A simulation framework for the modeling of adsorption related noise phenomena in electrochemical sensors

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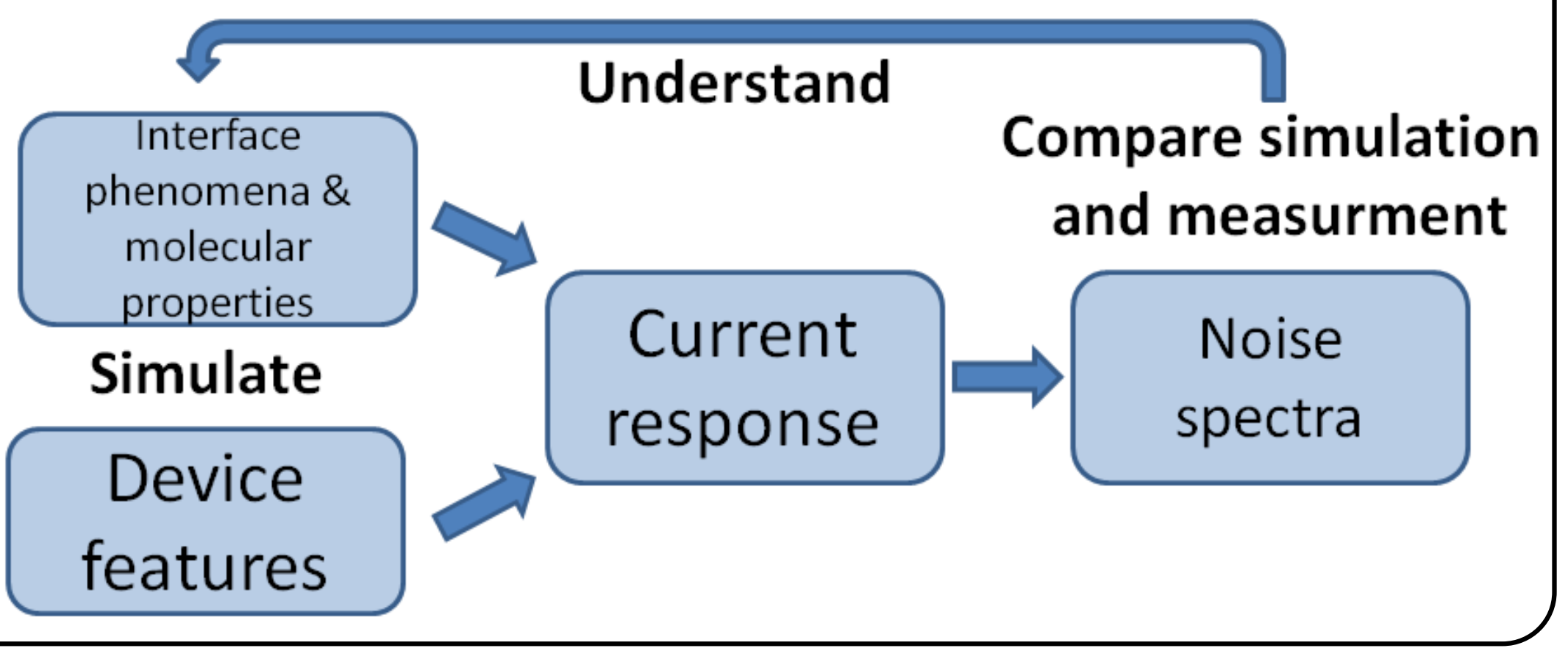
Introduction

Nanocavity redox cycling devices are a promising tool for sensing applications. In most studies, the temporal current response of these devices is investigated. However, the spectrum of the recorded traces also offers unique information on the system allowing fluctuation effects to be investigated in the frequency regime[1]. Here we use a random walk model to investigate the impact of adsorption on the power spectra of redox cycling devices.

Motivation

Simulate electrochemical devices at the molecular level for a deeper understanding of the device response.



