

BremHLR Kompetenzzentrum für Höchstleistungsrechnen Bremen

# Statusbericht 2021

# des

# Kompetenzzentrums

für

# Höchstleistungsrechnen Bremen

# -BremHLR-

Bremen, September 2022



www.bremhlr.uni-bremen.de



BremHLR

# Das Berichtsjahr 2021 in Stichpunkten

- Stabiler Betrieb des HLRN 4 im Endausbau
- Weiter ansteigende Bremer Nutzung der Ressourcen des Norddeutschen Verbunds für Hoch- und Höchstleistungsrechnen (HLRN)
- > Hochschule Bremen ist neuer Kooperationspartner des BremHLR seit Juli 2021



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# 1 BremHLR: Aufgaben und organisatorische Struktur

# 1.1 Aufgaben

Das Land Bremen beteiligt sich am Norddeutschen Verbund für Hoch- und Höchstleistungsrechnen – HLRN – um an dem rasanten Fortschritt der Computer- und Softwaretechnologie Teil zu haben. Das Kompetenzzentrum für Höchstleistungsrechnen Bremen – BremHLR – unterstützt dazu Wissenschaftler im wissenschaftlichen Rechnen insbesondere im Land Bremen. Die Fachberater des BremHLR leisten Unterstützung für Projekte sowohl in der Konzeption, der Antragstellung als auch der Durchführung. Der Schwerpunkt der Unterstützung liegt hierbei auf Projekten auf dem HLRN-System. Seit 2005 Betreuung aber auch auf Rechenprojekte an den nationalen wurde die Höchstleistungsrechenzentren wie z. B. dem Jülich Supercomputing Centre (JSC) ausgeweitet.

Als Bestandteil im Kompetenznetzwerk des HLRN beteiligt sich BremHLR unter anderem an der fachspezifischen Nutzerberatung, der Pflege von Software-Paketen und der Veranstaltung überregionaler Nutzerworkshops. Die Geschäftsstelle des BremHLR ist an der Universität Bremen im Zentrum für Technomathematik angesiedelt.

Das BremHLR wurde am 1. Juli 2003 als Kooperation zwischen der Universität Bremen (UB), der Jacobs University Bremen (JUB) und dem Alfred-Wegener-Institut Helmholtz-Zentrum für Polar- und Meeresforschung (AWI) gegründet. Seit April 2008 ist die Hochschule Bremerhaven (HBHV) Kooperationspartner des BremHLR. Neuer Kooperationspartner des BremHLR ist seit Juli 2021 die Hochschuhe Bremen (HSHB). Das Kompetenzzentrum wird von den beteiligten Kooperationspartnern sowie der Bremer Senatorin für Wissenschaft und Häfen (SWH) anteilig finanziell getragen. Seit Januar 2014 ist die JUB als ideelles Mitglied beitragsfrei gestellt. Im Jahr 2021 konnte eine Weiterfinanzierung des BremHLR bis Ende 2024 sichergestellt werden.

#### 1.2 Struktur

Dem Lenkungsausschuss des BremHLR als oberstes beschlussfassendes und steuerndes Gremium gehörten in der Berichtsperiode folgende Vertreter der kooperierenden Einrichtungen an. Im Einzelnen sind dies:

- Prof. Dr. Alfred Schmidt (UB/Zentrum für Technomathematik ZeTeM)
- Prof. Dr.StephanFrickenhaus (AWI/Rechenzentrum, UB/FB3)
- Prof. Dr. Ulrich Kleinekathöfer (JUB)
- Prof. Dr. Henrik Lipskoch (HBHV)
- Prof. Dr. A. Baars (HSHB)
- Dr. Jörg Hofmann (SWH)

Die fachspezifische Betreuung der Projekte am Norddeutschen Verbund für Hoch- und Höchstleistungsrechnen (HLRN) sowie von Projekten an anderen nationalen Höchstleistungsrechenzentren wird von den Fachberatern des BremHLR geleistet, die ebenfalls den Einrichtungen der Kooperationspartner angehören. Im Berichtszeitraum waren folgende Fachberater tätig:

