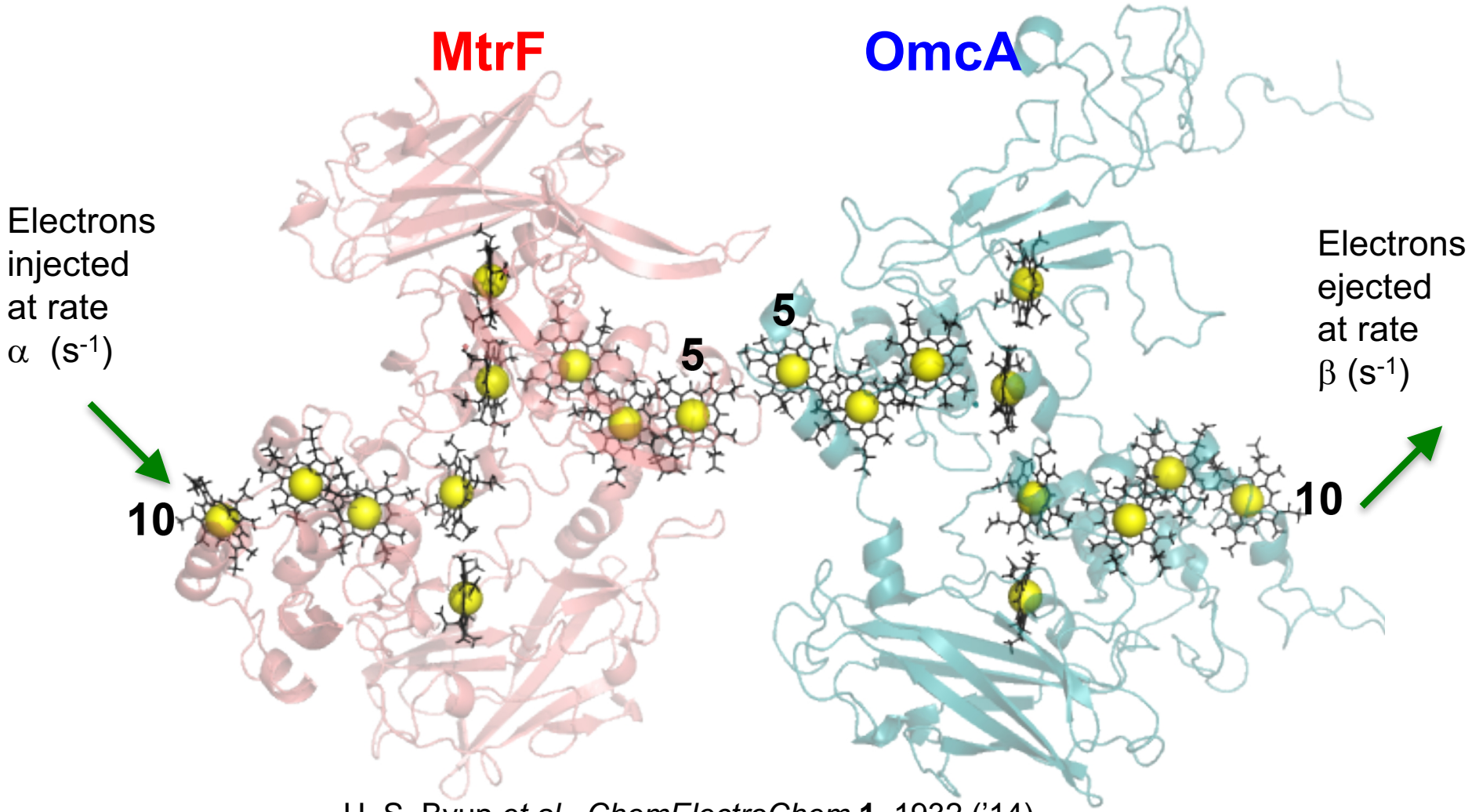
- **Outer-membrane cytochromes, MtrF & OmcA, are hypothesized media for ET, but how they are assembled into a conducting complex remains a mystery**
- ***Goal*: Determine the structure of MtrF-OmcA complex & visualize ET dynamics in it to understand electric conduction mechanisms**



