

Kinetic Monte Carlo Simulation of Electron Transfer

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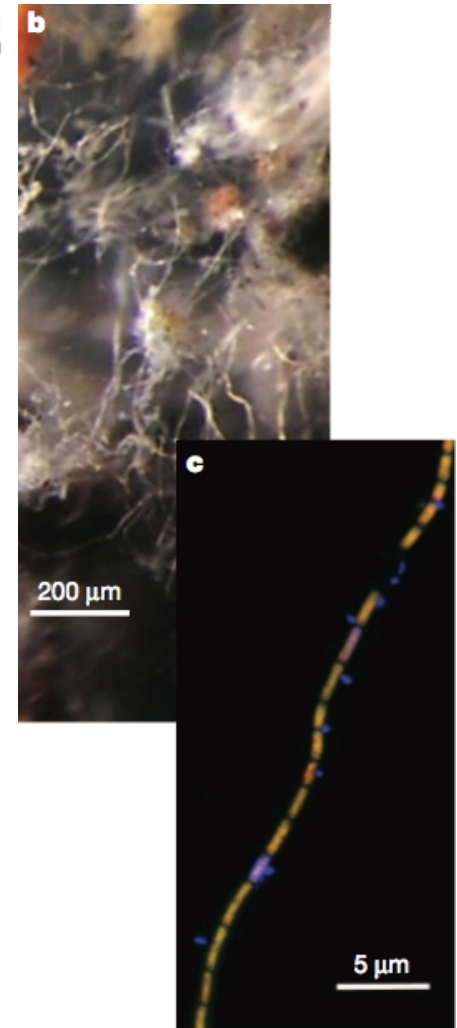
Biological Electron Transfer

Filamentous bacteria transport electrons over centimetre distances

Christian Pfeffer¹, Steffen Larsen², Jie Song³, Mingdong Dong³, Flemming Besenbacher³, Rikke Louise Meyer^{2,3}, Kasper Urup Kjeldsen¹, Lars Schreiber¹, Yuri A. Gorby⁴, Mohamed Y. El-Naggar⁵, Kar Man Leung^{4,5}, Andreas Schramm^{1,2}, Nils Risgaard-Petersen¹ & Lars Peter Nielsen^{1,2}

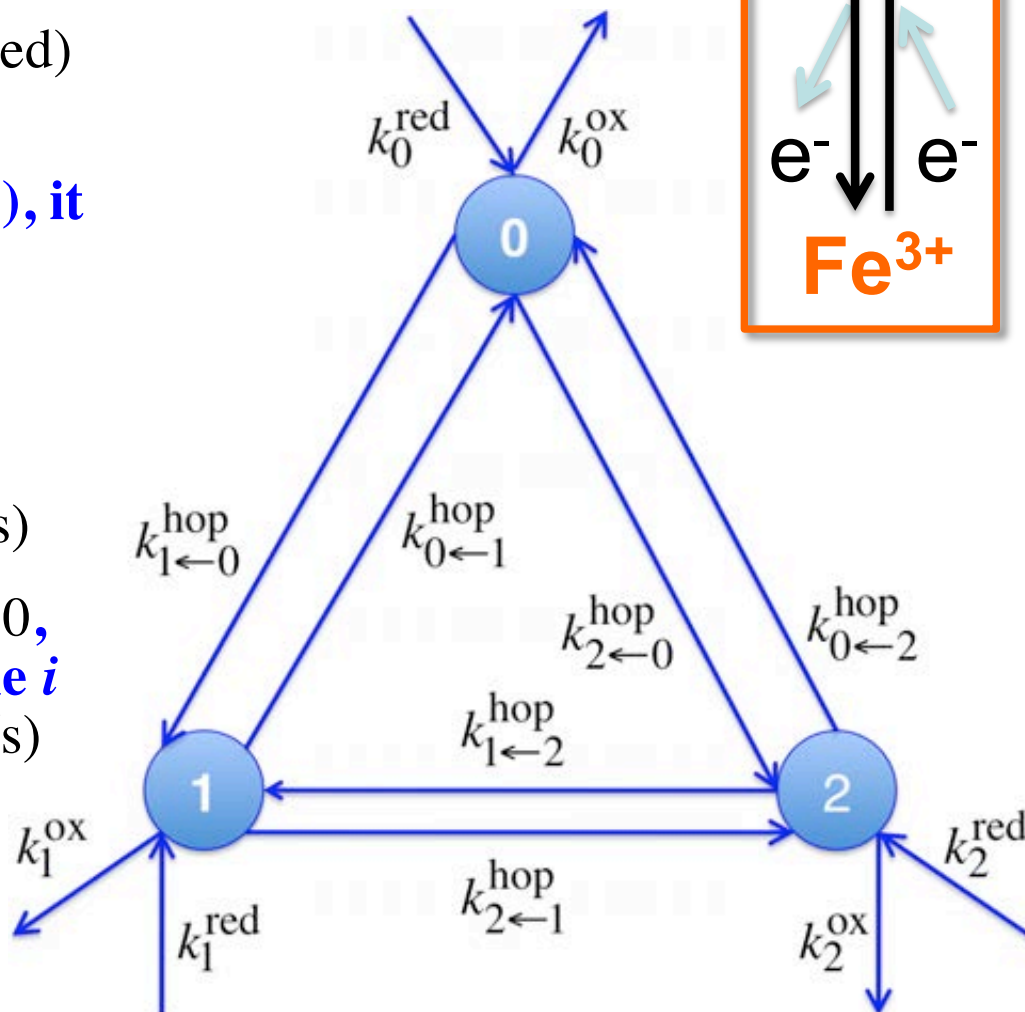
218 | NATURE | VOL 491 | 8 NOVEMBER 2012

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.



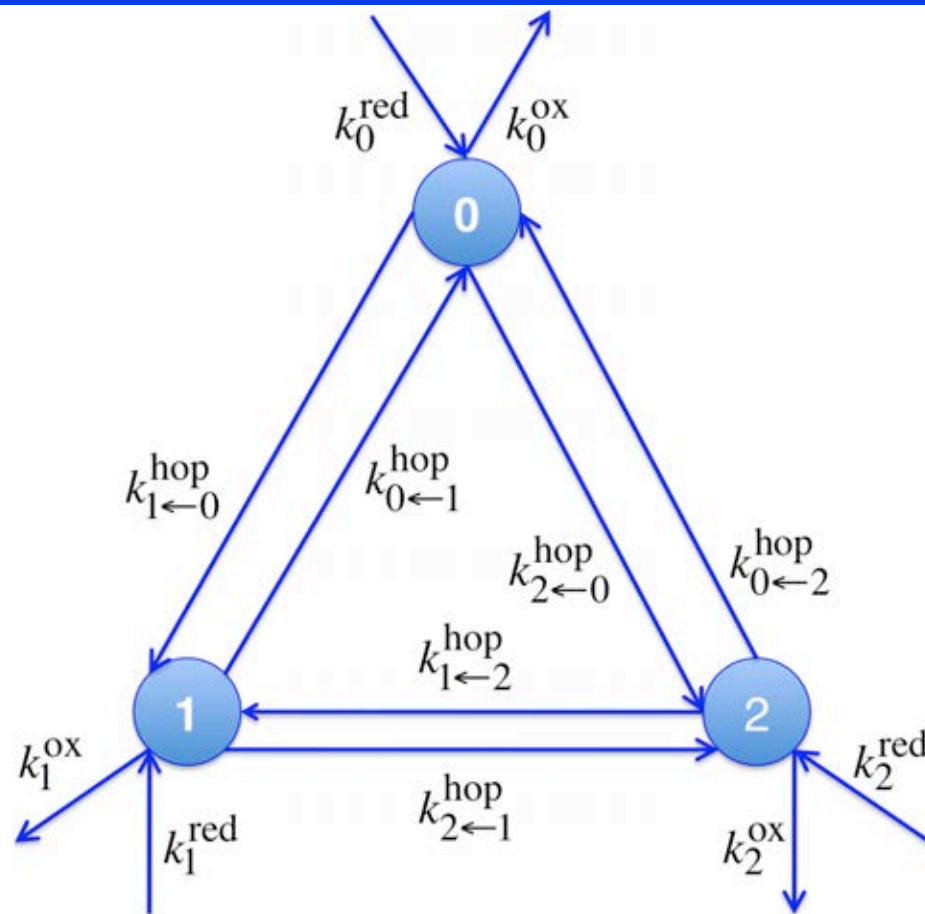
Model Definition

- 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^{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 $k_{j \leftarrow i}^{\text{hop}}$ (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 (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)**