- Dr. Lars Nerger (AWI/Rechenzentrum, UB/ZeTeM, Leiter Geschäftsstelle)
- Thorsten Coordes (UB/ZARM)
- Dr. Achim Geleßus (JUB/CLAMV)
- Dr. Natalja Rakowsky (AWI/Rechenzentrum)

Die Geschäftsstelle ist verantwortlich für die Organisation der Workshops (siehe Abschnitt Veranstaltungen) und die Unterstützung der Nutzer, insbesondere im Antragsverfahren. Im Jahr 2021 wurde das Sekretariat der Geschäftsstelle kommissarisch betreut von

• Birgit Michaelis und Sabine Schulz.

Die Sekretariatsstelle wird absehbar im Jahr 2022 wieder dauerhaft besetzt werden.

# 2 Tätigkeitsprofil des BremHLR im Berichtszeitraum

#### 2.1 Unterstützung der HLRN-Nutzung im Land Bremen

Ein Schwerpunkt der Aktivitäten des BremHLR lag auch in diesem Berichtszeitraum in der Unterstützung der HLRN-Nutzung. Neben den Tätigkeiten von Prof. Dr. Stephan Frickenhaus als Mitglied der Technischen Kommission sowie Prof. Dr. Alfred Schmidt als Mitglied des Wissenschaftlichen Ausschusses bestand die Unterstützung des HLRN durch das BremHLR hauptsächlich in der Fachberatung für Bremer Projekte am HLRN von der Antragstellung bis zur Begleitung rechenintensiver Projekte während der gesamten Projektlaufzeit.

Eine wesentliche Aufgabe im Berichtsjahr war die weitere Unterstützung der Bremer Nutzer des HLRN bei der effizienten Nutzung des HLRN Hochleistungsrechner-Systems. Hierbei war ein Fokus den stabilen Forschritt der Projekte zu unterstützen.

#### 2.2 Weitere Aktivitäten des BremHLR

Bedingt durch die Covid-19 Pandemie musste der üblichlicherweise jährlich veranstaltete Workshop zur Einführung in die parallele Programierung leider ausfallen. Aufgrund der Abstandsregeln wäre eine Durchführung der im Workshop relevanten praktischen Anteile nicht möglich gewesen.

Die Fachberater des BremHLR beteiligten sich an Fachberaterworkshops des HLRN-Kompetenznetzwerks die im Jahr 2021 online stattgefunden haben. Bei diesen Workshops wurden unterschiedliche Themen des HLRN-Betriebs und der Nutzerbetreuung besprochen. Eine Übersicht über die Veranstaltungen ist in Abschnitt 4 zu finden.

# 3 Statistische Angaben zu den Bremer Höchstleistungsprojekten

Auch im Jahr 2021 wurde der HLRN intensiv durch Bremer Projekte genutzt. Über das Jahr wurde auf den HLRN-Systemen ein prozentualer Anteil von 7,1 % an der gesamten Rechenleistung des HLRN erreicht. Dieses liegt deutlich über dem investiven Anteil von etwa 3,5% des Landes Bremen am HLRN. Über die gesamte Laufzeit seit Einrichtung des HLRN-Verbunds wurde durch Bremer Projekte ein Anteil von 7,8% der verfügbaren Rechenzeit abgenommen.

Mit dem Abschluss der Ausbauarbeiten des HLRN-IV Systems im vierten Quartal 2020 wurde ein stabiler Betrieb erreicht der auch eine stabile Nutzung ermöglicht. Diese zeichnet sich durch eine hohe Nutzung von ca. 4,7 Mio. NPL pro Quartal aus. Hiervon weicht nur das dritte Quartal, vermutlich bedingt durch die Sommerferien, ab. Insgesamt wurden im Jahr 2021 etwa 17.800.000 NPL<sup>1</sup> durch Bremer Projekte am HLRN abgenommen. Dieses ist die größte bisher am HLRN abgenommene Rechenkapazität durch Einrichtungen im Land Bremen.