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

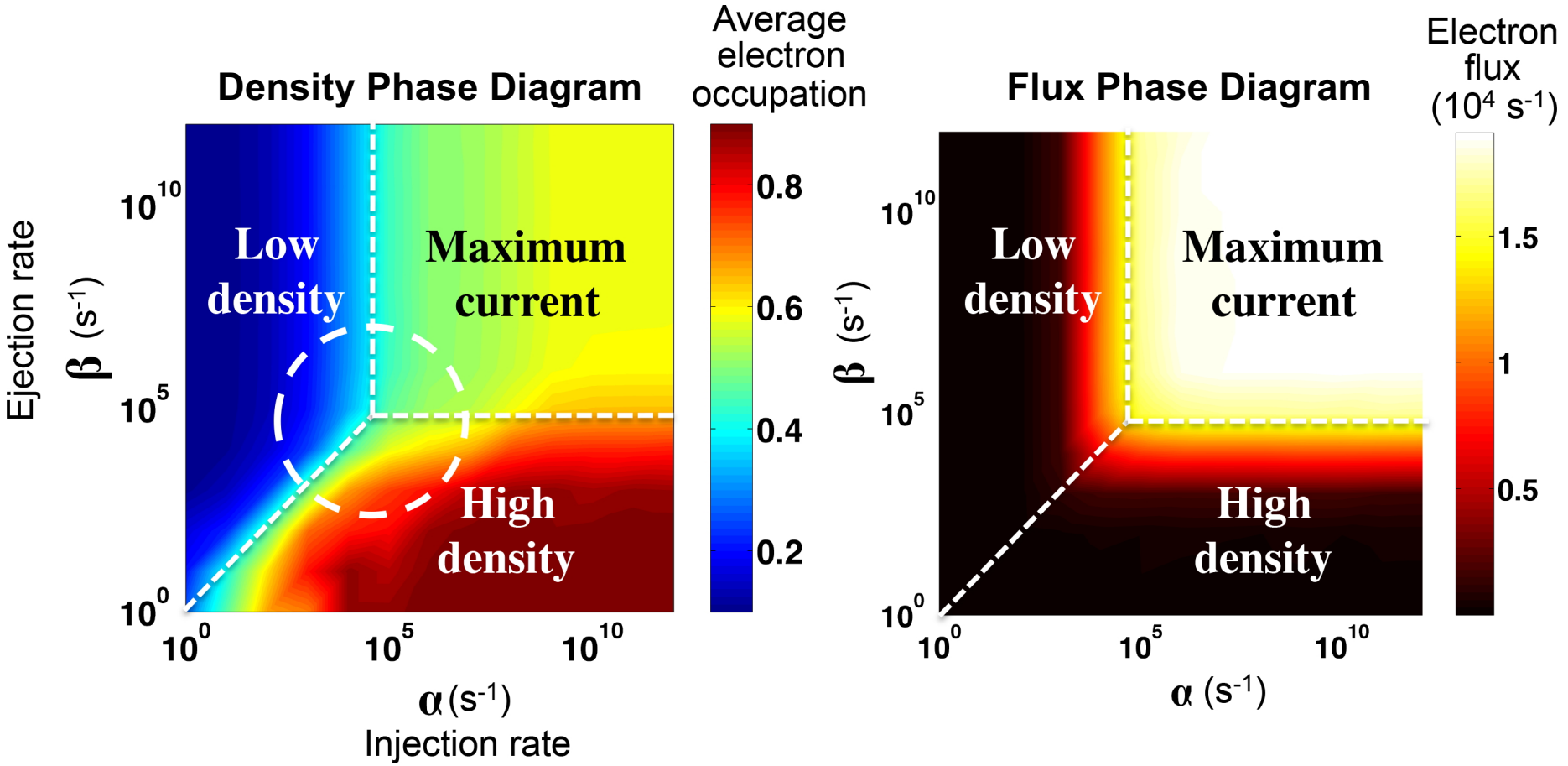
Result: Complex Structure

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)
H. Byun *et al*., *Comput. Phys. Commun*. **219**, 246 ('17)