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

Many-body effects

Algorithm

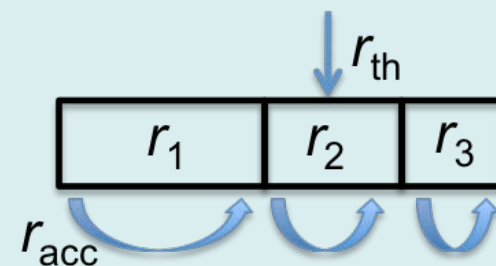
```

occ[i] ← 0 (i = 0 to N-1)
nred ← 0 // number of injected electrons
nox ← 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
        rth ← r*rand()/RAND_MAX
        racc ← 0
        for i ← 0 to N-1
            if (rth < (racc += rate_occ[i][0])) // reduction occurs
                occ[i] ← 1; print t, ++nred, nox; break
            else if (rth < (racc += rate_occ[i][1])) // oxidation occurs
                occ[i] ← 0; print t, nred, ++nox; break
            else
                for k ← 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]] ← 1; occ[i] ← 0; break
            if (rth < racc) break

```

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

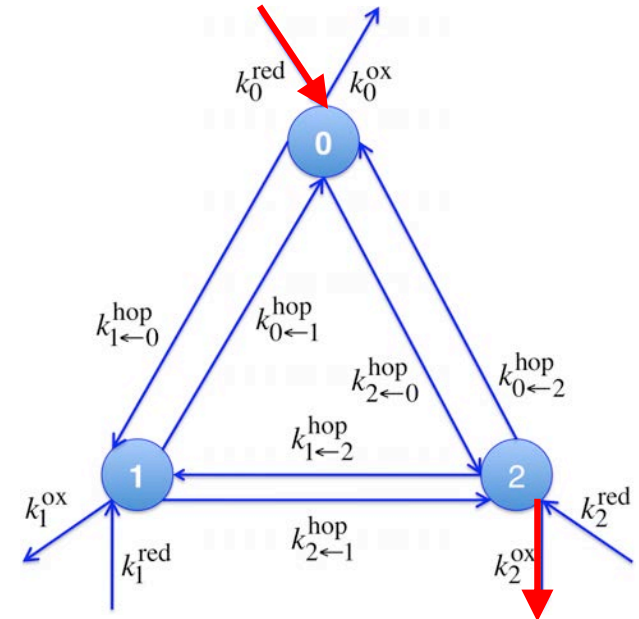
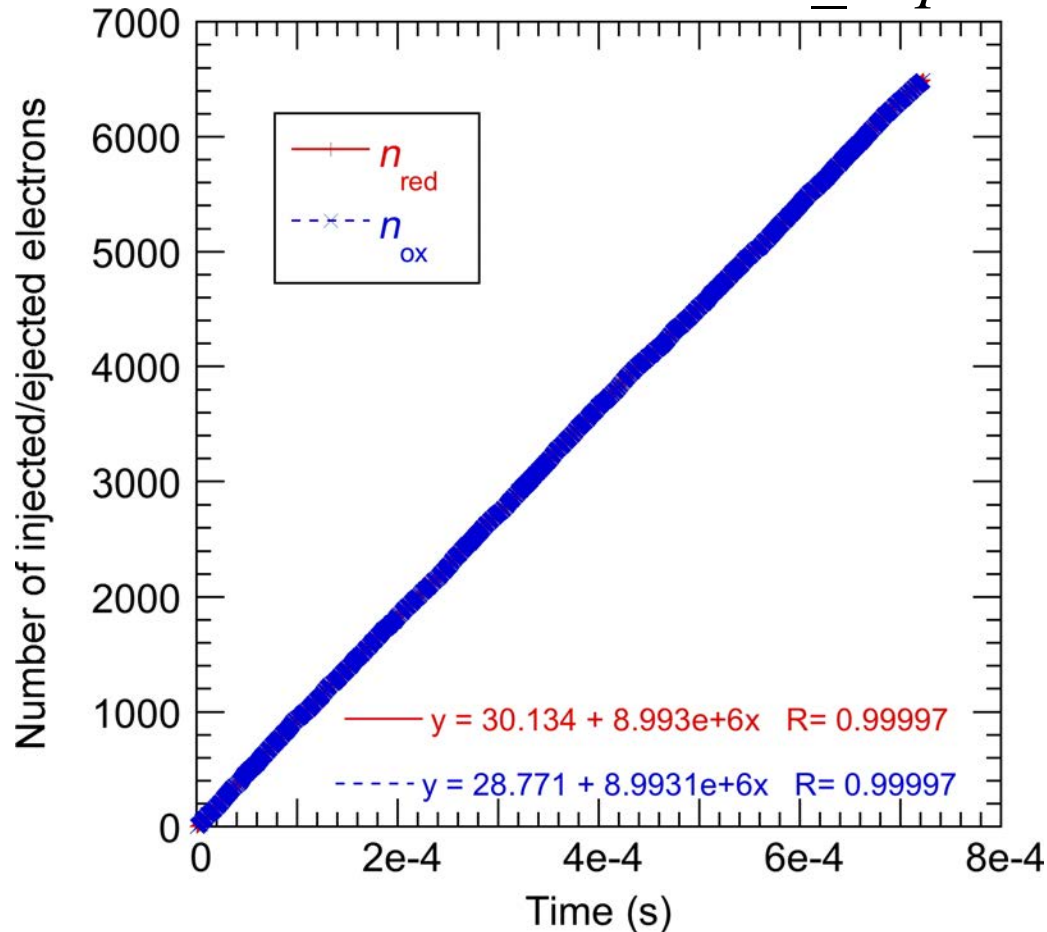
$$\Delta t = -\ln(u_{random})/r$$