Abbildung 3.1 zeigt die quartalsweise Nutzung des HLRN durch die Bremer Projekte. Während der Umbauphase von HLRN-III auf HLRN-IV wurden die NPL teilweise unvollständig erfasst.



**Abbildung 3.1:** Quartalsweise Rechenzeitnutzung der Bremer HLRN-Großprojekte seit Anfang 2018 auf den HLRN-III und HLRN-IV Systemen in der HLRN-Leistungseinheit NPL. Die Farben zeigen die Verfügbarkeit der unterschiedlichen Ausbaustufen des HLRN-Systems. Im vierten Quartal 2019 war der Betrieb durch die Umbaumaßnahmen beeinträchtigt und weitgehend nur das HLRN-IV System in Göttingen verfügbar. Im ersten Quartal 2020 waren die Nutzer vielfach mit Portierungsarbeiten befasst. Seit dem vierten Quartal 2020 befindet sich das HLRN-IV System im Endausbau.

Eine Übersicht zu allen vom BremHLR betreuten Projekten geben die Tabellen 3.1 und 3.2. Im Jahr 2021 wurden vom BremHLR 48 Projekte am HLRN betreut. 15 neue Projekte mit teilweise sehr großem Rechenzeitbedarf wurden im Jahr 2021 beantragt und vom Wissenschaftlichen Ausschuss des HLRN bewilligt. 14 Projekte wurden im Berichtsjahr beendet.

<sup>&</sup>lt;sup>1</sup>Norddeutsche Parallelrechner-Leistungseinheit: Auf dem Göttinger HLRN-IV System der Ausbaustufe 1 entspricht die Nutzung eines Knotens über eine Stunde 6 NPL. Auf den Systemen der Ausbaustufe 2 entspricht die Nutzung eines Knotens über eine Stunde 14 NPL.



# 4 Veranstaltungen mit Beteiligung des BremHLR

#### 39. HLRN-Fachberater-Workshop

Veranstalter: GWDG Datum: 3. Juni 2021

Ort: Online

Teilnehmerzahl: 18

**Teilnehmende Institutionen**: BremHLR (AWI, ZARM), GWDG/Uni Göttingen, TU Braunschweig, Uni Hamburg, Uni Kiel, Uni Oldenburg, ZIB

#### 40. HLRN-Fachberater-Workshop

Veranstalter: GWDG

Datum: 11. November 2021

Ort: Online

#### Teilnehmerzahl: 26

**Teilnehmende Institutionen**: BremHLR (AWI, ZARM), FU Berlin, GWDG/Uni Göttingen, IOW, TU Braunschweig, Uni Hamburg, Uni Kiel, Uni Oldenburg, Uni Potsdam, ZIB

Tabelle 3.1:	Übersicht	neu	begon	nener	Bre	mer	HF	PC-Projek	cte,	die	inne	erhalb	des
	Berichtszei	itraums	vom	Brem⊦	ILR	betre	ut	wurden.	Stat	us:	E =	Erstar	ntrag,
	X = Projekt	ende ir	n Jahr	2021; k	NPL	: Kont	ing	ent im Ja	hr 20	)21 ir	n taus	send N	٦L.