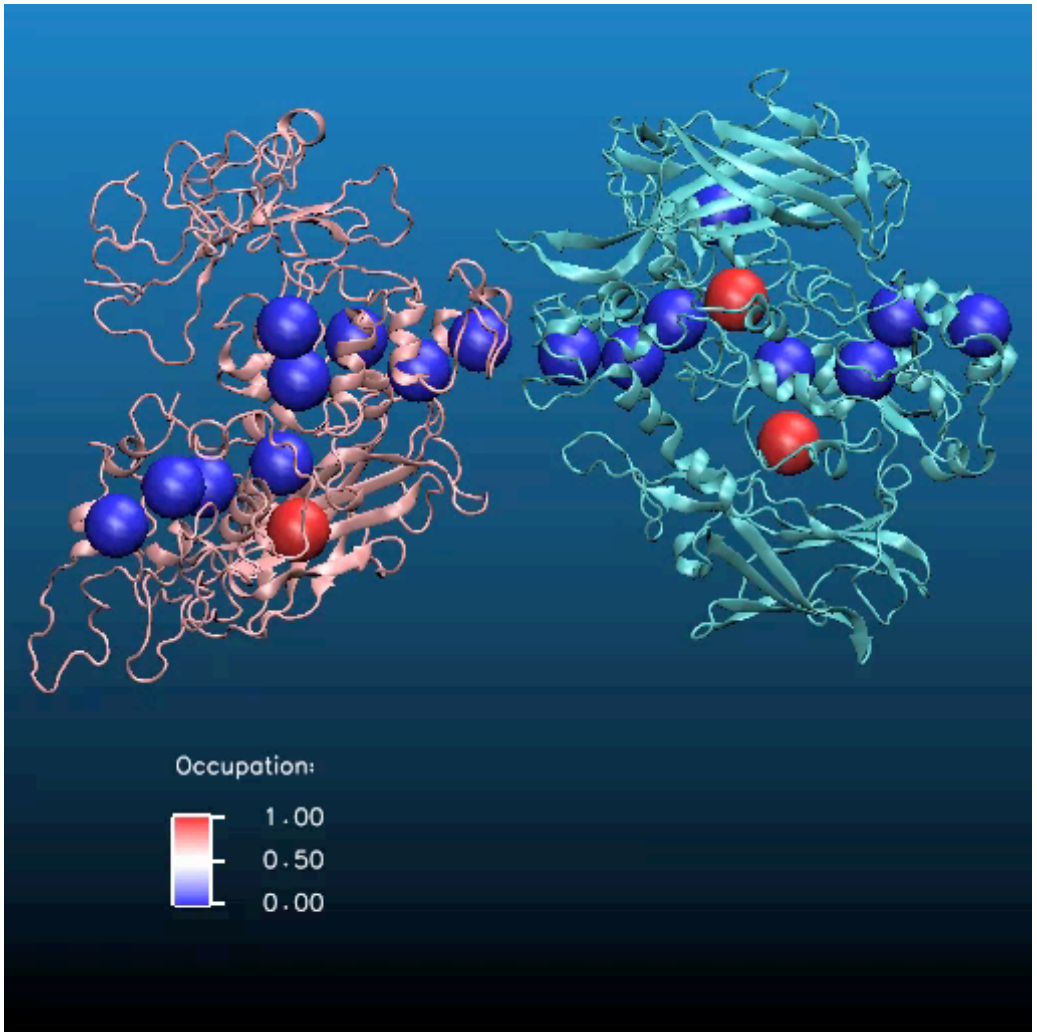
Result: ET Phase Diagram



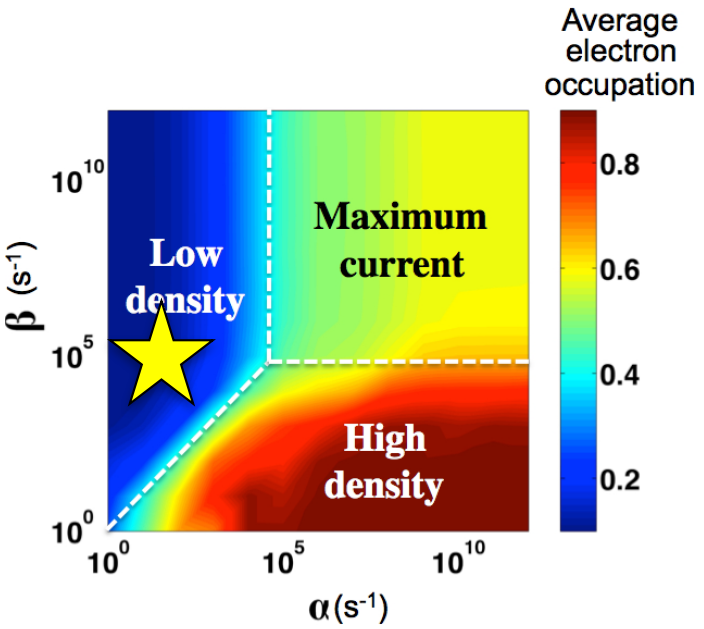
- KMC results exhibit a nonequilibrium phase transition from low-density to high-density phases for increased ratio of electron injection rate (α) to ejection rate (β)