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	$2e7$	$2e7$	$4e9$

$Max_step = 10^6$

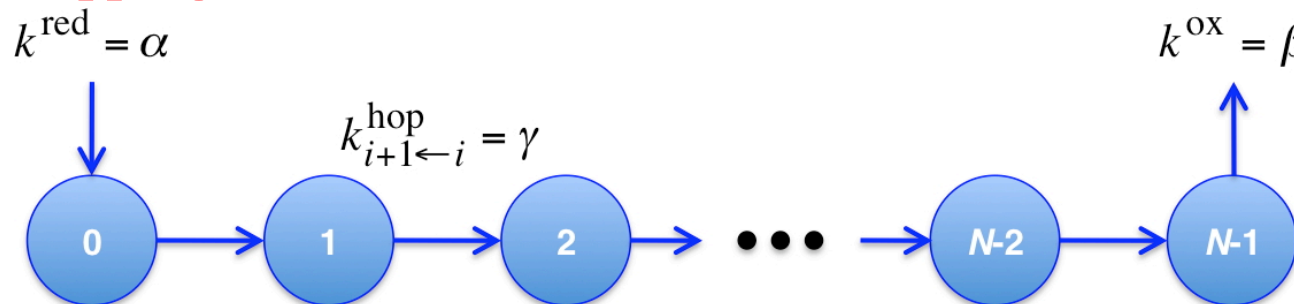


Electric current

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

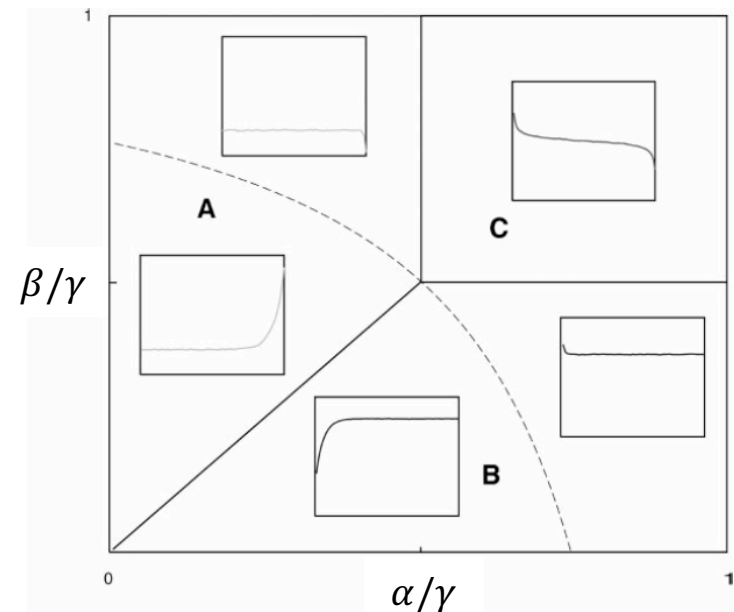
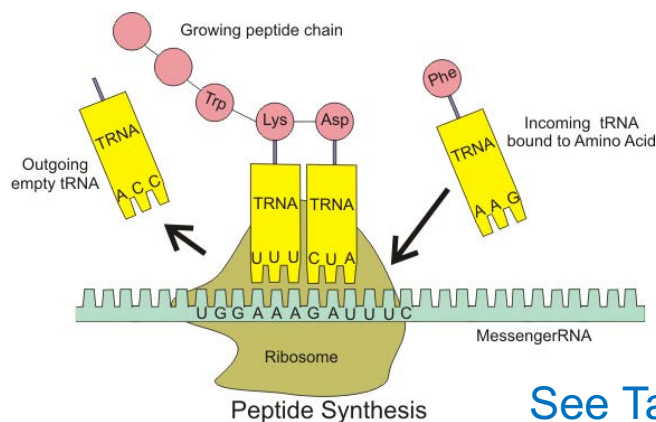
Asymmetric Simple Exclusion Process

- 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 α/β
- Applications in traffic flow and ribosome motion on mRNA during translation



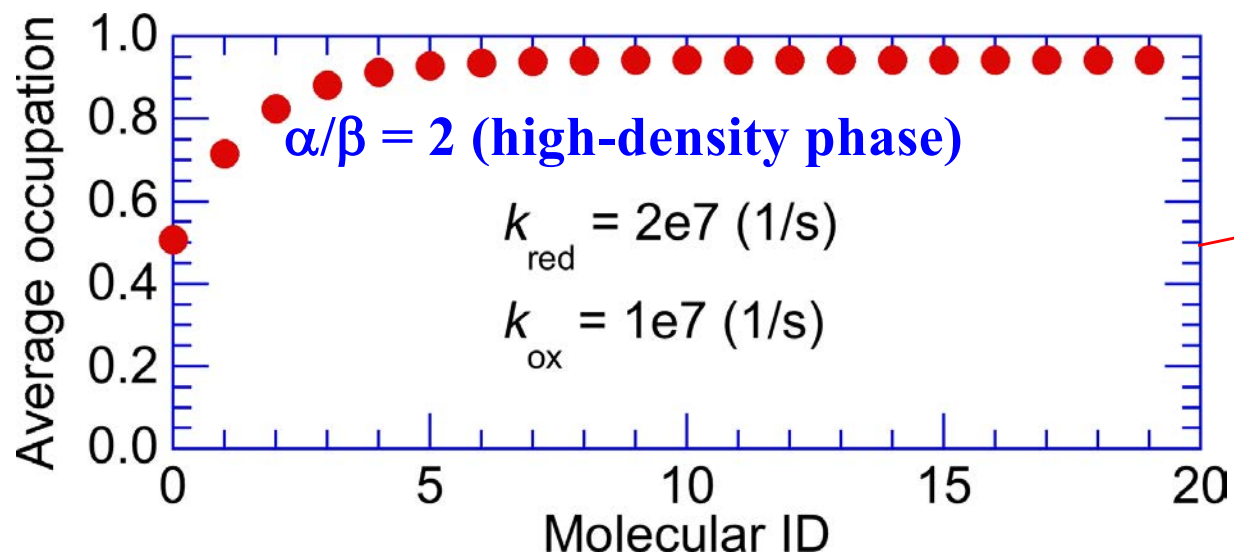
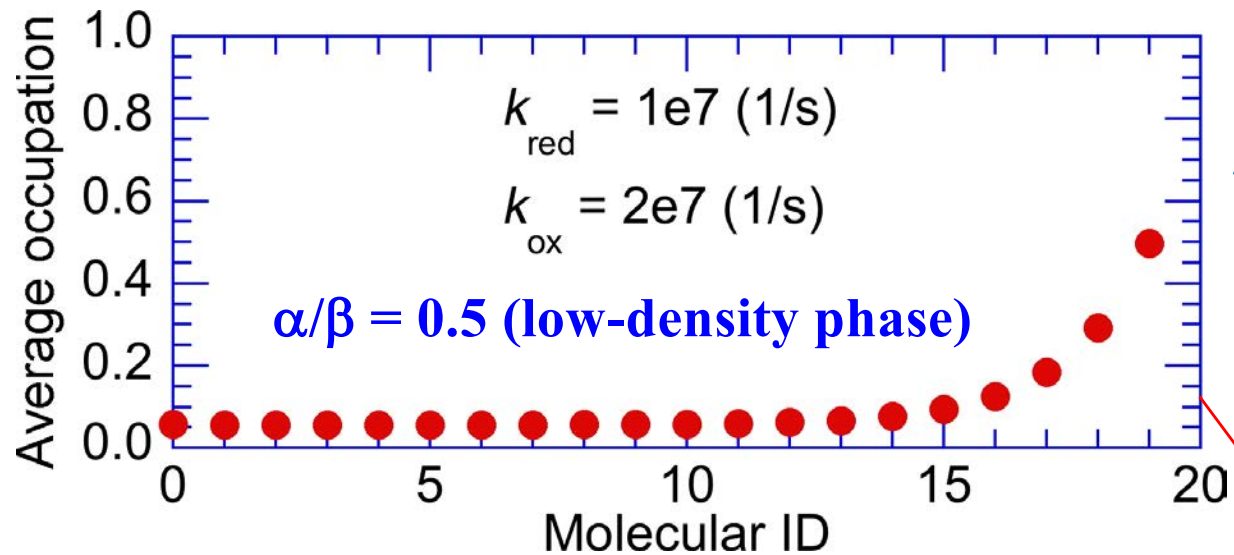
A. Shadschneider, *Physica A* **285**, 101 ('00)