Kennung	Projektleiter	Institut	Laufzeit	kNPL	Status
hbc00049	Dr. P. Guo	UB/BCCMS	I/21 – I/22	217	Е
hbc00051	Dr. Q. Duy Ho	UB/ZARM	I/21 — I/22	320	Е
hbc00053	Prof. Dr. L. Colombi Ciacchi	UB/BCCMS	II/21 – I/22	225	Е
hbc00056	Dr. M. Fischer	UB/Geo	III/21 – II/22	140	Е
hbc00057	Dr. M. Delle Piane	UB/BCCMS	III/21 – II/22	180	Е
hbc00060	Dr. B. Aradi	UB/BCCMS	IV/21 – III/22	40	Е
hbc00061	Dr. L. Moskaleva	UB/Chemie	IV/21 – III/22	125	Е
hbi00050	PD Dr. Y. Jin	UB/ZARM	I/21 – I/22	100	Е
hbi00051	Prof Dr. R. Groll	UB/ZARM	III/21 – II/22	384	Е
hbi00053	Prof. Dr. M. Avila	UB/ZARM	IV/21 – III/22	158	Е
hbk00083	Prof. Dr. B. Rost	AWI & UB	II/21 – IV/22	711	Е
hbk00084	Prof Dr. A. Bracher	AWI & UB	IV/21 – III/22	140	Е
hbk00085	Prof. Dr. M. Schulz	UB/MARUM	IV/21 – III/22	500	Е
hbk00087	Prof. Dr. T. Kanzow	AWI & UB	IV/21 – III/22	455	Е
hbp00070	Prof. Dr. T. Wehling	UB/Physik	II/21 – I/22	450	Е

Tabelle	Übersicht	der	fortgeführten	Bremer	HPC-Projekte,	die	innerhalb	des
3.2:	Berichtszei	traum	s vom BremHL	R betreut	wurden. Status	s: F =	Fortsetzung,	X =
	Projektende	e im Ja	ahr 2021; kNPL	: Kontinge	ent im Jahr 2021	in tau	isend NPL.	

Kennung	Projektleiter	Institut	Laufzeit	kNPL	Status
hbb00001	Prof. Dr. L. Colombi Ciacchi	UB/BCCMS	III/20 – II/22	404	F
hbc00029	Dr. L. Moskaleva	UB/Chemie	I/18 — I/22	326	FX
hbc00030	Dr. M. Fischer	UB/Geo	II/18 – III/21	90	FX
hbc00045	Prof. Dr. T Neudecker	UB/Chemie	II/20 – III/22	195	F
hbc00046	Dr. M. Delle Piane	UB/BCCMS	II/20 – II/21	110	FX
hbc00047	Dr. S. Köppen	UB/BCCMS	II/20 – II/21	30	FX
hbc00048	Dr. M. Michaelis	UB/BCCMS	III/20 – III/21	140	FX
hbi00033	Prof. Dr. M. Avila	UB/ZARM	l/17 – ll/21	100	FX
hbi00036	Prof. Dr. U. Fritsching	UB/FB4	II/17 – I/22	310	F
hbi00037	Prof. Dr. U. Fritsching	UB/FB4	II/17 – I/22	121	F
hbi00042	Prof. Dr. A. Baars	HS Bremen	IV/19 – III/22	1325	F
hbi00045	Prof. Dr. C. Büskens	UB/ZeTeM	III/20 – II/22	376	F
hbi00046	Dr. M. Castillo	UB/ZARM	III/20 – III/21	2	FX
hbi00048	Dr. Yan Jin	UB/ZARM	III/20 – III/21	90	FX
hbi00049	Prof. Dr. U. Fritsching	UB/IWT	IV/20 – I/22	147	F
hbk00032	Prof. Dr. T. Jung	AWI & UB	II/12 – III/21	200	FX
hbk00034	Prof. Dr. T.Kanzow	AWI & UB	III/13 — I/22	1800	F
hbk00038	Prof. Dr. T. Kanzow	AWI & UB	III/14 – III/21	900	FX
hbk00059	Prof. Dr. M. Schulz	UB/MARUM	III/17 – II/22	765	F
hbk00062	Dr. A. Rozanov	UB/IUP	IV/17 – III/22	360	F
hbk00064	Prof. Dr. T. Jung	AWI & UB	l/18 – III/21	776	FX
hbk00071	Prof. Dr. M. Schulz	UB/MARUM	I/19 – IV/22	2650	F
hbk00075	Prof. Dr. D. Wolf-Gladrow	AWI & UB	IV/19 – IV/22	1800	F
hbk00079	Prof. Dr. B. Rost	AWI & UB	II/20 – IV/22	1008	F
hbk00080	Prof. Dr. M. Schulz	UB/MARUM	III/20 — I/22	1203	F
hbk00082	Dr. K. Purkiani	UB/MARUM	III/20 – III/21	20	FX
hbp00041	Prof. Dr. C. Lämmerzahl, Prof. Dr. S. Rosswog	UB/ZARM	I/17 – I/22	255	F
hbp00054	Dr. M. Lorke	UB/Physik	II/20 – III/21	28	FX
hbp00058	Prof. Dr. U. Kleinekathöfer	Jacobs U	II/20 – II/22	246	F
hbp00067	Prof. Dr. T. Frauenheim	UB/BCCMS	IV/20 – III/22	320	F
hbp00068	Prof. Dr. U. Kleinekathöfer	Jacobs U	IV/20 – III/22	730	F
hbp00069	Prof. Dr. T. Wehlling	UB/Physik	II/20 – III/21	141	FX
nak00001	Dr. H. Gößling	AWI	II/19 – II/22	204	F