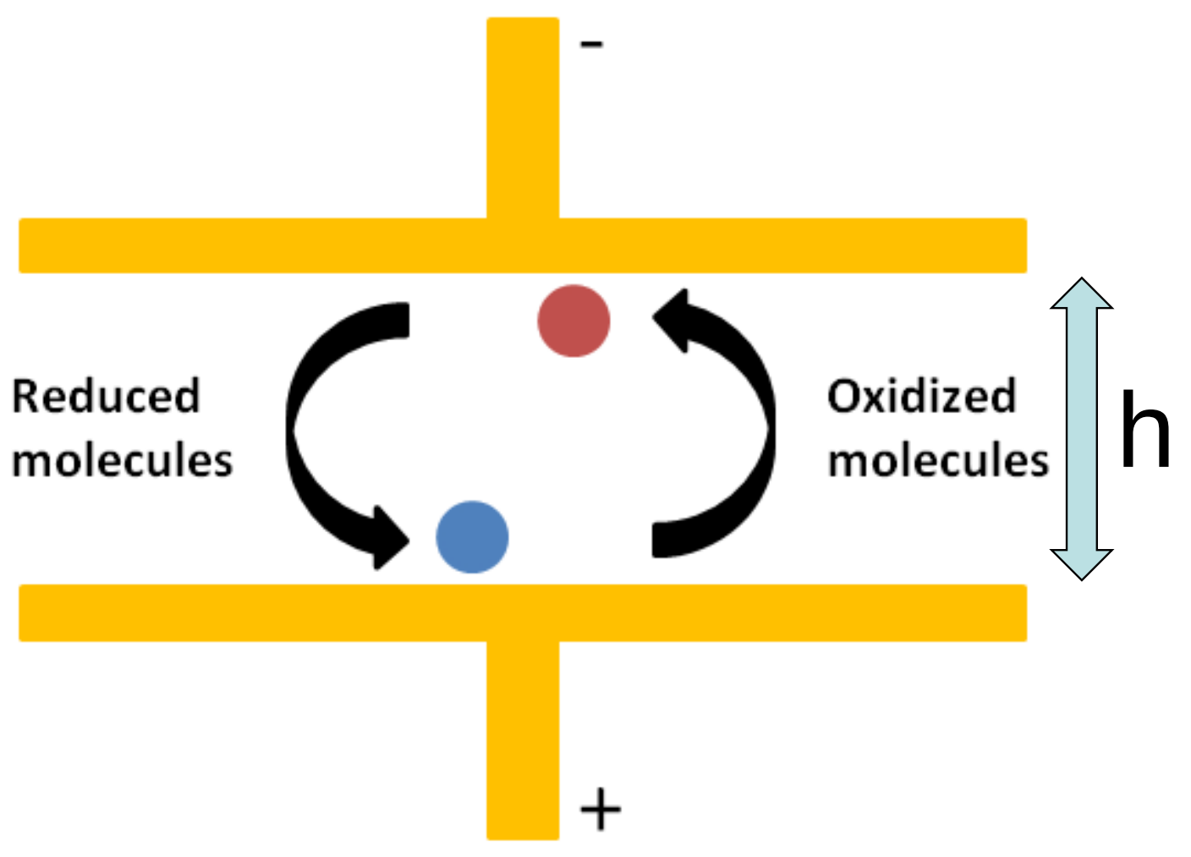
Electrochemical detection and redox cycling

- Diffusive molecular movement in between two individually biased electrodes enables repetitive redox reactions at the two electrodes.

- Amplified net current across the gap:

$$I = \frac{e_0 z D n}{h^2}$$

$e_0 z$ = transferred charge per reaction
n = number of molecules in between the electrodes
D = diffusion constant