- When both α & β exceed the smallest k_{ij}, another transition to the maximum-current phase was found
- Observed respiration rates (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: $\alpha = 10^2\ s^{-1}$



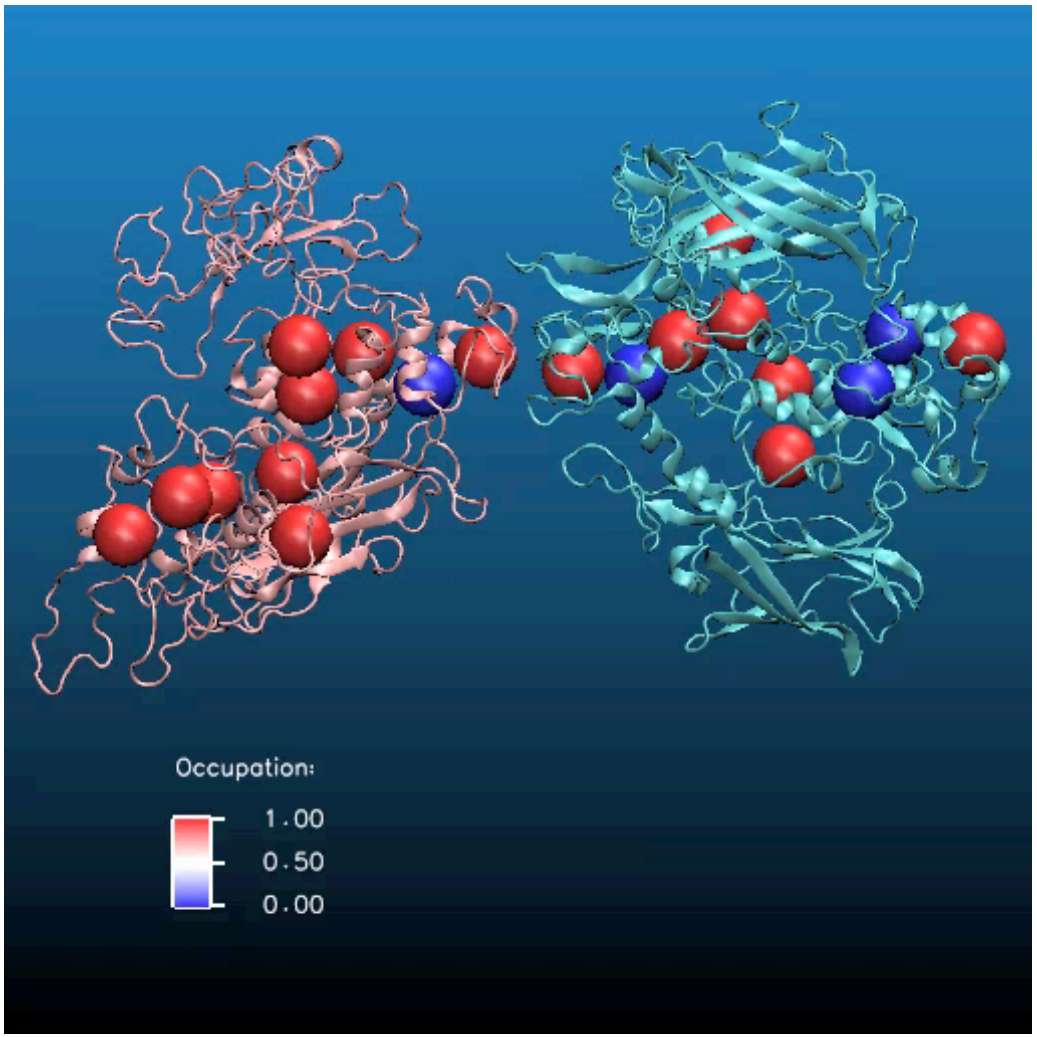
Electron ejection rate: $\beta = 10^5\ s^{-1}$