# 5 Informationen zur Infrastruktur: Endausbau des HLRN-IV Systems zum Ende des Jahres 2020

Am 25.11.2020 wurde die zweite Ausbaustufe des HLRN-IV in Göttingen für alle Nutzer zugänglich gemacht. Damit ist der Ausbau der HLRN-IV Systeme vollständig. Teilweise werden noch kleine Erweiterungen vorgenommen, z.B. wurden in 2021 in Göttingen die Knoten mit großem und sehr großem Speicher mit SSDs ausgestattet.

Die Systeme wurden von der Firma Atos geliefert. Die Systeme sind wie folgt konfiguriert:

# Göttingen:

Phase 1:

- 432 Dual-Socket Knoten mit einer standard Speicheraustattung von 192 GB
- 16 Dual-Socket Knoten mit einer großen Speicherausstattung von 768 GB
- 3 GPU-Knoten mit 768 GB Speicher und 4x NVIDIA Tesla V100 mit 32 GB
- Jeder Knoten ist ausgestattet mit
  - 2 Intel XEON Skylake Gold (6148) mit 2,4 GHz Taktung und jeweils 20 Prozessorkernen
  - o 480 GB Solid-State Disk

# Phase 2:

- 956 Dual-Socket Knoten mit einer standard Speicheraustattung von 384 GB
- 16 Dual-Socket Knoten mit einer großen Speicherausstattung von 768 GB
- 2 Dual-Socket Knoten mit einer sehr großen Speicherausstattung von 1,5 TB
- Jeder Knoten ist ausgestattet mit
  - 2 Intel XEON Cascade Lake Platinum (9242) mit 2,3 GHz Taktung und jeweils 48 Prozessorkernen
  - o 1 Intel Omni-Path Netzwerkadapter

Netzwerk und Filesysteme werden von beiden Rechnersystemen gemeinsam genutzt:

- Netzwerk: Intel Omni-Path in Fat Tree Topologie
- 8,1 PB paralleles Lustre Dateisystem ("WORK") über Omni-Path Netzwerk
- 340 TB Heimat-Dateisystem

# Berlin:

- 1236 Dual-Socket Knoten mit einer standard Speicheraustattung von 384 GB
- 32 Dual-Socket Knoten mit einer großen Speicherausstattung von 768 GB
- 2 Dual-Socket Knoten mit einer sehr großen Speicherausstattung von 1,5 TB
- Jeder Knoten ist ausgestattet mit
  - 2 Intel XEON Cascade Lake Platinum (9242) mit 2,3 GHz Taktung und jeweils 48 Prozessorkernen
- Netzwerk: Intel Omni-Path mit 14 TB/s Bisektions-Bandbreite
- 8,1 PB paralleles Lustre Dateisystem ("WORK" zur Speicherung von Simulationsdaten) über Omni-Path Netzwerk
- 340 TB Heimat-Dateisystem

Das Göttinger System wurde nach Emmy Nöther "Emmy" benannt und das Berliner System nach Lise Meitner "Lise". Zum Abschluss des Ausbaus wurde im November 2020 das Berliner System auf der Top500 Liste der weltweit schnellsten Supercomputer auf Platz 55, und das Göttinger System auf Platz 47 eingestuft. In Deutschland standen die beiden Systeme auf den Plätzen 5 und 7.



