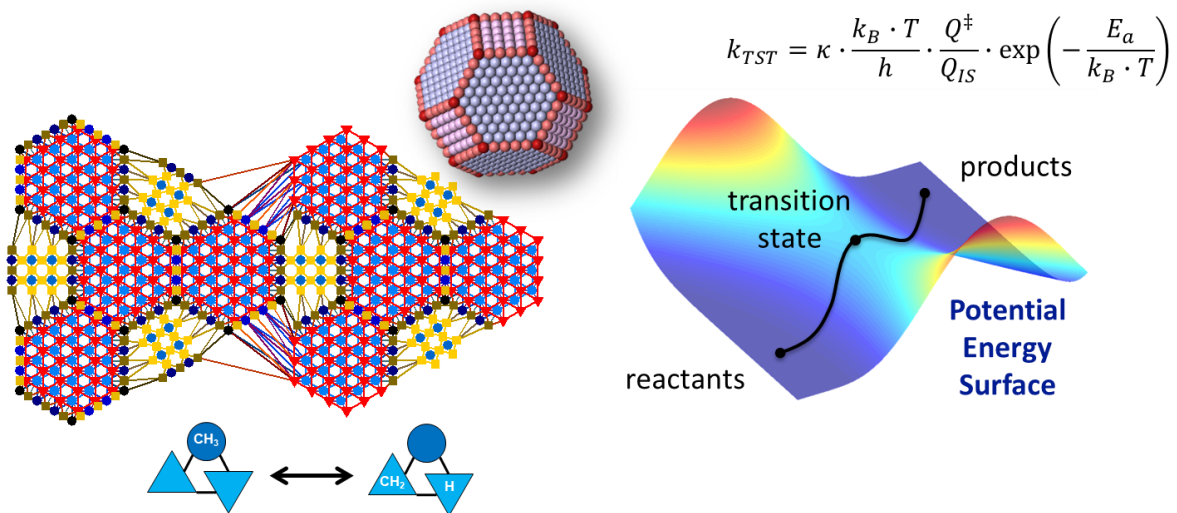# Workshop:
# KMC as a Tool for Understanding Catalytic Function

Fritz Haber Institute, Berlin, Germany

8th – 10th May 2023

# Welcome!

A very warm welcome to all the invited speakers as well as the participants of this Workshop! For a few years now, we have been contemplating the idea of organising such a Workshop on kinetic Monte Carlo (KMC) in Europe, after running a few smaller-scale such events in the USA and Japan. The COVID-19 pandemic unfortunately meant that we had to delay things, but here we got eventually, and I am more than happy to welcome you to the Fritz Haber Institute in Berlin for this event!

I am very grateful to our host Prof. Dr. Karsten Reuter at the Fritz Haber Institute who enabled this opportunity, Julia Pach for administrative support, as well as Steffen Kangowski, Dr. Christoph Scheurer, Dr. Sebastian Matera and their researchers for IT Support. Many thanks also to the researchers at my group at UCL, who developed material for the tutorials and KMC lectures. Finally, none of this would have been possible without support from the Thomas Young Centre (the London Centre for the Theory and Simulation of Materials) and funding from the Alexander von Humboldt Foundation (Bessel Research Award), and the European Commission (grant agreement 814416).
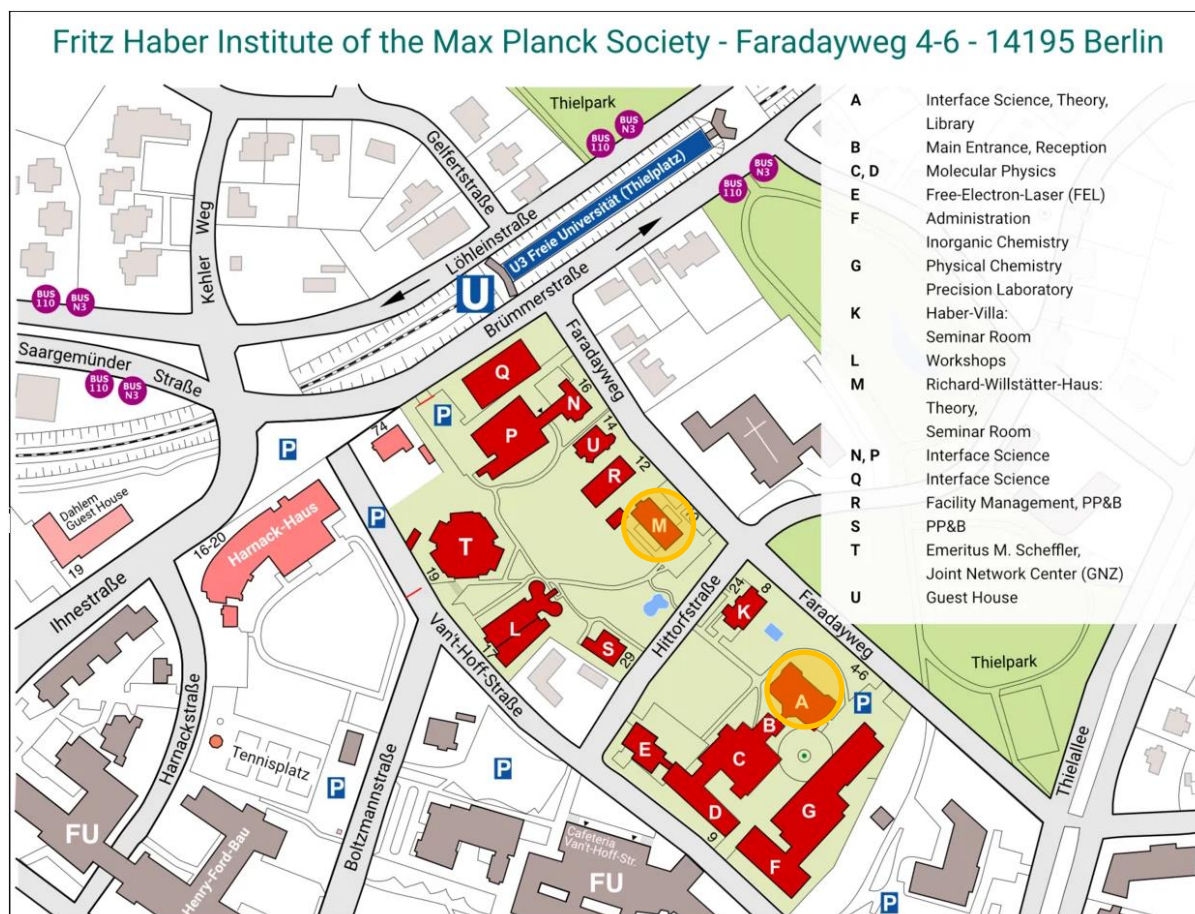
Welcome again, and I hope you have a productive three days with us in Berlin!

Sincerely,

Michail Stamatakis

# Time and Place

The Workshop will take place at the **Fritz Haber Institute** from **8 to 10 May 2023** (three full days). The talks and poster sessions will be held in [Building M, Richard-Willstätter-Haus, Faradayweg 10, 14195 Berlin, Germany](). The hands-on computer practical sessions (tutorials) will take place in [Building A, Faradayweg 4-6, 14195 Berlin, Germany](). These buildings are highlighted with orange circles in the map below. Instructions on how to reach the FHI can be found in: [https://www.fhi.mpg.de/directions](https://www.fhi.mpg.de/directions).