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

ASEP Occupation Profile

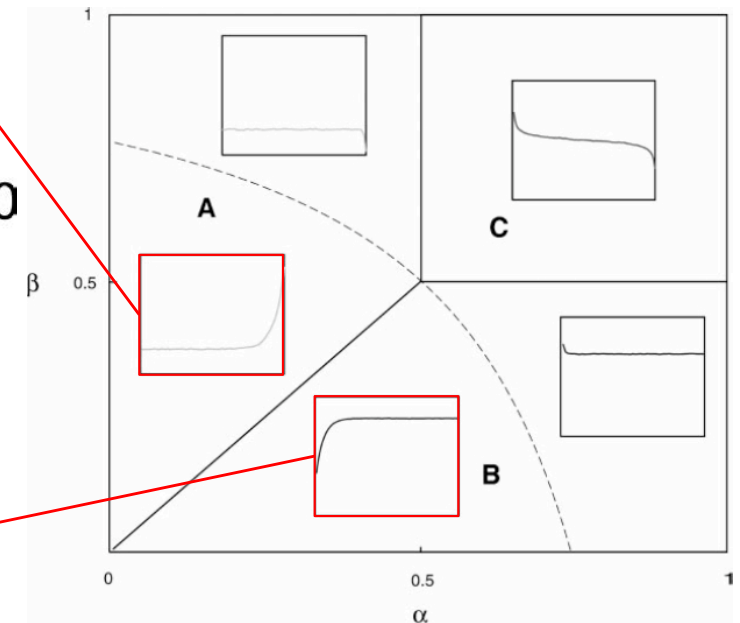
KMC simulation results

$N = 20$; $k_{\text{hop}} = 1\text{e}9$ (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

```

occ[i] ← 0 (i = 0 to N-1)  N = 20
nred ← 0 // number of injected electrons
nox ← 0 // number of ejected electrons
t ← 0      Max_step = 106

```

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**

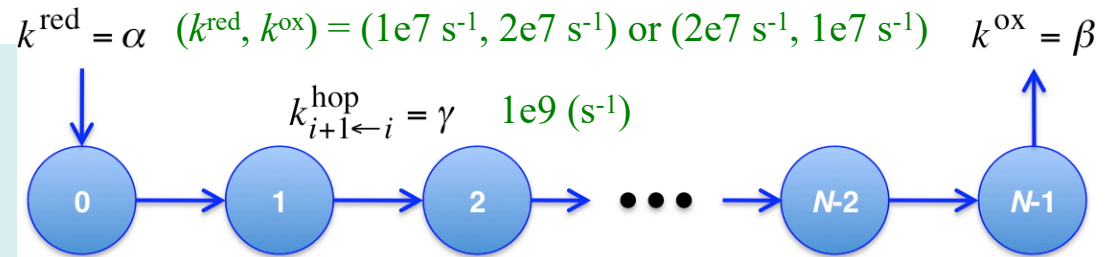
else

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

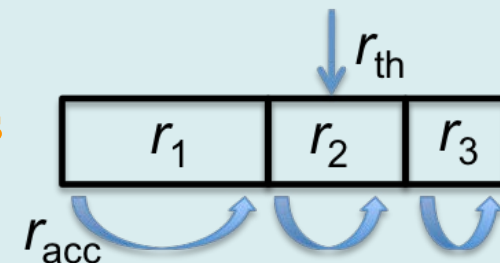
 occ[lsngb[i][k]] ← 1; occ[i] ← 0; **break**