# 6 Projektberichte<sup>2</sup>

# 6.1 *hbb00001:* Exploring the conformational phase space of *N*-linked glycans using enhanced MD and sketch-map analysis

HLRN Project ID:	hbb00001
Run time:	III/2020 – II/2022
Project Leader:	Dr. Lucio Colombi Ciacchi
Project Scientists:	Isabell L. Grothaus
Affiliation:	University Bremen

#### Overview

Glycosylation is one of the bulkiest post-translational modification of proteins but has long been overlooked in molecular dynamics simulations, despite its omnipresence in the cell. However, the structure, function and interaction of many biochemical systems is governed by *N*-glycans covalently linked to asparagine residues in specific protein sequences. Due to the flexibility of their glycosidic linkages and their sugar units, *N*-glycans assume many different conformations, unlike the more rigid protein structure to which they are attached. A complete description of the conformational phase space requires thus the consideration of their large number of internal degrees of freedom.

During the course of this project, we showed that an enhanced-sampling molecular dynamics scheme based on enhancing transitions of all relevant barriers with concurrent onedimensional energy potentials in the framework of metadynamics can in fact capture effectively all biologically relevant global conformers of branched glycans, importantly also including the monomer puckering states. This approach was so far tested only for free *N*-glycans in solution as the convergence and reliability of the simulation protocol first had to be assessed. In a consecutive step we were now searching for a glycoprotein, suiting as a model system for the study of protein bound *N*-glycans.

Together with our collaboration partners from the AG Kelm of the glycobiochemistry group at the University of Bremen, we focused on the trans-sialidase enzyme from the African parasite *Trypanosoma congonlense* (TconTS). It is known as an important virulence factor for the disease animal trypanosomiases in Sub-Saharan Africa. As the disease is causing persistent cases of illness and huge economical losses, investigations about molecular mechanisms of TconTS1 are required. The enzyme TconTS1 preferentially transfers  $\alpha$ 2,3-linked sialic acids (Sia) from host-cell glycoconjugates to terminal  $\beta$ -galactose residues of glycoproteins present on the parasite's surface. We were able to shown experimentally that a recombinantly expressed TconTS is highly glycosylated with high-mannose type *N*-glycans on its surface and that theses *N*-glycans have an effect on the substrate affinity, altering enzyme kinetics.

<sup>&</sup>lt;sup>2</sup> Für den Inhalt der Projektberichte sind ausschließlich die genannten Projektleiter bzw. die Projektbearbeiter verantwortlich.



#### Results

In order to verify and validate the above observed experimental phenomenum, we performed molecular dynamics (MD) simulation of the glycoprotein in solution. The influence of the *N*-glycan shield on the overall protein structure and in detail on catalytic amino acids can be investigated on an atomistic scale, which would not be possible in wet-lab experiments.

Based on mass spectrometry experiments, N-glycans of the structure Man<sub>5</sub>GlcNAc<sub>2</sub> were attached at protein positions N45, N113, N206, N240, N281 and N693 (Fig. 1A) and 500 ns of classical MD performed.