Fritz Haber Institute of the Max Planck Society - Faradayweg 4-6 - 14195 Berlin

| | |
|---|---|
| A | Interface Science, Theory, Library |
| B | Main Entrance, Reception |
| C, D | Molecular Physics |
| E | Free-Electron-Laser (FEL) |
| F | Administration<br>Inorganic Chemistry |
| G | Physical Chemistry<br>Precision Laboratory |
| K | Haber-Villa:<br>Seminar Room |
| L | Workshops |
| M | Richard-Willstätter-Haus:<br>Theory,<br>Seminar Room |
| N, P | Interface Science |
| Q | Interface Science |
| R | Facility Management, PP&B |
| S | PP&B |
| T | Emeritus M. Scheffler,<br>Joint Network Center (GNZ) |
| U | Guest House |

# Technical Program Grid

| | Day 1<br>Monday, May 8 | Day 2<br>Tuesday, May 9 | Day 3<br>Wednesday, May 10 |
|---|---|---|---|
| 9.30-10 | Registration / welcome | Invited Speaker 3<br>Karoliina Honkala | Invited Speaker 6<br>Henrik Grönbeck |
| 10-10.30 | Invited Speaker 1<br>Hannes Jonsson | Invited Speaker 4<br>Sebastian Matera | Invited Speaker 7<br>Franklin Goldsmith |
| 10.30-11 | Invited Speaker 2<br>Franziska Heß | Invited Speaker 5<br>Mie Andersen (ONLINE) | Break |
| 11-11.30 | Break | Break | Invited Speaker 8<br>Felix Studt |
| 11.30-12 | Lecture 1: statistical mechanics<br>Romain Réocreux | Lecture 3: lateral interactions<br>Hector Prats | Invited Speaker 9<br>Ivo Filot |
| 12-12.30 | Lecture 2: the KMC method<br>Raz L. Benson | Lecture 3: lateral interactions<br>Hector Prats | Lunch |
| 12.30-13 | Lunch | Lunch | Lunch |
| 13-13.30 | Lunch | Lunch | Lunch |
| 13.30-14 | Lunch | Lunch | Lecture 4: stiffness<br>Michail Stamatakis |
| 14-14.30 | Tutorial 1: the ZGB model<br>Weitian Li | Tutorial 2: lattices<br>Raz L. Benson and Romain Réocreux | Tutorial 3: the WGSR<br>Hector Prats |
| 14.30-15 | Tutorial 1: the ZGB model<br>Weitian Li | Tutorial 2: lateral interactions<br>Raz L. Benson and Romain Réocreux | Tutorial 3: the WGSR<br>Hector Prats |
| 15-15.30 | Tutorial 1: the ZGB model<br>Weitian Li | Tutorial 2: lateral interactions<br>Raz L. Benson and Romain Réocreux | Tutorial 3: the WGSR<br>Hector Prats |
| 15.30-16 | Break | Break | Break |
| 16-16.30 | Internal Speaker 1<br>Hector Prats | Internal speaker 2<br>Romain Réocreux | Internal speaker 3<br>Raz L. Benson |
| 16.30-17 | Poster session / Q&A | Poster session / Q&A | Poster session / Q&A |
| 17-17.30 | Poster session / Q&A | Poster session / Q&A | Poster session / Q&A |

# Zoom Invitation and Link for Invited Talks and KMC Lectures

Michail Stamatakis is inviting you to a scheduled Zoom meeting.

**Topic: KMC Workshop: Invited talks, KMC Lectures**
Time: May 8, 2023 09:00 AM Amsterdam, Berlin, Rome, Stockholm, Vienna
       Every day, until May 10, 2023, 3 occurrence(s)
       May 8, 2023 09:00 AM
       May 9, 2023 09:00 AM
       May 10, 2023 09:00 AM
Please download and import the following iCalendar (.ics) files to your calendar system.
Daily: https://ucl.zoom.us/meeting/tJYodu-gqTIsHNK4mDjIUAGe6giItAYaMIDt/ics?icsToken=98tyKuCqqzosEtOcth-BRowQGYj4M_zwtlhdgo12yBLBCQlmQyTzYOVLG6ZeKdn9

Join Zoom Meeting
https://ucl.zoom.us/j/92516879666?pwd=bStiQlU2RHJuNHNFditPV3ZXZ244Zz09

Meeting ID: 925 1687 9666
Passcode: 815875
One tap mobile
+17193594580,,92516879666#,,,,*815875# US
+19292056099,,92516879666#,,,,*815875# US (New York)

Dial by your location
       +1 719 359 4580 US
       +1 929 205 6099 US (New York)
       +1 253 205 0468 US
       +1 253 215 8782 US (Tacoma)
       +1 301 715 8592 US (Washington DC)
       +1 305 224 1968 US
       +1 309 205 3325 US
       +1 312 626 6799 US (Chicago)
       +1 346 248 7799 US (Houston)
       +1 360 209 5623 US
       +1 386 347 5053 US
       +1 507 473 4847 US
       +1 564 217 2000 US
       +1 646 931 3860 US
       +1 669 444 9171 US
       +1 669 900 6833 US (San Jose)
       +1 689 278 1000 US
Meeting ID: 925 1687 9666
Passcode: 815875
Find your local number: https://ucl.zoom.us/u/aQmixm4Z7

# Instructions for the Hands-on Tutorial Sessions

## Option 1: Setting up Virtual Machine in Your Own Laptop

This is the preferred option. You will be setting up a Virtual Machine in your computer, which contains the *Zacros* code and the trial version of *Zacros*-post. To do this:

1. Download and install a Virtual Machine manager. We recommend VirtualBox, which supports several host operating systems. It can be obtained from the following link (make sure you download the installation file appropriate for your system):

   https://www.virtualbox.org/wiki/Downloads

2. Download the Virtual Machine appliance for the KMC Workshop from (this is a ~10 GB file so it may take a while, depending on your connection):

   http://zacros.org/files/handson2023_v4.1.ova

3. Open VirtualBox and import the Virtual Machine appliance using File > Import Appliance, as shown in the snapshots below (note that importing can take several minutes):
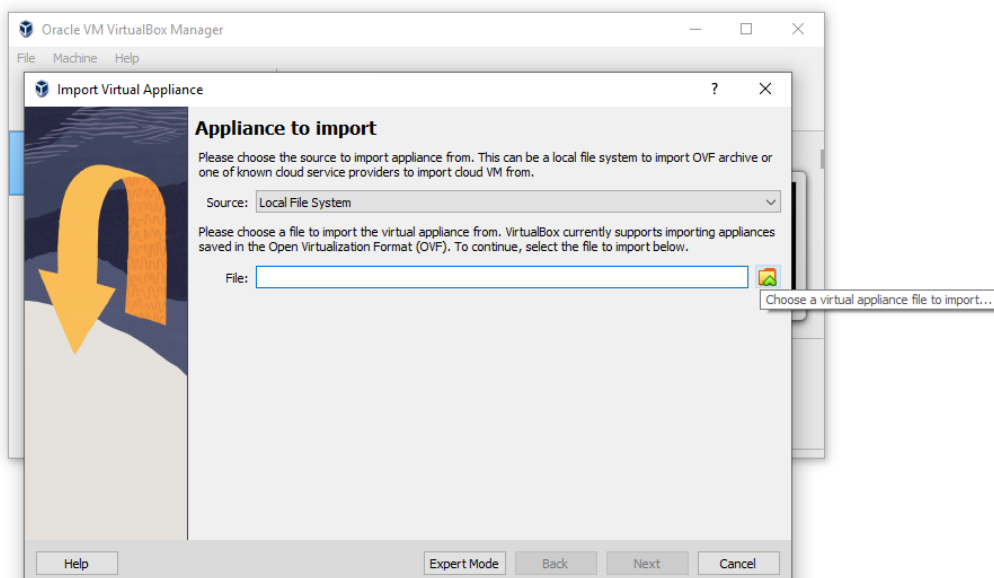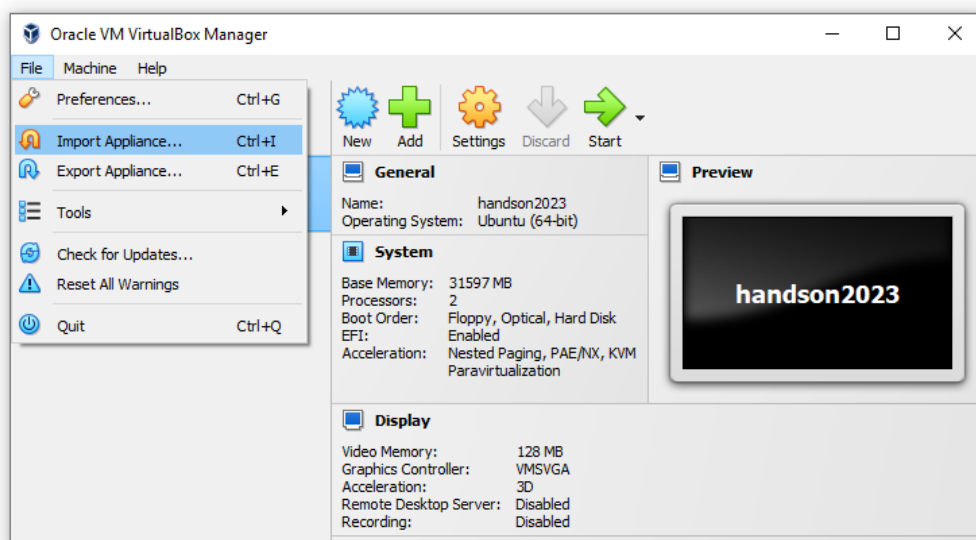
4. Once the Virtual Machine is set up in your system, click on the green right-arrow icon (marked "Start") to fire-up the machine and then login using the following credentials:

username: handson
password: handson2023

5. The *Zacros* distribution files and the *Zacros*-post installation can be found by navigating to Home/Documents from the Desktop, or accessing the full path /home/handson/Documents using Nautilus (the "file explorer" of Ubuntu), or simply by clicking on "Documents" in the top taskbar:
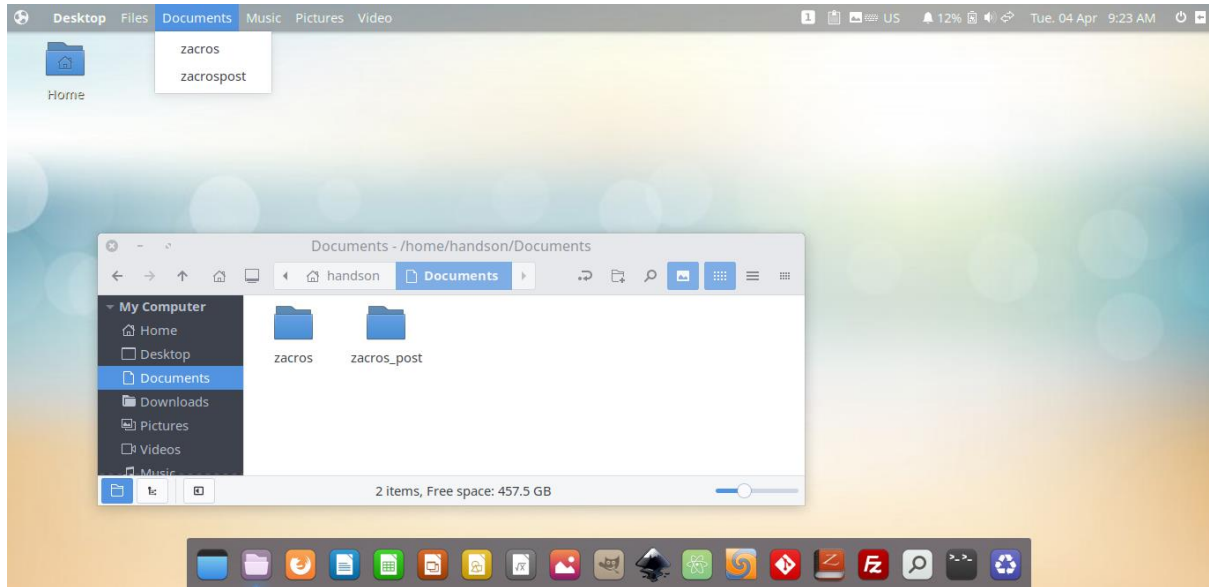


Note: if you have not yet obtained licenses for *Zacros* v3.01 and *Zacros*-post, please do so by following the instructions in:

https://zacros.org/software

Use of the *Zacros* and *Zacros*-post software installed in the Virtual Machine is subject to the terms and conditions outlined in the respective licenses, which can be found in the pages below (click on the links "*Preview terms*" therein):

https://xip.uclb.com/product/zacros-3

https://xip.uclb.com/product/zacros-post

## Option 2: Accessing Virtual Machine in the FHI Cluster

For participants who had issues installing the Virtual Machine in their laptop, we have made available a Virtual Machine in a local cluster at Fritz Haber. To log into to this Virtual Machine the participant will need two accounts: one in the Max Planck computing platform (this will be referred to the "mpcdf guest account") and one separate account in the Virtual Machine. Participants' user accounts on the Virtual Machine are named such that Albert Einstein would have aeinstein as account name (note that the mpcdf guest account name might differ). The participant will also need a key pair and default user password, which are available on request. We have already set up such accounts and shared the key pair for participants who informed us they had issues with Option 1. If you had issues but you have not been given account credentials and the key pair for Option 2, please let us know as soon as possible.

### Linux/Mac Systems

To access the Virtual Machine on the cluster via a **Linux (or Mac) system**:

1. In a terminal on your laptop create a couple of new directories:

   ```
   mkdir ~/.ssh/zacros_workshop/
   ```

   ```
   mkdir ~/.ssh/zacros_workshop/key_pairs/
   ```

   and, using your file explorer (e.g., *Nautilus* in Ubuntu or *Finder* in macOS), navigate to the `~/.ssh/zacros_workshop/key_pairs` directory and place the key pair (two files: `zacros_rsa` (private key) and `zacros_rsa.pub` (public key)) in that directory.

   Note: the .ssh directory may be hidden, so you may have to manually type the directory name (path) in the search bar. In Ubuntu's Nautilus this can be done using Ctrl+L and then typing the path. In Finder there is a menu option Go > Go to Folder.

2. Open the SSH configuration file for editing. This is typically located in the user's home directory, e.g. `~/.ssh/config`. If it does not exist, you can create it with:

   ```
   touch ~/.ssh/config
   ```

   Open the file with your favourite text editor and add the following lines:

   ```
   Host fhi_gate_mstam
    ServerAliveInterval 120
    ControlMaster auto
    ControlPersist 12h
    ControlPath ./an-%C
    Hostname gatezero.mpcdf.mpg.de
    # Change [mpcdf username] to the actual
    #  mpcdf user name of the participant, below:
    User [mpcdf username]
    Port 22

   Host hpc-cloud-mstam-workstation-root
    Hostname 10.186.1.53
    # Change [VM username] to the actual VM user name, below:
    User [VM username]
    Port 22
    # You may need to replace the path ~/.ssh/zacros… below with
    #  the actual path where the user's private key is located:
    IdentityFile ~/.ssh/zacros_workshop/key_pairs/zacros_rsa
    ProxyCommand ssh fhi_gate_mstam -W %h:%p
   ```

3.  Install the TigerVNC Viewer (`tigervnc-viewer`) on your system. For Ubuntu, the TigerVNC Viewer can be easily found in the Software app (use the name of the program as keyword). For other systems, see https://tigervnc.org/ for instructions (section Downloads).

4.  In a terminal in your laptop run:

    ```
    <on your laptop>$ ssh hpc-cloud-mstam-workstation-root
    ```

    If you are asked whether you want to continue connecting type `yes` and enter. You will be asked to provide your password and your one-time password (OTP). These are the credentials you should have been given (or that you set up, e.g. for the OTP), that allow you to connect to the MPCDF gateway.

5.  In the same terminal where you ran the above command (and which should now be connected to the VM on the cluster), run:

    ```
    vncserver
    ```

    At this step you will be asked to set up a password, which will be for accessing the graphical environment of the VNC server. Keep your password in a safe place. Also, make a note of the display because it will be used in the next step. Specifically, note the number that appears after "desktop at :" in the message:

    ```
    New 'mstam-workstation:1 (mstam)' desktop at :1 on machine mstam-workstation
    ```

6.  Run from a **new** terminal in your laptop:

    ```
    <on your laptop>$ ssh -L 2345:localhost:5901 hpc-cloud-mstam-workstation-root
    ```

    The number 5901 (which signifies a port in the remote system), will have to be changed to 5900 + n, where n is the number that appeared after "desktop at :" in the message of the previous step. So, if you got "`desktop at :2`", you should have 5902 in your command above. Keep in mind that you will need you MPCDF password and OTP to connect.