if (r_{th} < r_{acc}) **break**



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

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



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

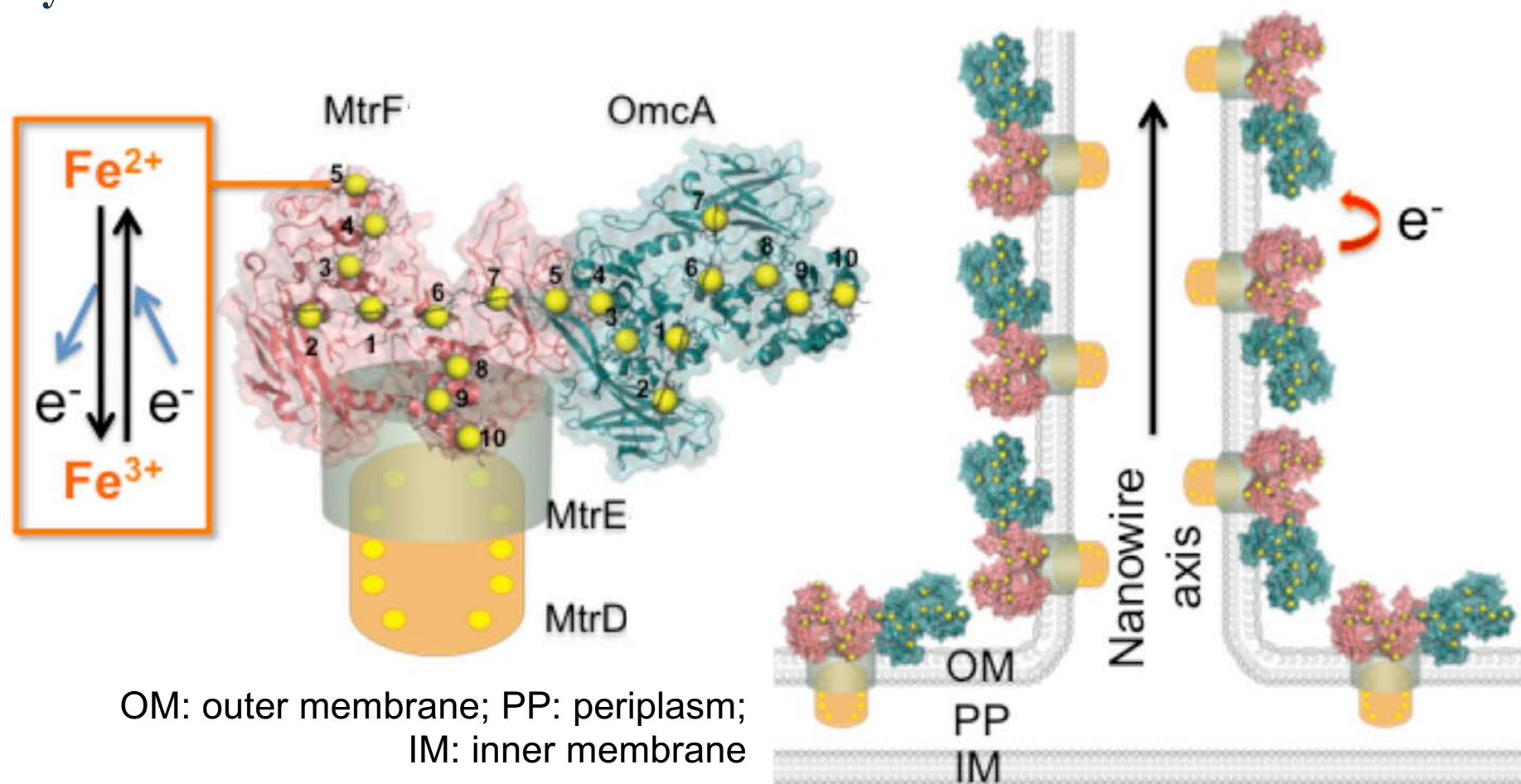


Shewanella emitting electrically conducting nanowires



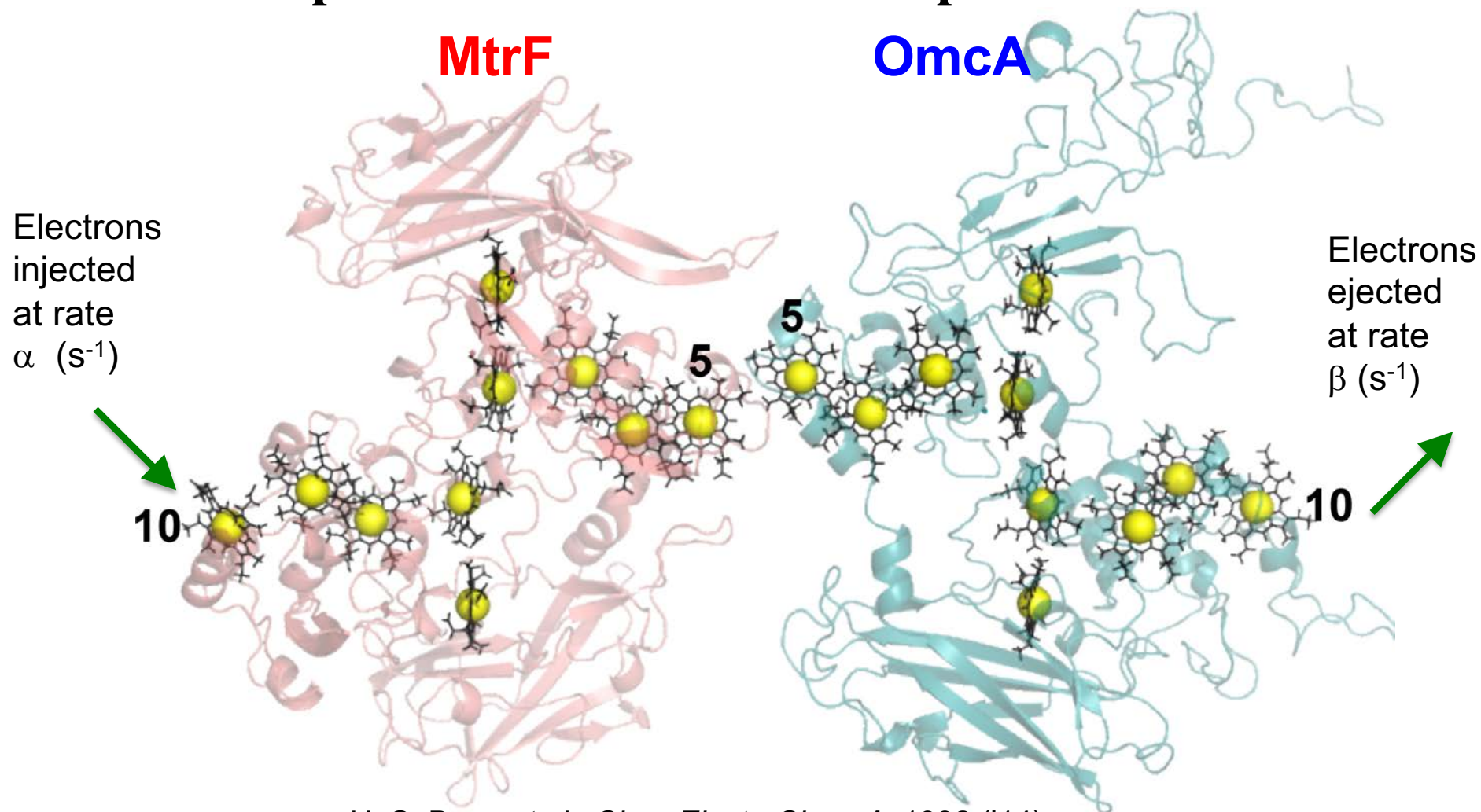
Scientific Problem & Research Goal

- 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



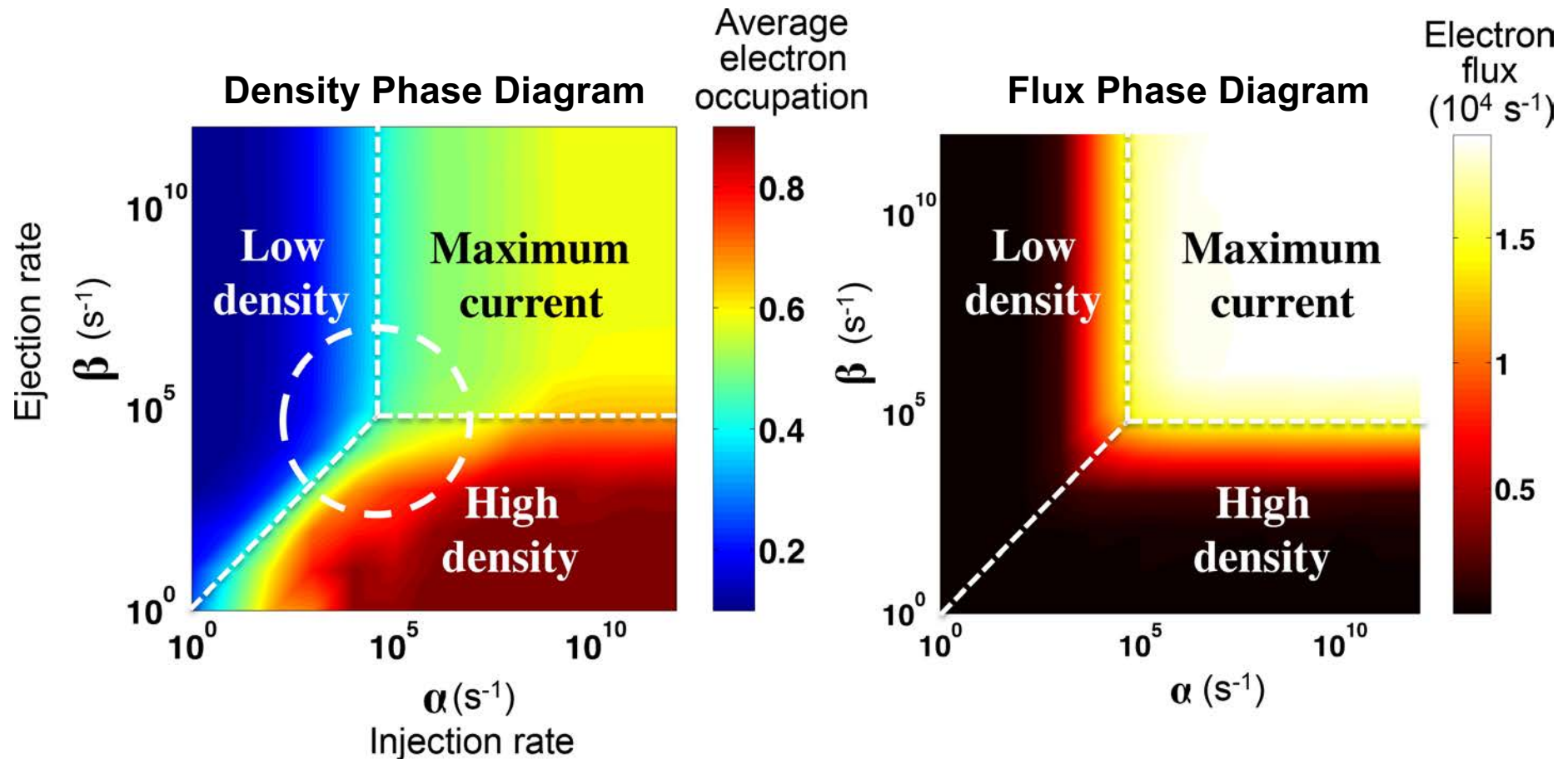
Result: Complex Structure

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)