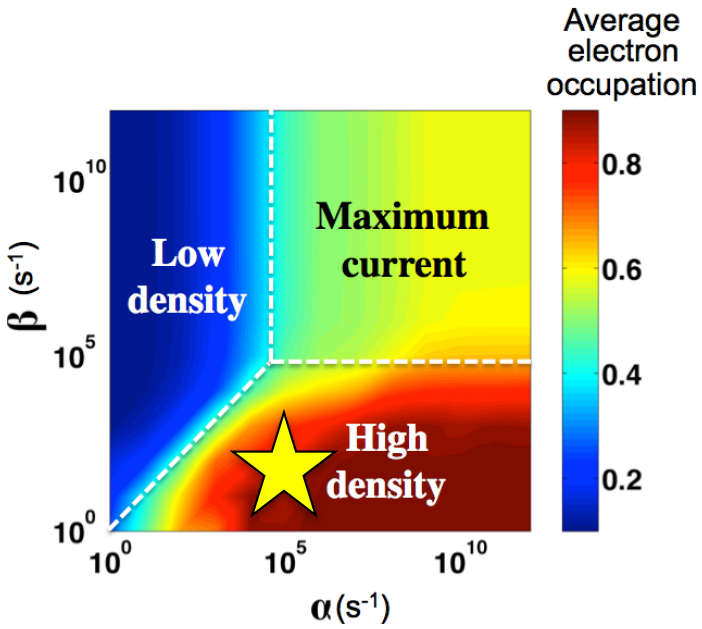
- **Electron flow is limited by the small number of electrons**