7.  Then in a new terminal in your laptop run:

    ```
    vncviewer localhost:2345
    ```

    and enter the VNC password you just set when prompted.

## Windows Systems

It is assumed that OpenSSH is installed in your Windows machine, therefore if you open a Windows PowerShell and type ssh + Enter, you should see the help message of ssh. If you get an error, consult the following page on how to install OpenSSH in your machine: https://learn.microsoft.com/en-us/windows-server/administration/openssh/openssh_install_firstuse?tabs=gui

Then, to access the Virtual Machine on the cluster via a **Windows system**:

1. Use Windows explorer, and navigate to `C:\Users\YourUserName\.ssh\`, where `YourUserName` should be replaced by your own user name. Then create one directory there named `zacros_workshop`, and inside that directory create another one `key_pairs`. Finally, place the key pair (two files: `zacros_rsa` (private key) and `zacros_rsa.pub` (public key)) in that directory in that directory. At the end of this step, the Explorer window should like the following:
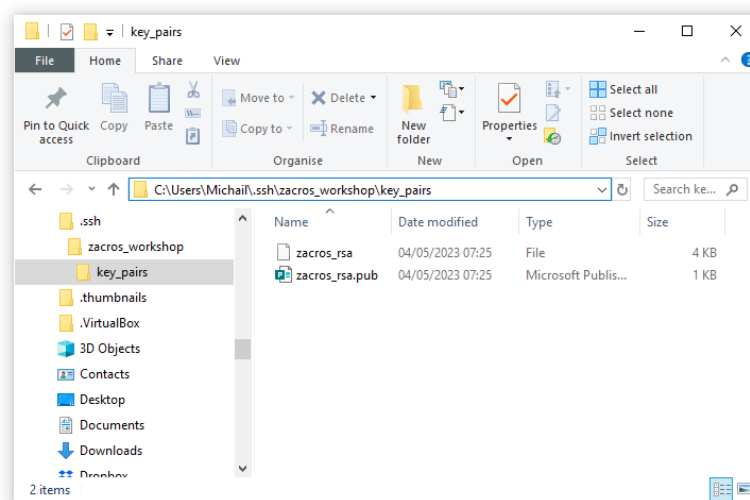


2. Open the SSH configuration file for editing. The path of this file is typically `C:\ProgramData\ssh\ssh_config` (to be clear, `ssh_config` is the filename and it is located in directory `C:\ProgramData\ssh\`). If it does not exist, you can open notepad as Administrator create it and save it in the aforementioned directory. To do this, click on the Start icon of Windows at the bottom left of your screen, type "notepad" and then right click on the top option and select *Run as administrator*:



10
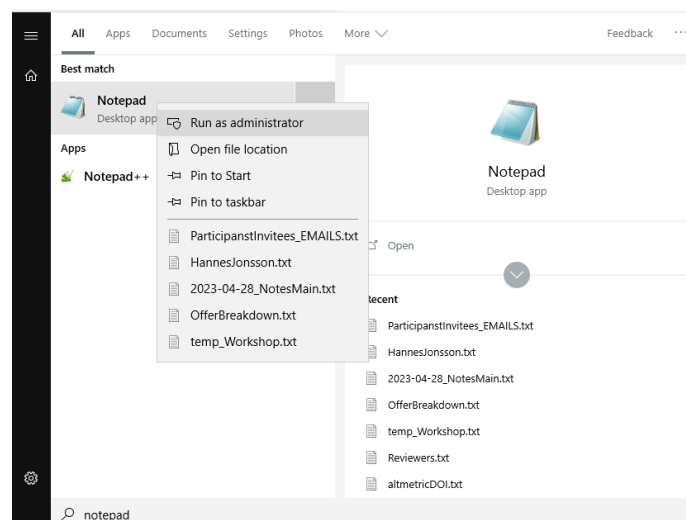
In the `ssh_config` file (which is now open in notepad) add the following lines, then save and close it:

```
Host fhi_gate_mstam
  ServerAliveInterval 120
  Hostname gatezero.mpcdf.mpg.de
  # Change [mpcdf username] to the actual
  #  mpcdf user name of the participant, below:
  User [mpcdf username]
  Port 22

Host hpc-cloud-mstam-workstation-root
  Hostname 10.186.1.53
  # Change [VM username] to the actual VM user name, below:
  User [VM username]
  Port 22
  # Replace path below with path where the private key
  #  is located:
  IdentityFile C:\Users\Michail\.ssh\zacros_workshop\key_pairs\zacros_rsa
  # The ssh path below must be a full path.
  #  Amend it, if ssh.exe is located elsewhere in your computer:
  ProxyCommand C:\Windows\System32\OpenSSH\ssh.exe fhi_gate_mstam -W %h:%p
```

3. Download the RealVNC Viewer for Windows from:
   https://www.realvnc.com/en/connect/download/viewer/

4. Open a PowerShell terminal on your laptop and run:

   ```
   <on your laptop>$ ssh hpc-cloud-mstam-workstation-root
   ```

   If you are asked whether you want to continue connecting type `yes` and enter. You will be asked to provide your password and your one-time password (OTP). These are the credentials you should have been given (or that you set up, e.g. for the OTP), that allow you to connect to the MPCDF gateway.

5. In the same terminal where you ran the above command (and which should now be connected to the VM on the cluster), run:

   ```
   vncserver
   ```

   At this step you will be asked to set up a password, which will be for accessing the graphical environment of the VNC server. Keep your password in a safe place. Also, make a note of the display because it will be used in the next step. Specifically, note the number that appears after "desktop at :" in the message:

```
New 'mstam-workstation:1 (mstam)' desktop at :1 on machine mstam-workstation
```

6. Run from a **new** PowerShell terminal in your laptop:

```
<on your laptop>$ ssh -L 2345:localhost:5901 hpc-cloud-mstam-workstation-root
```

The number 5901 (which signifies a port in the remote system), will have to be changed to 5900 + n, where n is the number that appeared after "desktop at :" in the message of the previous step. So if you got "`desktop at :2`", you should have 5902 in your command above. Keep in mind that you will need you MPCDF password and OTP to connect.

7. Open RealVNC Viewer in in the top bar type:

```
localhost:2345
```

Hit Enter to start the connection and provide the VNC password you just set when prompted.

# Kinetic Monte Carlo without predefined table of transitions and applicable to disordered systems

Hannes Jónsson[1],[*]

[1] *Faculty of Physical Sciences, University of Iceland, Sæmundargata 2, 102 Reykjavík, Iceland*

[*]*Email: hj@hi.is*

A brief introduction to the kinetic Monte Carlo method will be given, following the evolution from the use of rates fitted to observations, to the use of empirical potential functions as a means of determining the relevant mechanisms and rates of transitions to electronic structure calculations accelerated with machine learning. A formulation of the KMC method where a table of possible events is not specified beforehand but rather constructed during the simulation for each state visited (referred to as 'adaptive', 'on-the-fly', or 'self-learning') will be presented, along with an approach based on absorbing Markov chains for dealing with disparate time scales. Examples of applications to diffusion and island formation on ordered and disordered surfaces as well as diffusion along grain boundaries will be given.

# Model fitting: pitfalls and solutions, or: "How to fit an elephant…"

Franziska Hess[1,*]

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[*]*Email: f.hess@tu-berlin.de*

Fitted models represent complex data in a simple functional form by relying on a limited number of fitted parameters that enable the quick, on-the-fly evaluation of the output variable(s) based on input variable(s). In bottom-up multiscale modeling, fitted models are often used as surrogate for computationally demanding electronic structure calculations. Here, the acquisition of sufficient data is a severe bottleneck in the overall modeling process, resulting in typically small datasets with limited statistical significance. Yet, the ability of the resulting models to reliably predict new data points is the core requirement for successful subsequent integration into other models. Models that are fitted with the exclusive goal of representing the original data as accurately as possible sometimes fall into the pit of overfitting, which renders them unable to predict new data with the same accuracy as they reproduce the original data, while underfitted models often fail at both. This contribution will give an introduction on how to use statistical diagnostics to measure the reliability of models based on small datasets by examining statistical leverage and the influence of individual data points on the predictions in order to identify "problem areas" in the model that require revision, more data or additional fitting. Finally, it will be demonstrated how to use these tools to select data in order to minimize the number of computations that need to be run while maximizing the reliability of the resulting model within given constraints.