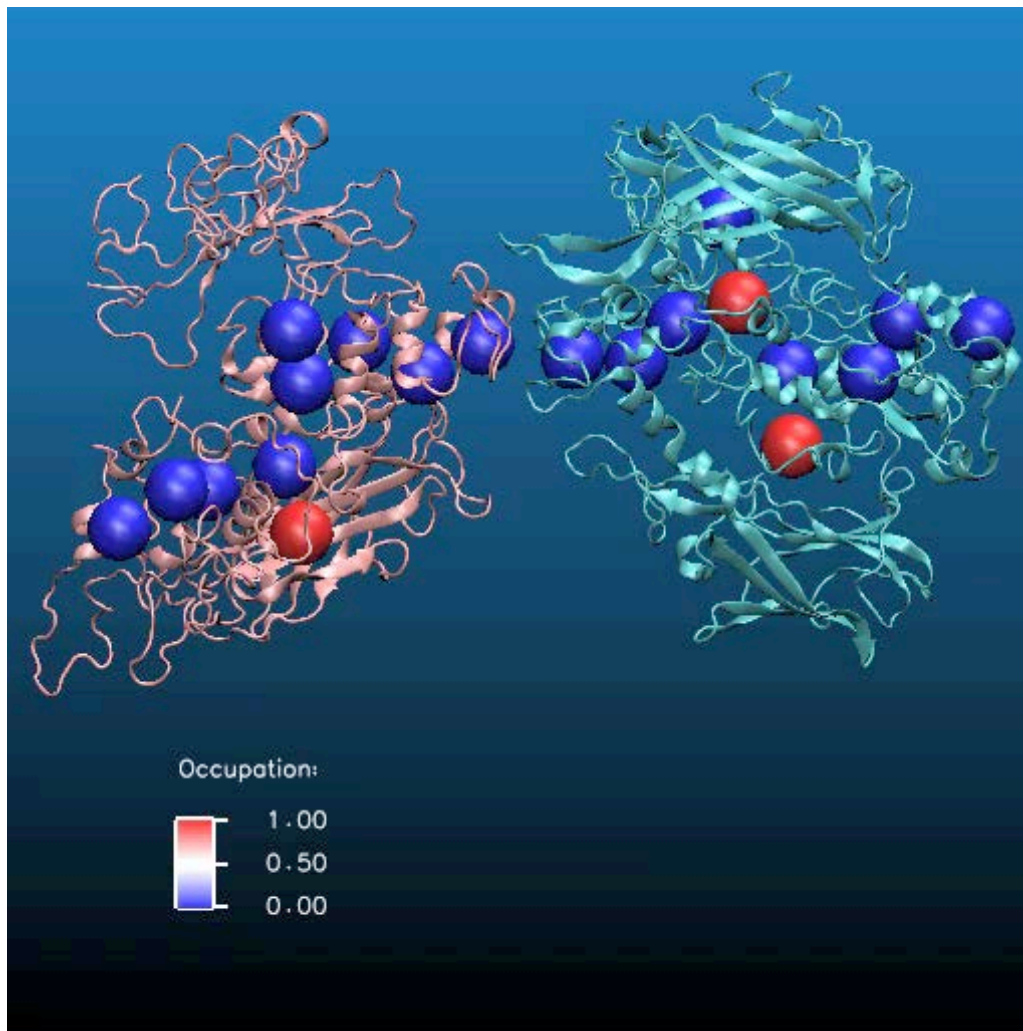
Result: ET Phase Diagram



- KMC results exhibit a nonequilibrium phase transition from low-density to high-density phases for increased ratio of electron injection rate (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 (10³-10⁴ 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

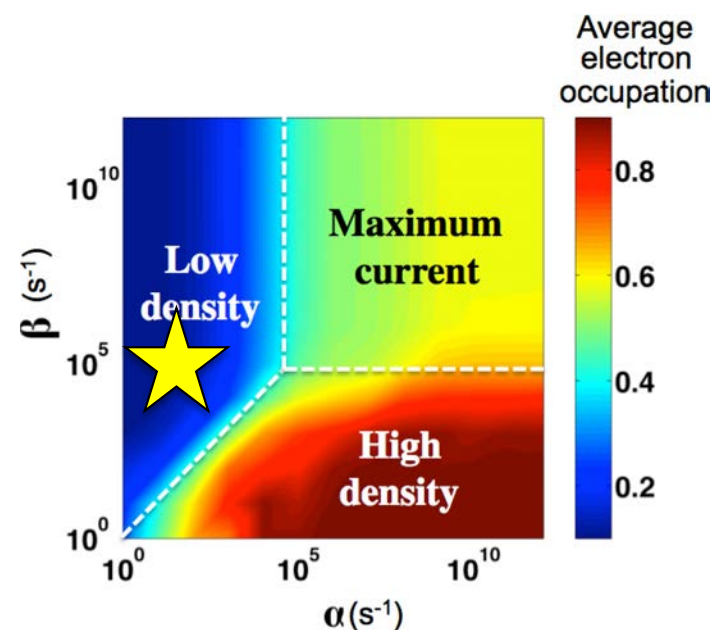
Electron
injection
rate:
 $\alpha = 10^2 \text{ s}^{-1}$