Animation: High-Density Phase

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



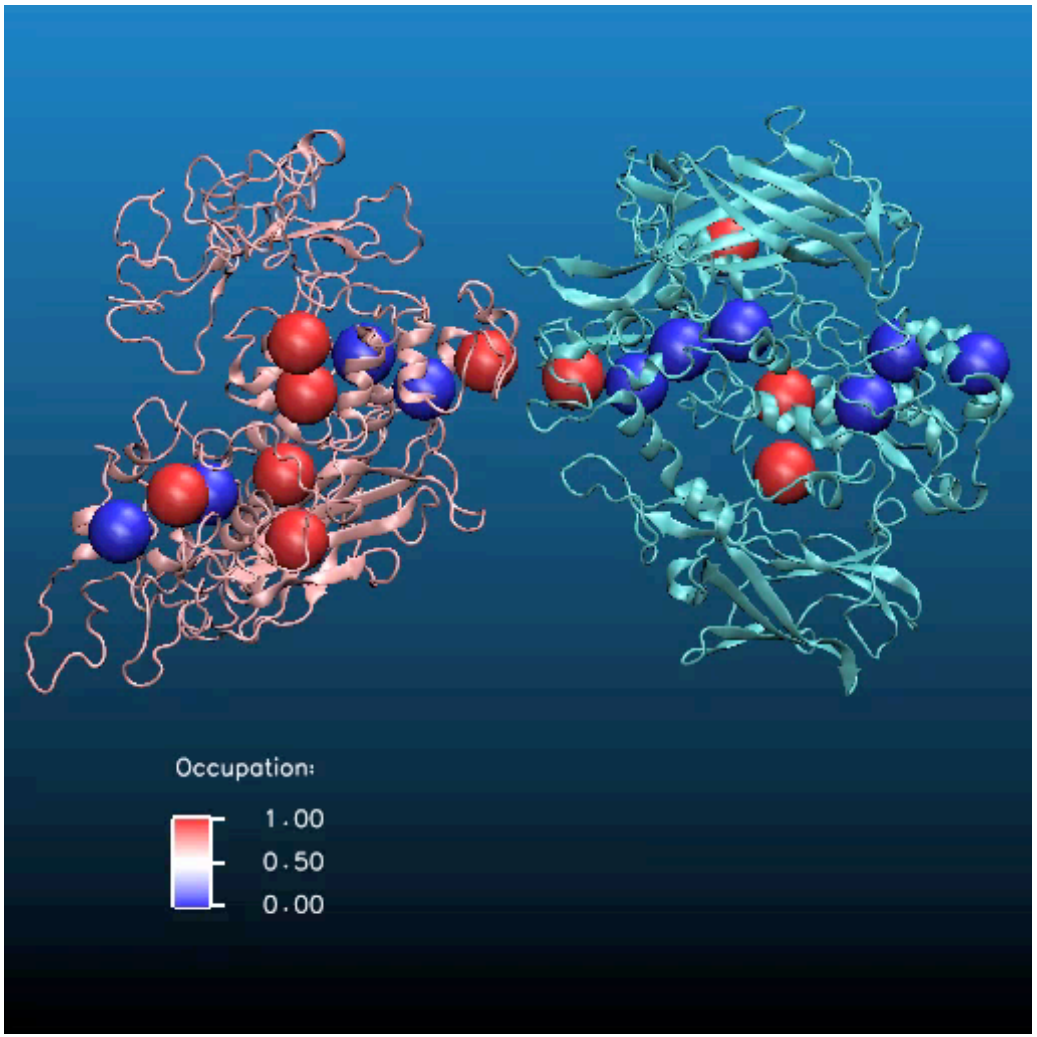
Electron ejection rate: $\beta = 10^2\ s^{-1}$



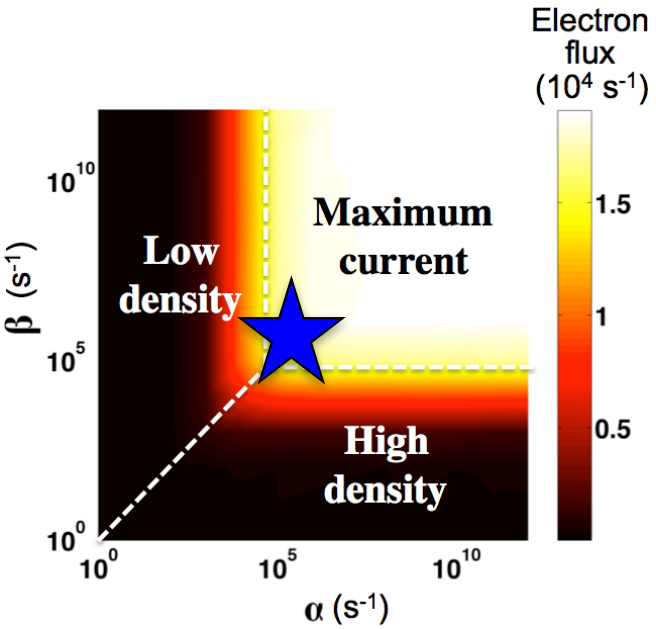
- **Electron flow is limited by the congestion of electrons**