# Modelling electrocatalytic NO reduction by KMC

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[*]*Email: karoliina.honkala@jyu.fi*

The reduction of NO has been identified as a key step in the electrochemical denitrification of nitrites and nitrates.  Combining density functional theory calculations and kinetic Monte Carlo simulations, the reduction reaction was studied on Pt(100) [1]. This approach describes the effects of coverage-dependent adsorbate-adsorbate interaction, reaction thermodynamics, water-mediated protonation kinetics, and transient potential sweeps on product rates and selectivity. KMC simulations can predict electrochemical NO stripping curves in nice agreement with experiments and provide an elementary mechanistic interpretation of observed current peaks. The DFT-KMC methodology provides a full reaction profile and reveals the sensitive balance between thermodynamics and kinetics in NO reduction. However, the computational approach is sufficiently general to be applicable to other electrocatalytic processes on metal catalysts that are technologically and environmentally important.
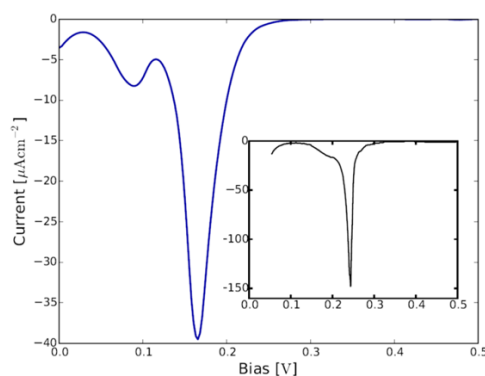


**Figure 1:** The Voltametric profile for the reductive stripping of NO from KMC simulations at the initial NO coverage of 0.5 ML. The inset gives the experimental profile extracted from the work of Rosca and Koper [2].

## References

[1] H.J. Chon, V. Apaja, A.Clayborne, K. Honkala, J. Greeley, *ACS Catal.* **7**, 3869 (2017).
[2] V. Rosca, M.T.M. Koper, *J. Phys. Chem. B* **109**, 16750 (2005).

# Beyond rate-controlling steps:
# Global sensitivity analysis for first principles kinetic models

Sebastian Matera[1,2,*] Sandra Döpking[2], Sina Dortaj[1]

[1]*Theory, Fritz Haber Institute of the MPS, Faradayweg 4-6, 14195 Berlin, Germany*
[2]*Institute f. Mathematics, Arminallee 6, 14195 Berlin, Germany*
[*]*Email: matera@fhi.mpg.de*

Rate-controlling steps are determined by a local sensitivity analysis, i.e. how the turnover frequency respond to small errors in the reaction barriers. However, in first principles based kinetics, these barriers are obtained from Density Functional Theory and must be regarded as large. The intrinsic assumption of linearity behind local sensitivity analysis is then likely to break down and can provide misleading results. Global sensitivity analyses (GSA) overcome these limitations and can provide a well-grounded quantification of the error propagation in such multiscale models. I will present our recent progress on GSA for first principles based kinetic models. A special emphasis will be put on novel distribution based approaches to GSA which are particularly suited for first principles kinetic Monte Carlo (1p-kMC) models. Unlike prevalent approaches, these require neither derivative information nor surrogate models nor specialized sampling of the space of barriers. Each of these points would be very challenging even for the simplest 1p-kMC models. Instead, the distribution based approach allows for reasonably accurate results using Quasi Monte Carlo data sets of modest size. Moreover, distribution based GSA seems to be very robust against the simulation noise in 1p-kMC data. Hence, the sensitivity data can be accurately obtained from badly converged and computationally cheap simulations. This results in a GSA which comes at a similar (or even smaller) computational footprint as a local sensitivity analysis. At the same time, it provides of a much more reliable picture of the important uncertainties in the reaction energetics and hence can guide future steps to improve the accuracy of the model.

# Accelerated kinetic Monte Carlo simulations with lateral interactions applied to higher oxygenate synthesis over Rh-based catalysts

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[2]*Center for Interstellar Catalysis, Department of Physics and Astronomy, Aarhus University, 8000 Aarhus C, Denmark*

[*]*Email: mie@phys.au.dk*

The kinetic Monte Carlo (KMC) method is a powerful tool for microkinetic modelling in heterogeneous catalysis since it provides a statistically correct description of fluctuations and correlations in the coverage and binding sites of the adsorbates [1]. Furthermore, it allows for considering lateral interactions between the adsorbates through e.g., cluster expansion methods. However, the simulations can become computationally demanding when complex lateral interaction models are needed or when elementary steps in the reaction network occur with highly disparate timescales, e.g., slow reactions and fast diffusion [1-3]. Here, I will present some recent implementations in the KMC code kmos [4] (now kmcos) aimed at tackling these challenges (see Fig. 1) and show how they enable us to study highly complex reaction networks involving methane and higher oxygenate synthesis over Rh(111) and Rh(211) surfaces [5]. The KMC results are compared to corresponding microkinetic simulations employing the mean-field approximation parametrized to include a dependence on the adsorbate coverage in the rate equations. We show that the subtle selectivity trends observed in experiments can only be reproduced using the KMC approach and highlight the different roles lateral interactions can play for different catalytic systems. The results are important for understanding and designing active and selective heterogeneous catalysts.
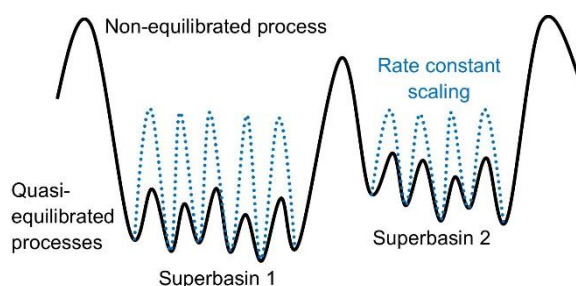


**Figure 1**: KMC acceleration algorithm [1-3].

## References

[1] M. Andersen, C. Panosetti, K. Reuter, *Front. Chem.* **7**, 202 (2019).
[2] M. Andersen, C. P. Plaisance, K. Reuter, *J. Chem. Phys.* **147**, 152705 (2017).
[3] E. C. Dybeck, C. P. Plaisance, M. Neurock, *J. Chem. Theory Comput.* **13**, 1525 (2017).
[4] M. J. Hoffmann, S. Matera, K. Reuter, *Comp. Phys. Comm.* **7**, 2138 (2014).
[5] M. Deimel, H. Prats, M. Seibt, K. Reuter, M. Andersen, *ACS Catal.* **12**, 7907 (2022).

# Importance of site-communication in hydrogenation reactions over dilute alloy nanoparticles

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[1]*Department of Physics and Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Göteborg, Sweden*

[*]*Email: ghj@chalmers.se*

Single atom alloy catalysts offer possibilities to obtain turn-over frequencies and selectivities unattainable by its mono-metallic counterparts. Examples are selective hydrogenation of acetylene to ethylene over Pd embedded in Cu [1] and direct formation of $H_2O_2$ from $O_2$ and $H_2$ over Pd embedded in Au hosts [2]. We use first principles based kinetic Monte Carlo simulations [3] to investigate the catalytic performance of Pd embedded in nanoparticles of Cu and Au. The simulations reveal an efficient site-separation where Pd monomers act as active centers for $H_2$ dissociation, whereas the hydrogenation steps proceed over under-coordinated Cu- and Au-sites. The simulations show that tuning the nanoparticle composition and reaction conditions can enhance the selectivity towards the desired product.

## References

[1] M. Jørgensen and H. Grönbeck, *J. Am. Chem. Soc.* **141**, 8541 (2019).
[2] R. Svensson and H. Grönbeck, (submitted).
[3] M. Jørgensen and H. Grönbeck, *J. Chem. Phys.* **149**, 114101 (2018).