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

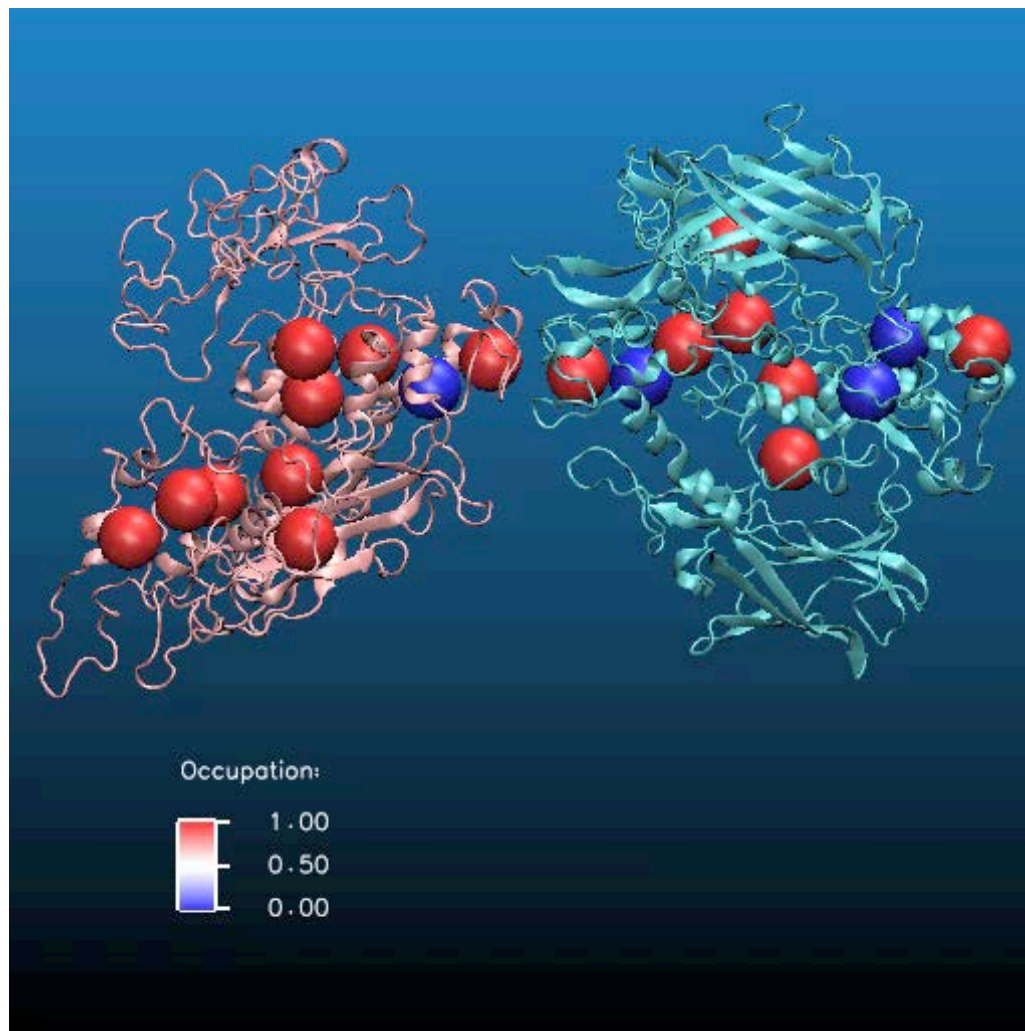


- Electron flow is limited by the small number of electrons



Animation: High-Density Phase

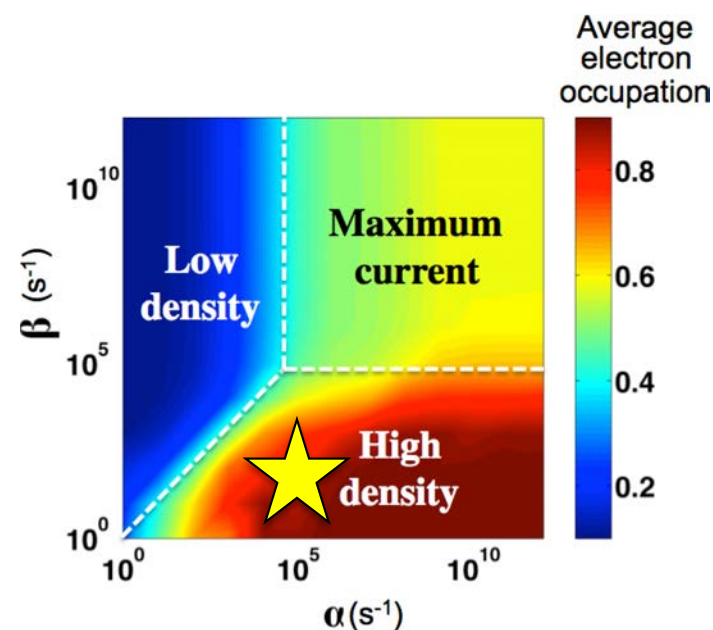
Electron
injection
rate:
 $\alpha = 10^5 \text{ s}^{-1}$



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

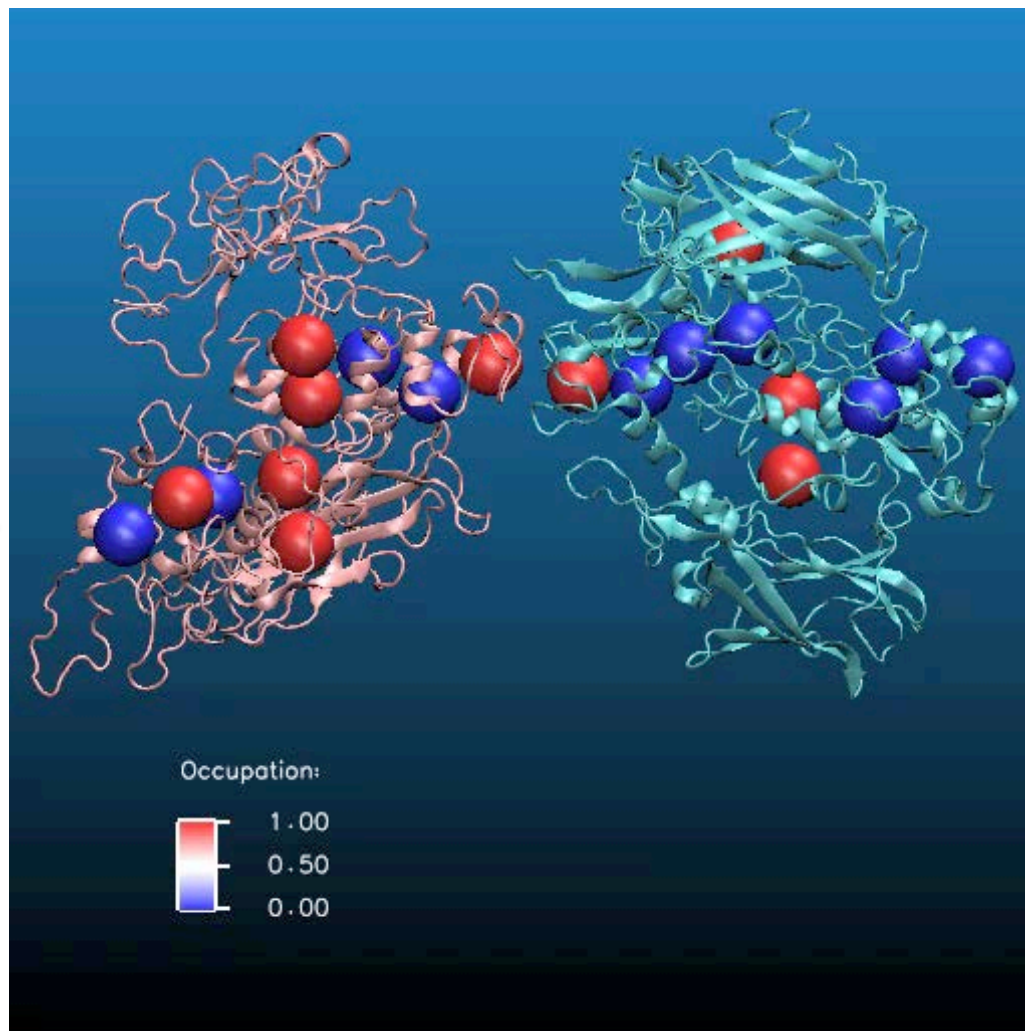


- Electron flow is limited by the congestion of electrons



Animation: Maximum-Current Phase

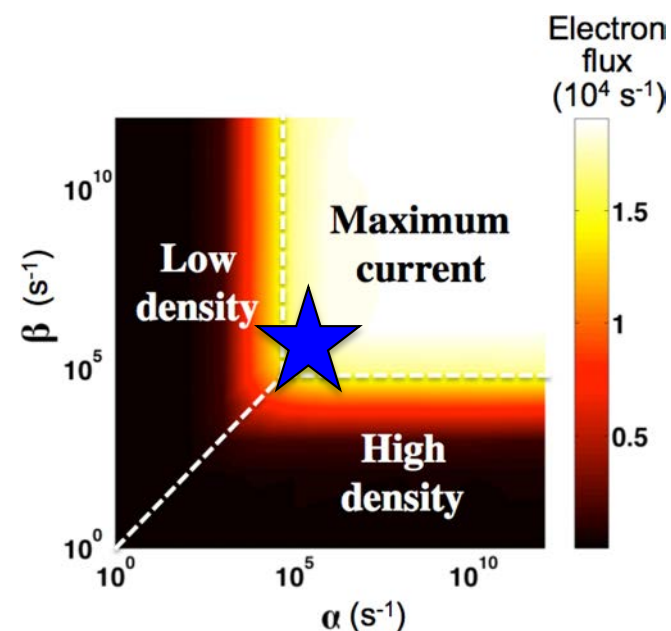
Electron
injection
rate:
 $\alpha = 10^5 \text{ s}^{-1}$