**Figure 1: Analysis of the dynamics of TconTS1's** *N***-glycan shield.** A) Atomistic model of TconTS1 with attached Man<sub>5</sub>GlcNAc<sub>2</sub> *N*-glycans (Man: green, GlcNAc: blue) at the asparagine residues (red). B) Interactions between N240 and N113 glycans mediated by hydrogen bonds observed during the MD simulations. C) Overlay of all *N*-glycan positions recorded every 5 ns over a simulation time of 500 ns, with the protein backbone (grey) aligned in all frames and the active site indicated by an orange circle. D) Same as C, with the protein rotated by 180°.

Interestingly, most *N*-glycans are attached at terminal loop positions, which provides a certain flexibility of these structural elements (Fig. 1B) enabling interactions among glycans in structural but not sequence proximity, for instance hydrogen bonds between *N*-glycans at positions N113 and N240. Large motion amplitudes due to internal flexibility of the *N*-glycan trees can further be seen when an overlay of the averaged glycan distribution recorded every5 ns during the simulation is plotted (Fig. 1C/D). A dense glycan coverage (shielding) of the protein can be observed, especially in the catalytic domain although the direct entrance to the active site is not covered (Fig. 1C).

Shifting from a global to a local analysis, the interaction of N-glycans with important catalytic amino acids like D150, Y211 and Y408 were investigated. D150 was observed to shift from the interior of the active site (Fig. 2A) towards an exterior position (Fig. 2B), increasing its



distance from the other catalytic amino acids Y211/Y408 over the simulation time. Interestingly, as a consequence of this shift, a hydrogen bond formed between D150 and the N206 glycan keeping D150 at a distance from the catalytic center (Fig. 2C). Aspartate at position 150 acts as a proton donor in the enzymatic transfer of Sia and is therefore crucial for substrate conversion.



**Figure 2:** Protein-glycan interactions drive active site rearrangements observed in MD simulations of TconTS1. A) Amino acids of the catalytic site were in close proximity at the beginning of the simulation (Snapshot at 100 ns). B) D150 moved out of the catalytic site and formed hydrogen bonds with glycan N206 until the end of the simulation (Snapshot at 350 ns). C) Detail of the hydrogen bonds (black dashed lines) between D150 and glycan N206 at its terminal mannose branches. D150 is circled in yellow and the ligand-binding residues Y211 and Y408 are circled in orange and represented in ball-and-stick with the following color code: oxygen (red), carbon (cyan), nitrogen (blue), hydrogen (white). The underlying protein structure is represented in cartoon style in grey with asparagine residues of *N*-glycosylation sites labelled in red spheres. Glycan color code: Man (green), GlcNAc (blue).

Its position being influenced by *N*-glycan interactions might suggest some regulatory function of *N*-glycans. This open conformation of the binding site (due to outward movement of D150) might lead to higher substrate-binding affinity and would explain experimental findings.

#### Outlook

We demonstrated experimentally and by computer-based simulations that *N*-glycans can influence the function of TconTS1, presenting an interesting model system for our further analysis of protein bound *N*-glycans. Due to the rather basic simulation protocol using only classical MD simulations, we aim at sampling the conformation of N-glycans when attached to TconTS1 by our previously developed enhanced sampling protocol in future studies.



#### Publications

Jana Rosenau, Isabell Louise Grothaus, Yikun Yang, Lucio Colombi Ciacchi, Sørge Kelm, Mario Waespy. *N-glycosylation modulates enzymatic activity of Trypanosoma congolense trans-sialidase.* bioRxiv 2021.12.13.472379; doi:10.1101/2021.12.13.472379

#### Presentations

Isabell Louise Grothaus, Jana Rosenau, Nilima Dinesh kumar, Lucio Colombi Ciacchi, Sørge Kelm, Mario Waespy. *Role of N-glycosylation on structure-function relations of Trypanosoma congolense trans-sialidase* (Poster), Society for Glycobioloogy - Annual Meeting, (virtual) Phoenix (Arizona, USA), November 2020



# 6.2 *hbc00029:* Understanding the catalytic performance of rare-earth oxides: Toward a knowledge-driven design of catalysts from first-principles calculations

HLRN Project ID:	hbc00029
Run time:	01/2021 – 12/2021
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#### Overview

 $La_2O_3$  doped by various metal cations has been extensively used in catalytic reactions[1-3]. Dopants can significantly modify the surface Lewis acidity/basicity which along with the stability of surface oxygen relates to the reactivity of the catalysts. In this project, we systematically investigate the influence of dopants on the surface geometries and the position of O2s2p band centers. We find a correlation between these geometric and electronic properties and the Lewis acidity/basicity of the surface oxygen atoms on the regular (no O vacancies) doped  $La_2O_3(0001)$  surface.