Redox cycling priciple

Random walk – Simulation of molecule movement

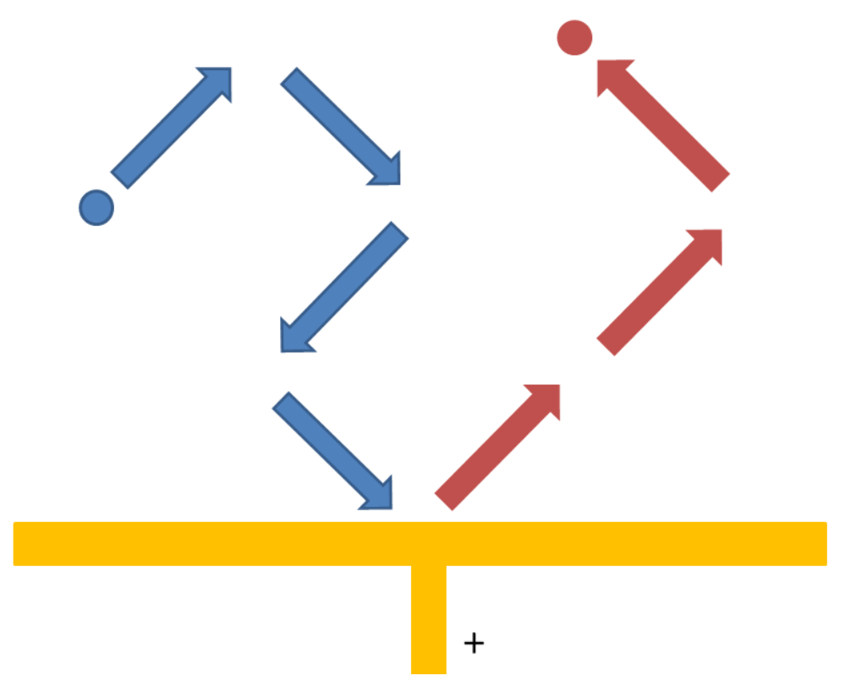
- Written in C/C++, supports parallel computing, freely available

- Independent random walks for each molecule

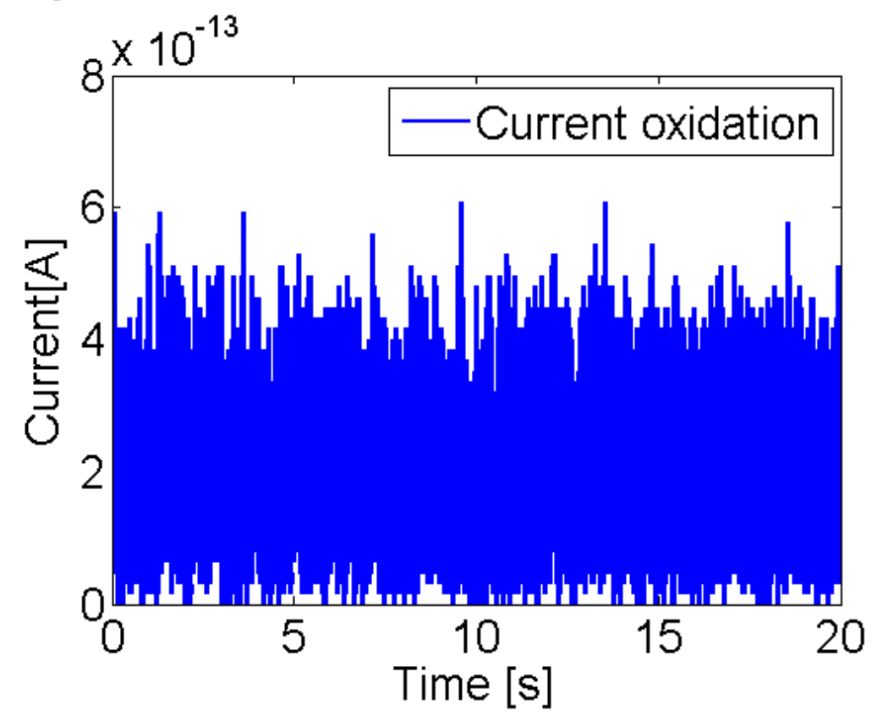
- Temporal and spatial step width match the diffusion equation