# Automated construction of elementary reaction mechanisms for kinetic Monte Carlo

C. Franklin Goldsmith[1,*]

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Elementary reaction networks in heterogeneous catalysis can be incredibly complicated. When the reactive intermediates contain two or more non-hydrogen atoms, a detailed microkinetic mechanism can require 10's of species and 100's of reactions.  Moreover, the size of the mechanism increases combinatorically with the size of reactants/products. This complexity presents a challenge for both experienced kineticists and novices alike. How do you determine which species and reactions to include? How do you obtain the corresponding parameters? How do you avoid bias? How can you maintain thermodynamic consistency? In this talk, we will discuss an open-source software, RMG (Reaction Mechanism Generator), that can automatically build detailed microkinetic mechanisms. The resulting mechanism can be used to populate the event list in a kinetic Monte Carlo simulation.

# DFT & kinetic modeling of the methanol to olefins process

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The methanol-to-olefins (MTO) process over the acidic zeolite H-SSZ-13 is investigated using periodic density functional theory (DFT) calculations corrected by higher level calculations (e.g. DLPNO-CCSD(T)), which are found to be crucial for sufficient accuracy. Using these data, a kinetic model of the autocatalytic carbon pool mechanism is employed to investigate the mechanistic details of the initiation kinetics through a batch reactor model. This model shows that initiation proceeds via oxidation of methanol to carbon monoxide, which subsequently forms the first carbon–carbon bond via carbonylation of methanol. The kinetic model also shows that only extremely small amounts of an olefin need to be formed for autocatalysis to start, implying that small impurities will dominate over initiation mechanisms. This work is extended to the use of ethanol instead of methanol to investigate the origin of olefins such as propene.
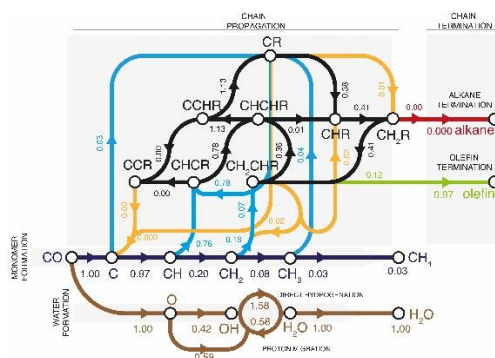
# Microkinetic modelling in heterogeneous catalysis

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Microkinetic modelling is a computational approach used in heterogeneous catalysis to understand the chemical reactions that occur on the surface of a catalyst. It involves breaking down the reaction mechanism into elementary steps and calculating the rate of each step based on the properties of the reactants and the catalyst surface. By simulating the reaction mechanism using microkinetic modelling, one can predict the catalyst's activity, selectivity, and stability under different conditions, which can help in the design and optimization of new catalysts.[1]



**Figure 1:** Flux-analysis of the Fischer-Tropsch reaction over $B_5$/Ru(11-21) active sites.

In this contribution, I aim to present a comprehensive overview of the microkinetic modelling procedure for heterogeneous catalysis, highlighting recent advances in the field. The focus will be on the simulation of large and complex chemokinetic networks[2], which may involve various active sites.[3] I will also discuss the integration of microkinetics into multiscale approaches[4] and the potential benefits of incorporating machine learning techniques to aid in microkinetic modelling[5] or to replicate the microkinetic modelling procedure. The catalytic processes of interest are related to chemical conversion processes for the production of fuels and chemicals, specifically Fischer-Tropsch synthesis[6] and $CO_2$ hydrogenation to methane and methanol.[7]

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# Unraveling complexity in catalytic materials

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Kinetic Monte Carlo (KMC) is a powerful method to unravel complexity in catalytic materials. For instance, it can be used to determine the dominant reaction mechanism or to identify the role of the distinct catalytic regions in multifunctional materials. In this talk, I will present some examples on the application of KMC to understand the reactivity of a complex reaction (i.e., the water-gas shift reaction, involving dozens of elementary steps) in several catalysts, from simple extended metal surfaces to more complicated supported metal clusters [1-4].
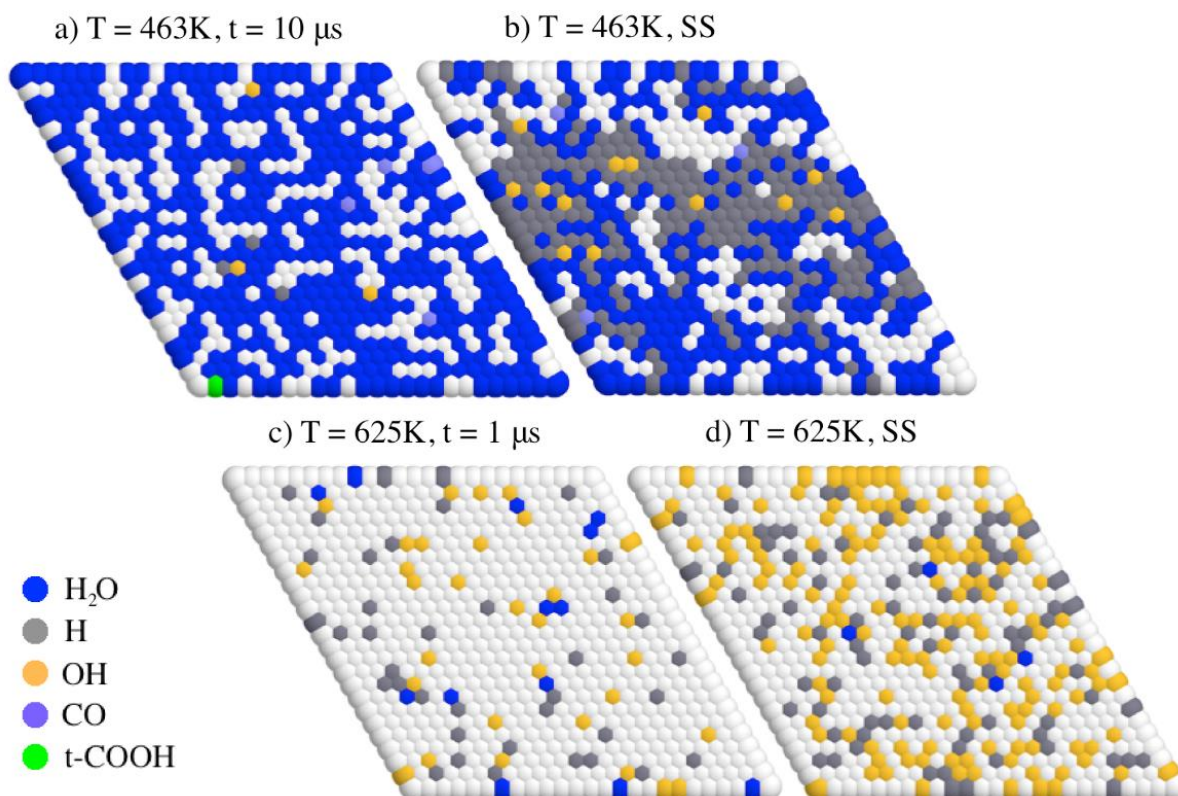


**Figure 1**: Snapshots of the lattice for a KMC simulation of the water-gas shift reaction on Cu(111)

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# Reactivity of hydrocarbons on single-atom alloys: comparison between experimental and simulated TPDs

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Embedding single atoms of transition metals into the surface of coinage metals (Cu, Ag and Au) has emerged as an effective atom-efficient approach to create new catalysts. These so-called Single-Atom Alloys (SAAs) are indeed active, selective and resistant to poisoning. They are therefore the perfect candidates for the conversion of hydrocarbons. To elucidate their reactivity, we teamed up with a group of surface science experimentalists and compared the experimental Temperature Programmed Desorption spectra with those obtained from DFT-parameterised KMC simulations.

By analysing these TPDs, we have showed that PtCu SAA acts as a bifunctional catalyst for the disproportionation of Ethyl ($C_2H_5$) into ethane ($C_2H_6$) and ethylene ($C_2H_4$). On this catalyst, the Cu sites perform the dehydrogenation reaction while the Pt sites catalyse the hydrogenation reaction. We have also showed that we can efficiently increase the selectivity for ethane by loading the surface with hydrogen atoms.