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

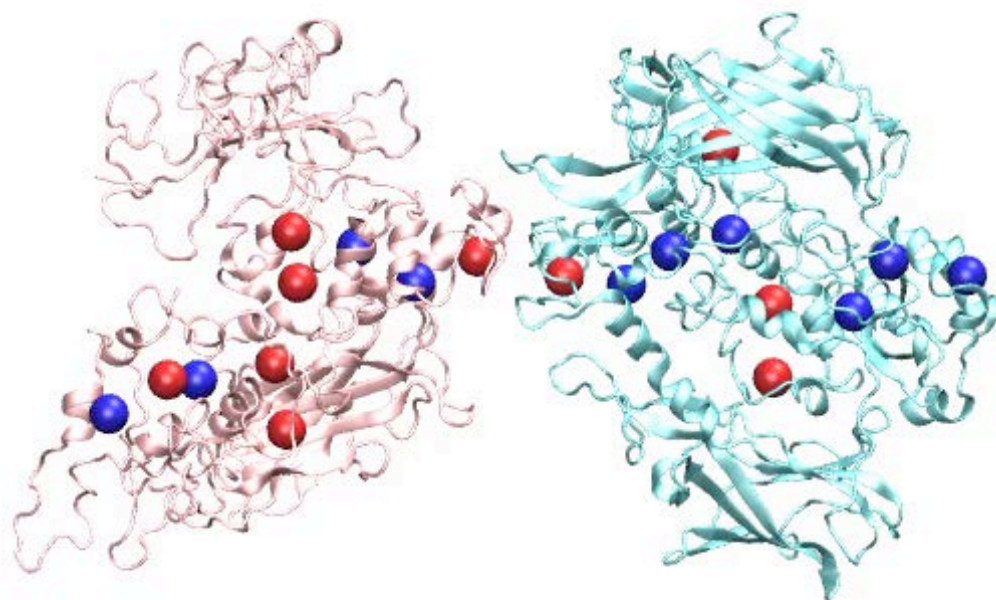


- Large electric current is facilitated by balanced electron injections & ejections
- Life operates around the triple junction

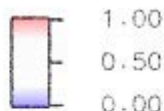


Animation: Maximum-Current Phase

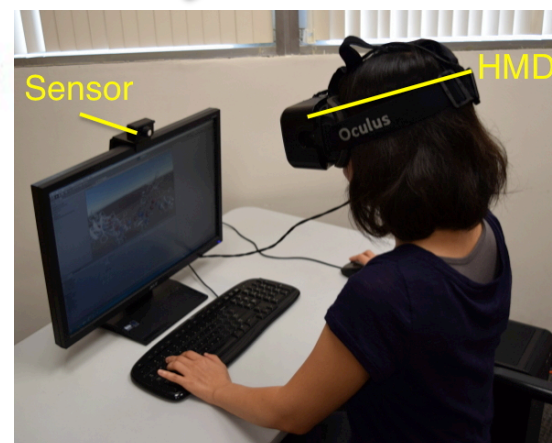
Electron
injection
rate:
 $\alpha = 10^5 \text{ s}^{-1}$



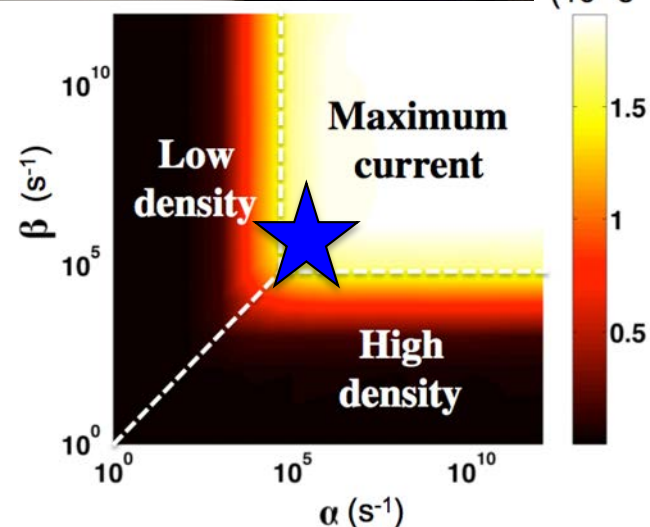
Occupation:



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



Electron
flux
(10^4 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



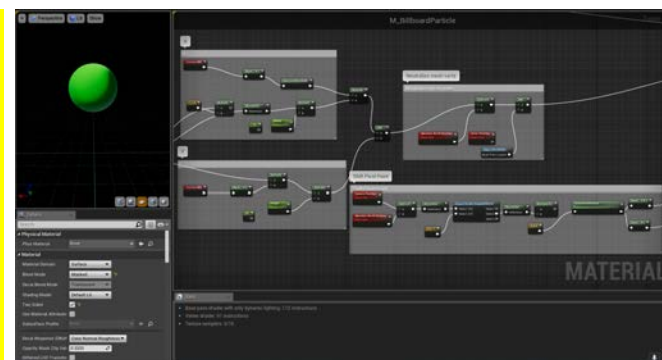
HTC Vive



Photoexcitation in MoSe₂

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

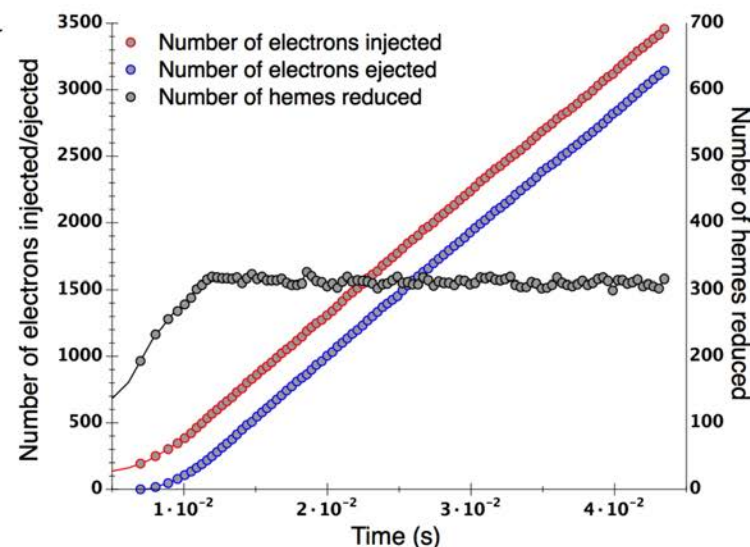
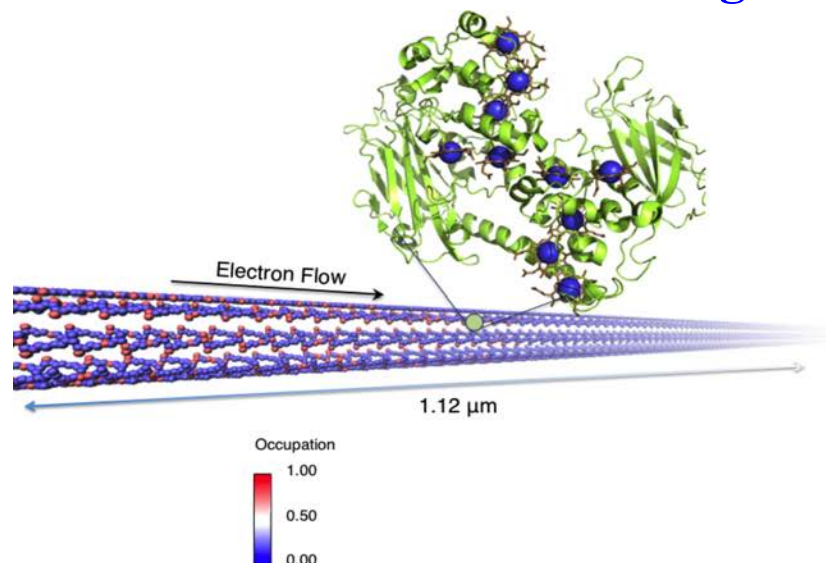


LammpsVR editor



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



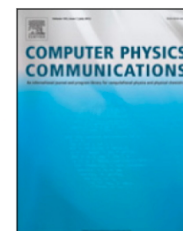
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A derivation and scalable implementation of the synchronous parallel kinetic Monte Carlo method for simulating long-time dynamics



Hye Suk Byun^a, Mohamed Y. El-Naggar^{a,b,c}, Rajiv K. Kalia^{a,d,e,f}, Aiichiro Nakano^{a,b,d,e,f,*},
Priya Vashishta^{a,d,e,f}