- Molecules can adopt two oxidation states

Count the number of electron transfer events per interval



Random walk principle

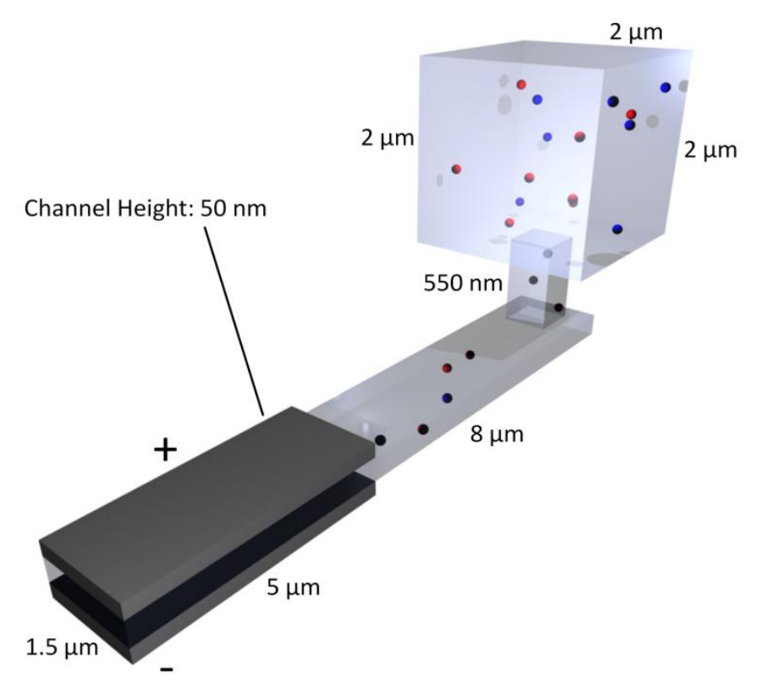


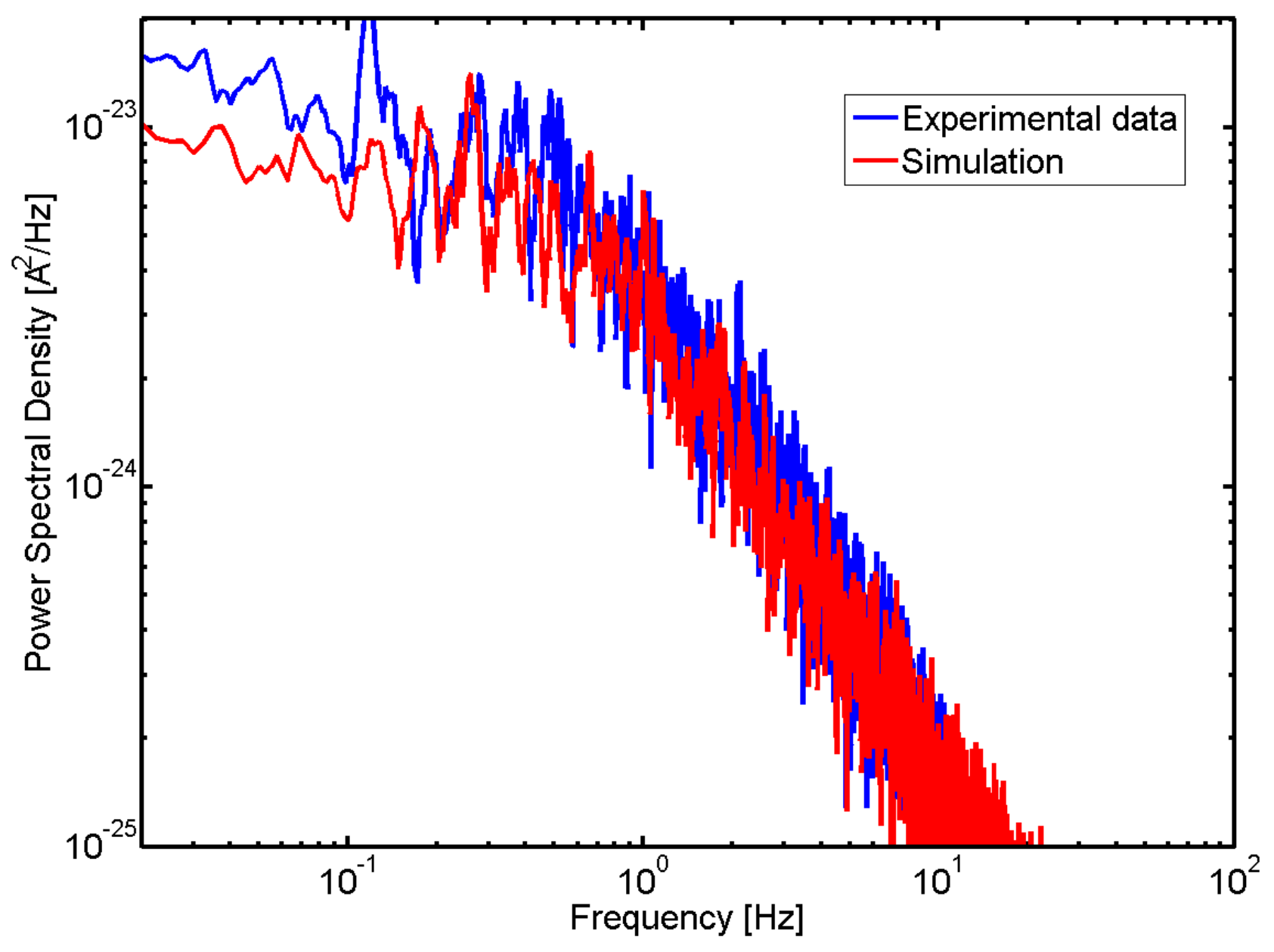
Simulated redox current

Simulation and experiment

- Blue: Experimental data, 50 µM $Fc(MeOH)_2$ solution.