Animation: Maximum-Current Phase

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



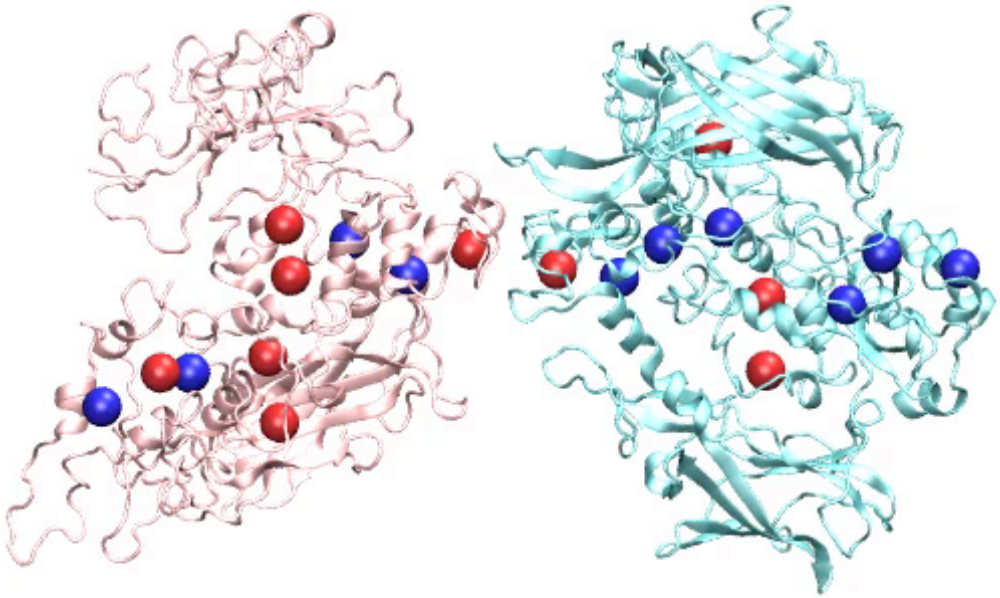
Electron ejection rate: $\beta = 10^5\ s^{-1}$



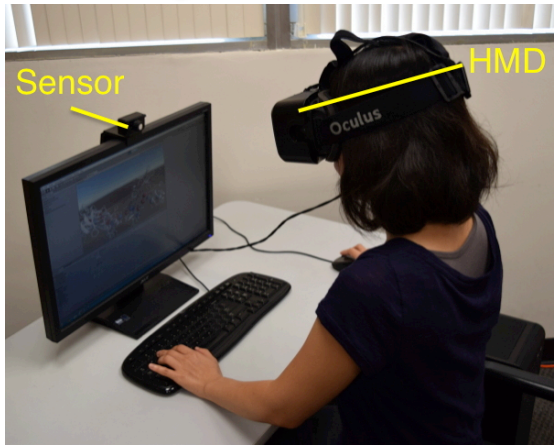
- **Large electric current is facilitated by balanced electron injections & ejections**
- **Life operates around the triple junction**

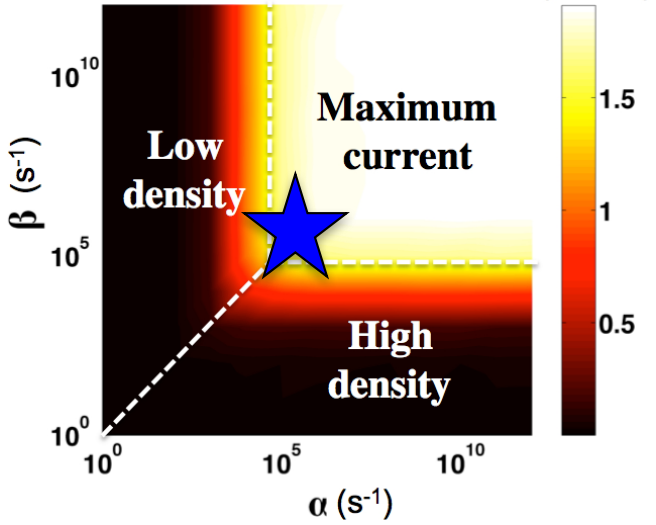
Animation: Maximum-Current Phase

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



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





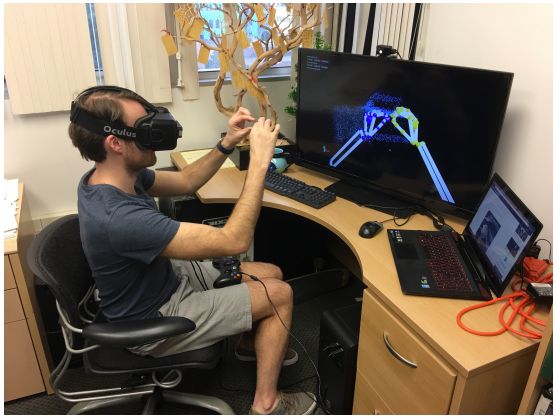
- **Each electron-transfer event is represented by a directed edge**