Moving on to Au-based SAAs, we have demonstrated that Ni and Pd dopants can perform C-C coupling reactions between two $sp^3$ carbons, a reaction that can usually only be catalysed in homogeneous conditions. Methyliodide was used as a probe molecule for the coupling (2MeI= $C_2H_6$+2I), therefore leaving iodine adsorbates on the surface. Far from being spectator, we showed that these iodine atoms can tune the reactivity of SAAs in an advantageous way.

Albeit simple, these systems reveal how we can use SAAs to design catalysts for the conversion of more complex molecules.
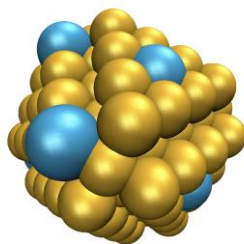


**Figure 1.** Structure of a Single-Atom Alloy Nanoparticle

# Recent developments towards accelerating KMC simulations with Zacros

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Lattice-based kinetic Monte Carlo (KMC) is unparalleled as a tool for accurately modelling heterogeneous catalytic processes [1]. However, KMC simulations of certain systems prove to be computationally highly demanding. Considerable effort has therefore been made to identify simulation bottlenecks and improve the underlying algorithms.

This talk will focus on advancements made towards mitigating two common sources of KMC complexity. First, long-range lateral interactions necessitate frequent and costly updates to activation energies. Generally, the adlayer energy is encoded in a cluster expansion (CE) Hamiltonian [2]; to evaluate it, one must detect all instances of each energetic pattern ('cluster') on the two-dimensional lattice. Within the graph-theoretical framework, this amounts to solving a series of subgraph isomorphism problems [3,4], which is currently achieved in Zacros using an adaptation of Ullmann's well-known algorithm [3-5]. We will show that simulation speed can be drastically increased by employing more sophisticated algorithms such as RI [6] in combination with shared-memory parallelisation.

Second, simulations of large (micron-scale) lattices can demand thousands of CPU hours. However, they are necessary for modelling systems exhibiting large-scale spatial inhomogeneities. Distributing the workload over processors without shared memory is complicated by the serial nature of KMC, but this has been achieved in Zacros by coupling the graph-theoretical framework with the 'Time-Warp' algorithm [7,8]. We will show that, despite significant overheads, distributed computing enables simulations incorporating millions of lattice sites that would otherwise be intractable.

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# A computational map of the probe CO molecule adsorption and dissociation on transition metal low Miller indices surfaces

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The adsorption and dissociation of carbon monoxide (CO) have been studied on 81 Transition Metal (*TM*) surfaces, with TMs having body centred cubic (*bcc*), face centred cubic (*fcc*), or hexagonal close-packed (*hcp*) crystalline structures. For each surface, CO, C, and O adsorptions, and C+O co-adsorptions were studied by density functional theory calculations on suited slab models, using the Perdew-Burke-Ernzerhof functional with Grimme's D3 correction for dispersive forces. CO dissociation activation and reaction energies, $\Delta E$, were determined. The values, including zero point energy, were used to capture chemical trends along groups, *d*-series, and crystallographic phases concerning CO adsorption and dissociation. Late *fcc* TMs are found to adsorb CO weakly, and perpendicularly, opposite to early *bcc* TMs, while *hcp* cases are distributed along these two extremes. The *d*-band centre, $\varepsilon_d$, is found to be the best descriptor for CO adsorptions and C + O co-adsorptions, $\Delta E$, and activation energies. The implications of the found trends and descriptors are discussed evaluating the activity of different surfaces as catalysts for processes requiring the breakage or the maintaining of the integrity of the CO.
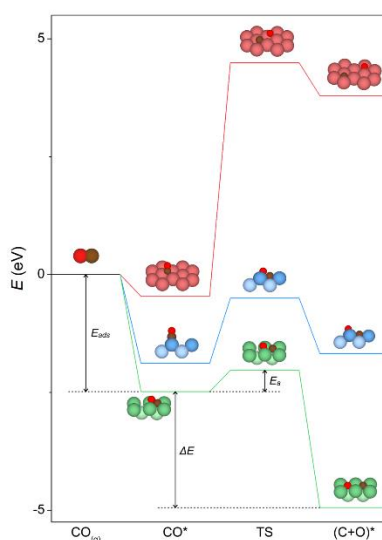


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# Computational insight into carbonyls formation and desorption on iron surfaces

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The formation of Iron pentacarbonyl (IPC) gas can be a significant issue in industrial processes, as it can cause metal loss, pipeline corrosion, and equipment contamination. Despite its early recognition, identification and experimental studies, an atomistic description of the carbonyl formation and desorption from iron surfaces has not been provided to date. In this work, we propose a mechanism for IPC formation on a pure bcc Fe surface using atomistic-level calculations based on electronic density functional theory (DFT). The research found that the desorption barriers for carbonyls on a clean Fe surface are too high for carbonyls to form and desorb at temperatures below 500K. However, a high CO surface coverage combined with Fe adatoms favors carbonyl formation and desorption towards the gas medium. The proposed IPC formation mechanism which is selected after exploring different possible paths, performing nudged elastic band and DFT based molecular dynamics AIMD, involves a two steps desorption, leading to iron adatom removal and its barrierless desorption as $Fe(CO)_5$ (IPC) gas.
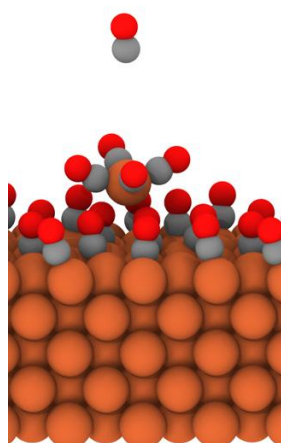
**Figure 1:** Ball and stick representation of Fe(110) surface with 0.6ML CO coverage, $Fe(CO)_4$ on top of CO adlayer, with COg molecule ready to react with the carbonyl forming IPC.

# What I talk about when I talk about my PhD: 4D-STEM, amorphous materials and crystallization mechanisms

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In recent years, four-dimensional scanning transmission electron microscopy has become an essential tool for the structural characterization of various materials[1–5]. Most systems studied are of inorganic materials that are crystalline or exhibit diffracting motifs[6–10]. On the other hand, organic crystals remain challenging to visualize as they are beam sensitive and require elaborate techniques to study their steady-state structure[1,11]. Furthermore, as they exhibit non-classical crystallization mechanisms, that go through various amorphous intermediates[12,13], most states are challenging to visualize, even under low-electron-dose regimes. In this poster, I will briefly summarize key aspects of our work in the fields of 4DSTEM method development, thin amorphous organic films, and organic crystallization.

Method development is done on both organic and inorganic thin-films, with the aim of increasing the amorphous-structure-characterization tool-box and making it accessible to many users. Our organic system of choice is Indomethacin, which is a pharmaceutical molecule that is used for the treatment of inflammation. Studying its amorphous structure, and its crystallization pathways can lead to improvement in drug bioavailability in pill forms.

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# Effect of terminations on the hydrogen evolution reaction mechanism on Ti$_3$C$_2$ MXene