- Red: Simulation, analytically corrected for adsorption(3).



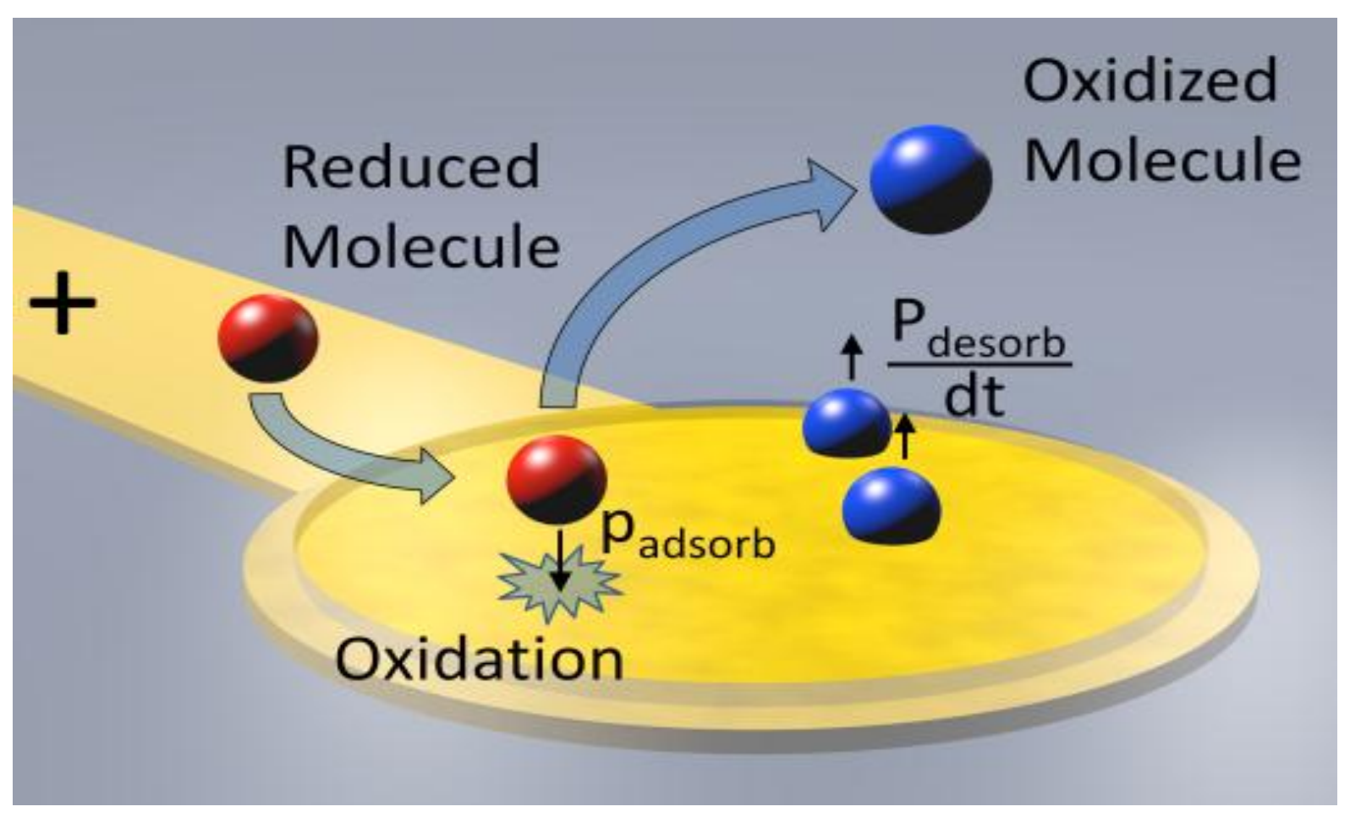


Comparison of the power spectral density of the redox current of experimental data and simulation results.