Navigation in Virtual Reality

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



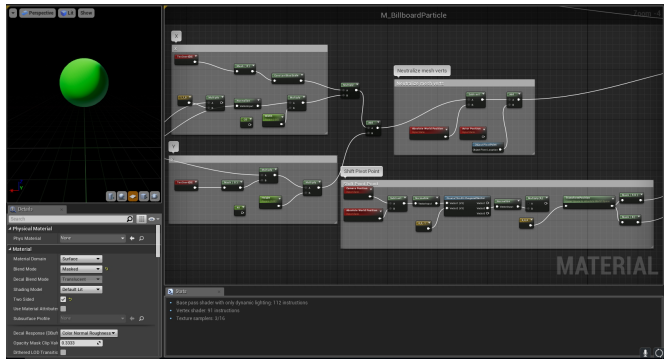
Oculus Rift + Leap Motion

HTC Vive

Photoexcitation in $MoSe_2$

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**



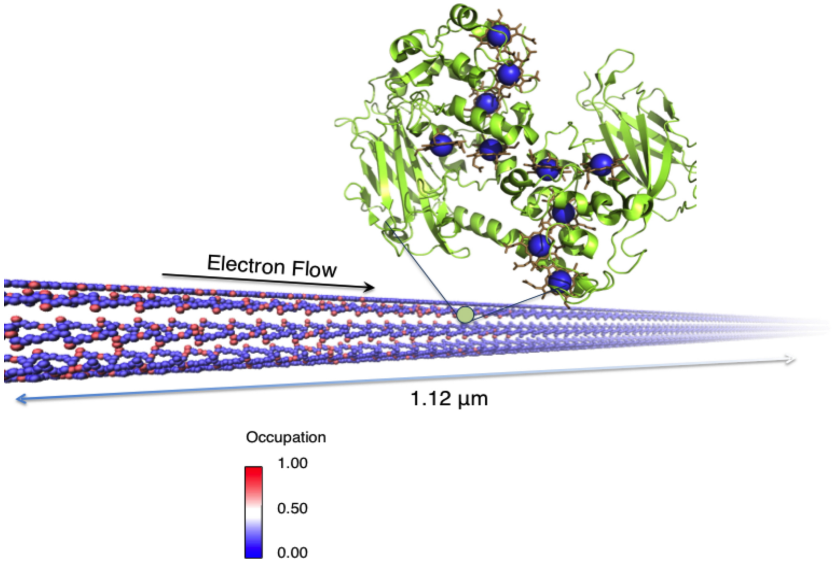
LammpsVR editor

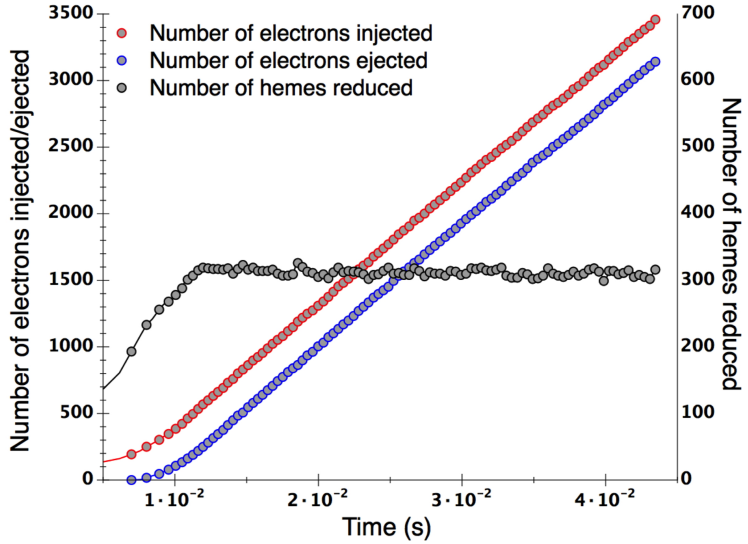
GEARS

https://github.com/USCCACS/GEARS

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**





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

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