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Two-dimensional (2D) MXene materials are proposed high-efficient hydrogen evolution reaction (HER) electrocatalysts [1]. Most computational studies addressed HER assuming a fully O-termination, even if as-synthesized MXenes feature a mixture of –O, –OH, –F, or even –H surface groups [2]. To better understand the electrocatalytic surface composition and mechanism under HER equilibrium conditions on Ti$_3$C$_2$ MXene model material, we composed Pourbaix diagrams considering *ca.* 450 topologically different surface terminations, including pristine Ti$_3$C$_2$, full –O, –OH, –F, and –H terminations, and binary and ternary situations with different group ratios. Realistic models built from Pourbaix diagrams near HER equilibrium conditions of low *pH* and *U* were used to investigate the Volmer-Heyrovsky and Volmer-Tafel mechanisms [3], with the particularity of considering, or not, the participation of H atoms from –OH or –H termination groups at different reaction stages. Results pointed out that the models close to HER equilibrium line, O$_{2/3}$OH$_{1/3}$, F$_{1/3}$O$_{1/3}$OH$_{1/3}$, and F$_{3/9}$O$_{4/9}$OH$_{2/9}$ require an almost negligible overpotential of 0.01 V, while surface charges explain the impact of higher ratios of –O groups on modulating the H bond, and the positive influence of having surface –F groups.
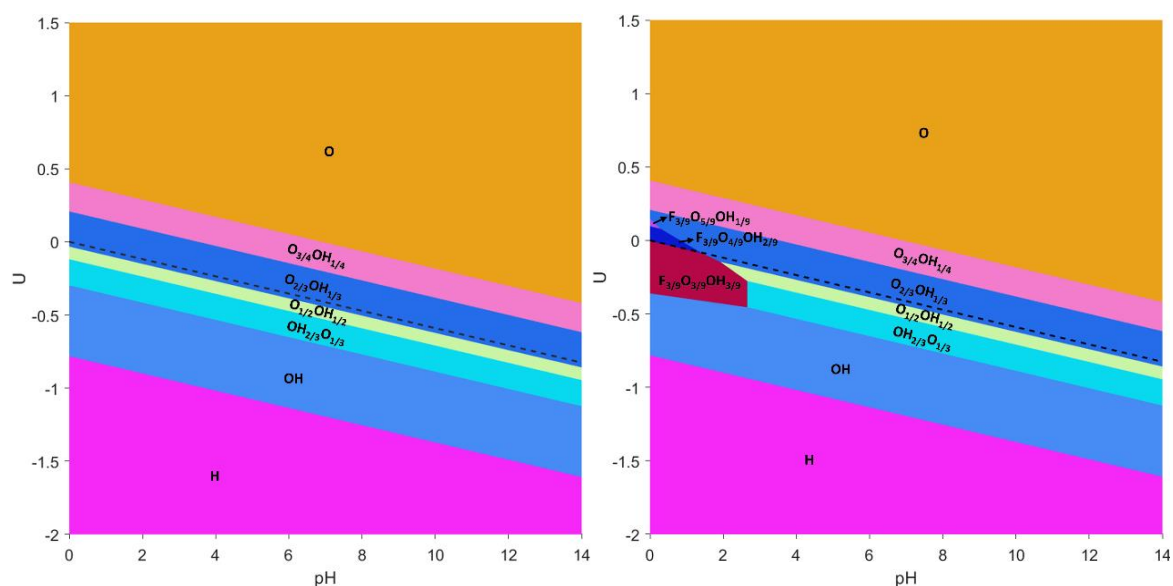


**Figure 1**: Pourbaix diagrams for Ti3C2 MXene (0001) surface regarding all single, binary, and ternary surface compositions including –O, –OH, –H, and –F terminations, as well as free sites. Left image corresponds to situations without any –F termination, while right image corresponds to situations when regarding–F termination. The black, dashed line indicates the HER equilibrium potential with respect RHE reference.

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# How the facet edge controls the overall CO oxidation in nanoporous gold: combined atomistic characterization/DFT study of residual Ag distribution and catalytic activity
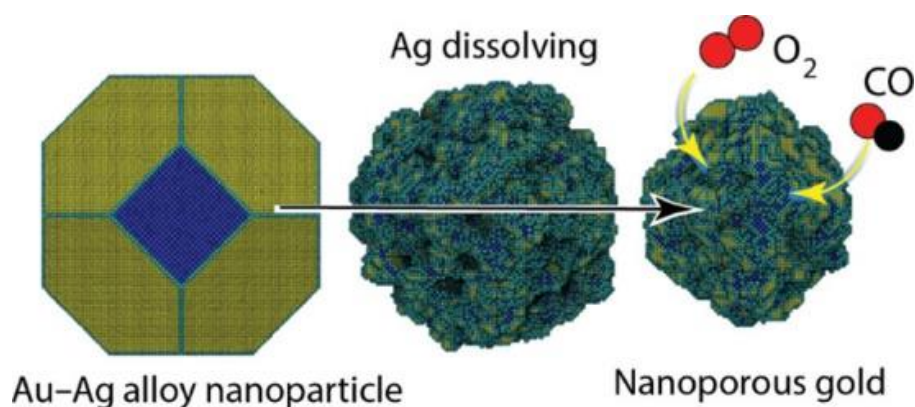
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Nanoporous gold (NPG) formed via dealloying/selective dissolution of the Au−Ag alloy is known to be catalytically active toward CO oxidation reaction (COR) even at room temperature. The atomistically resolved NPG structure is obtained by simulating the dealloying of $Au_{25}Ag_{75}$ nanoparticles using a combination of kinetic Monte Carlo and molecular dynamics. The effect of adsorbed O is included. The experiment-like NPG structures from these computer simulations are characterized. We map the surface of NPG, determine the diverse binding sites, and assess their role in catalysing the COR. Local surface Ag composition, population density of undercoordinated Au/Ag atoms, and cluster size distribution of surface Ag atoms are measured. A high density of dislocation defects is found in the simulated structure. The rate-determining steps, namely, $O_2$ binding and dissociation, are probed using density functional theory. We conclude that $O_2$ binding/dissociation is facilitated at the facet edge. Residual Ag at the edge aids in the capture of $O_2$. Subsequently, $O_2$ dissociates after spilling over to Au sites at the facet edge. These conclusions are confirmed by showing that the normalized facet edge length of NPG and supported Au nanoparticles is linearly correlated to the experimental turnover frequency [1].

**Figure 1**: Dealloying of Au-Ag NP to get NPG which has high catalytic activity for COR.

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# A probabilistic microkinetic modeling framework for catalytic surface reactions

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We present a microkinetic modeling (MKM) framework that incorporates the short-ranged order (SRO) evolution for adsorbed species (adspecies) on a catalyst surface. The resulting model consists of a system of ordinary differential equations. Adsorbate-adsorbate interactions, surface diffusion, adsorption, desorption and catalytic reaction processes are included in the model. Assuming that the adspecies ordering/arrangement is accurately described by the SRO parameters, we employ the reverse Monte Carlo (RMC) method to extract the relevant spatial correlations and pass them to the MKM. The reaction kinetics is faithfully captured as accurately as the kinetic Monte Carlo (KMC) method, but with a computational time requirement of few seconds on a standard desktop computer. KMC, on the other hand, can require several days for the examples discussed. The framework presented here is expected to provide the basis for wider application of the RMC-MKM approach to problems in computational catalysis, electrocatalysis and material science.

# Multiscale modelling evaluation of the InN growth under atomic layer deposition conditions

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Indium nitride (InN) has been extensively investigated for its potential applicability in photonic and electronic devices due to its high electron mobility and low band gap. [1] Therefore, it is important that this material is produced through appropriate methods that ensure high quality and crystalline purity. For instance, it has been demonstrated that atomic layer deposition (ALD) can enable InN thin film growth at low temperatures (T= 320 °C) and p= 0.006 bar with growth rate of 0.51 Å/cycle.[2] In this process, trimethylindium (TMI) and ammonia ($NH_3$) plasma are used as In and N precursors, respectively, that are added at different time slots to block any gas phase reactions between these species. This work aims at understanding the InN growth under the experimental conditions of interest by making use of a multiscale modelling approach, in other words, using density functional theory (DFT), microkinetic modelling and kinetic Monte Carlo (kMC) methods.

Initially, gas phase calculations were performed in Gaussian 16 [3] for the evaluation of TMI thermal stability under the experimental conditions. Thereafter, the thermokinetic data was supplied to the reaction engineering module in COMSOL[4] for calculation of the reaction rates. Similarly, periodic calculations in VASP program [5] were carried out to study different reaction mechanisms leading to the *In* layer formation, with further data used in Zacros [6] for the dynamic simulations. The outcomes [1,7] indicate that i) TMI is the physisorbed species in the process due to its high stability inside the chamber; ii) TMI diffusion is not plausible without decomposition, an observation associated with the presence of the -$NH_2$ layer from the *N* half-cycle; iii) instead methylindium (MI), which has low barrier for diffusion, is formed from TMI decomposition at the surface. In this mechanism, a second TMI molecule is necessary for H removal. Herein, the kMC simulations show the feasibility of this mechanism through the formation of a 2D thin film layer. Ultimately, the kMC simulations reveal the formation the triangle-shaped islands during the first stages of the film growth.

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