Reversible adsorption

- Adsorption probability p_{adsorb}

- Desorption probability p_{desorb} per random walk iteration dt

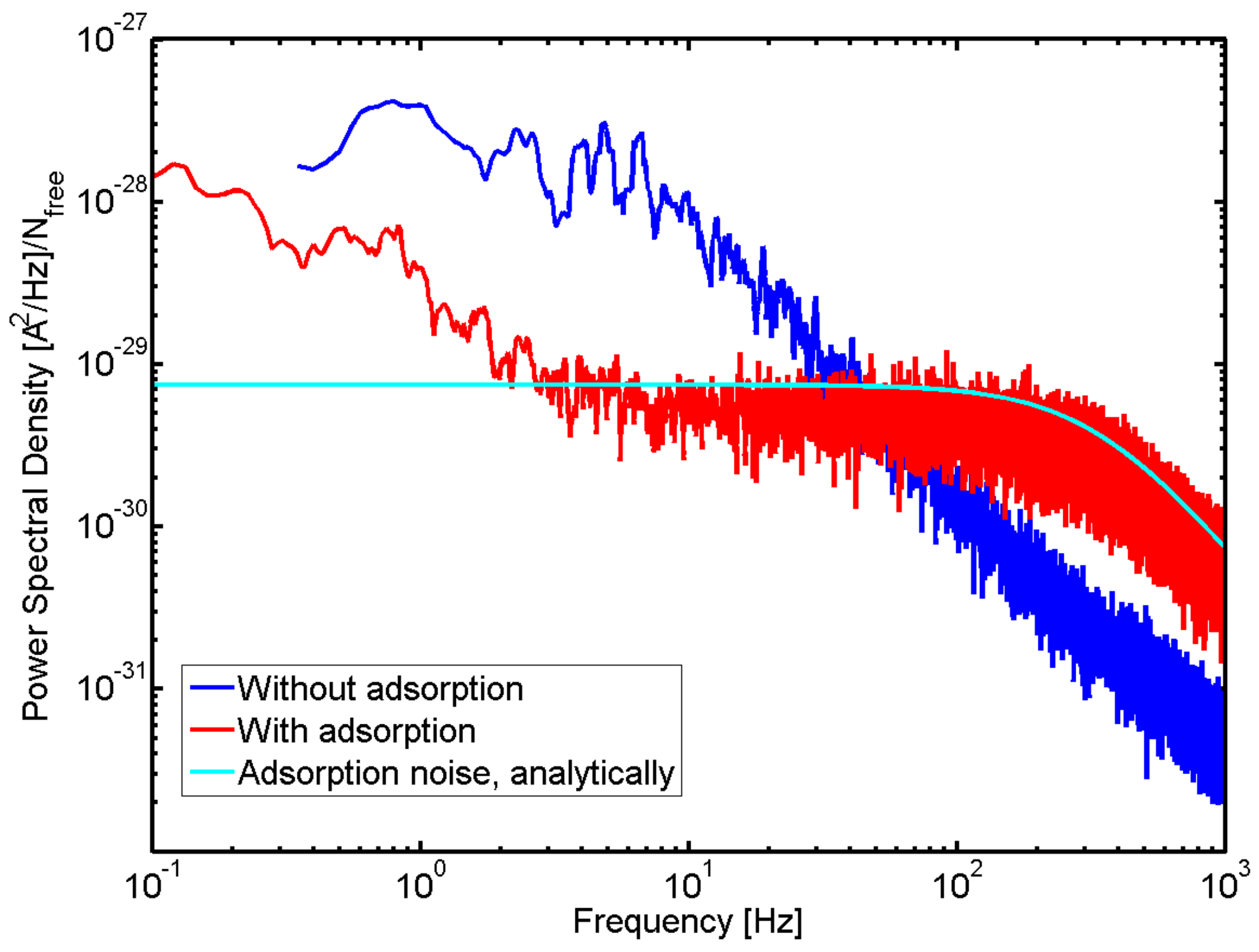


Power spectral density

- Due to the slower effective diffusion caused by adsorption, the spectrum is shifted to lower frequencies

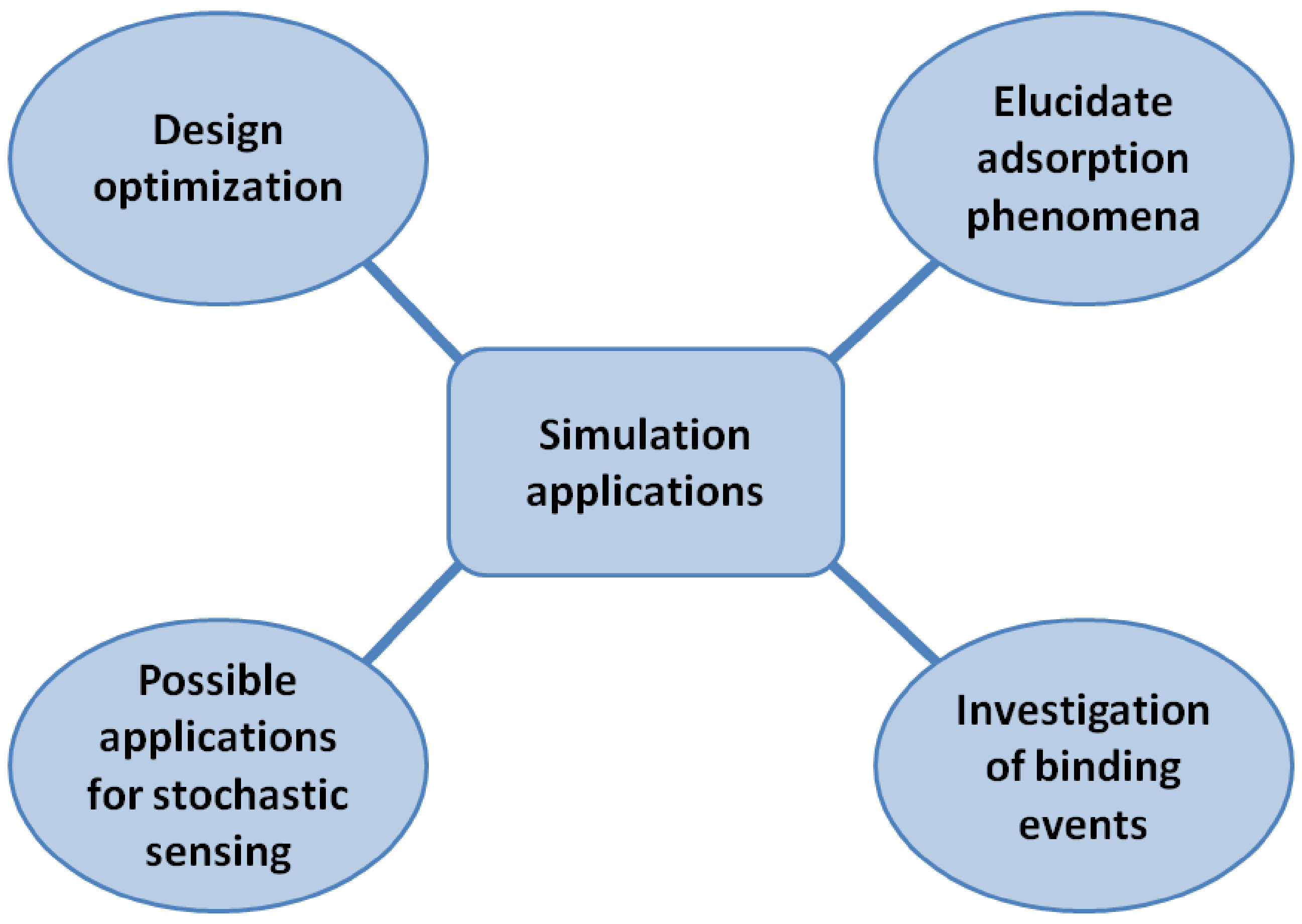
- In addition to the fluctuation noise plateau at low frequencies there is an adsorption noise plateau at higher frequencies

- The frequency regime of this plateau depends on the mean adsorption time



Power spectral density of the redox current with and without adsorption

Simulation applications



Conclusion

We present a simulation framework for the investigation of reversible adsorption on electrochemical redox cycling sensors. The code is freely available for further use and expansion[3].

Acknowledgements

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References

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(2) E. Kätelhön, B. Wolfrum, Phys. Status Solidi A, 209, No. 5, 881–884 (2012)
(3) E. Kätelhön, K. J. Krause, P. S. Singh, S. G. Lemay, B. Wolfrum, *J. Am. Chem. Soc.*, **135,** (2013) 8874-8881

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