#### Results

#### 1. The influence of dopants on the geometries of the regular $La_2O_3(0001)$ surface

To investigate the influence of various dopants in the surface geometry, we calculated the relative differences in bond lengths between the dopant atom (labelled as X) and the surrounding O atoms on the regular (with no oxygen vacancies) doped  $La_2O_3(0001)$  surface with respect to the undoped surface. The three surface O atoms surrounding the dopant site were denoted as Oupper, while the three subsurface O atoms were denoted as Olower. As shown in Figure 1, the bond lengths between a dopant atom and the six adjacent O atoms, namely d(X-O<sub>upper</sub>) and d(X-O<sub>lower</sub>) show various extent of elongation and contraction after the substitution of a La atom by a dopant. The X-O<sub>upper</sub> bond length generally increases, whereas the X-O<sub>lower</sub> bond length generally decreases relative to the La-O bond length of the undoped regular La<sub>2</sub>O<sub>3</sub>(0001) surface, indicating that the dopant atoms are lifted up in the direction normal to the surface to get closer to the O<sub>upper</sub> atoms and farther away from the O<sub>lower</sub> atoms. This trend is found for the alkali metal, alkali-earth metal and transition metal dopants except for Mo, whereas the lanthanide dopants and Mo shrink the adjacent X-O bonds resulting in negative values of both relative X-Oupper and X-Olower bond lengths. It can be seen from Figure 1 that transition metal dopants induce the largest change in the d(X-O<sub>upper</sub>) and d(X-O<sub>lower</sub>) distances, while lanthanide dopants only exert a very moderate change in the X-O bond lengths.





**Figure 1:** Relative differences in bond lengths between dopant atoms (X) and the surrounding O atoms calculated by subtracting the corresponding bond length on undoped regular La<sub>2</sub>O<sub>3</sub>(0001) surface from those on doped La<sub>2</sub>O<sub>3</sub>(0001) surfaces. O<sub>upper</sub> and O<sub>lower</sub> denote three surface O atoms and three subsurface O atoms near the dopant site, respectively. X-O<sub>upper</sub> and X-O<sub>lower</sub> denote the average bond lengths between dopant atom and three surface/subsurface O atoms.

#### 2. The influence of dopants on the O2s2p band center of the regular $La_2O_3(0001)$ surface

We calculated the O2s2p band center of the occupied states to measure the intrinsic Lewis basicity of the two types of surface O atoms,  $O_i$  (close to the dopant) and  $O_{ii}$  (far from the dopant), in comparison to the average Lewis basicity of surface O atoms (calculated as the average band center of all of the surface O atoms). By analogy to molecular systems, where the locations of the lowest unoccupied and molecular orbital and highest occupied molecular orbital, are related with the Lewis acidity (electron gain) and basicity (electron loss) of these systems. Lewis acidity and basicity of surfaces can be probed by identifying the location of the centers of unoccupied and occupied bands, respectively. A higher lying O2s2p band center indicates that the energy of the electrons occupying 2s2p orbitals is closer to Fermi level; therefore, these O atoms can easily serve as electron donors while interacting with other (acceptor) atoms. Hence, a higher lying O2s2p band center is associated with a stronger Lewis basicity of O atoms.

As shown in Figure 2, various dopants shift the O2s2p band center up or down compared to the undoped  $La_2O_3(0001)$  surface. Doping with Ca, Er, Eu, Gd, Ho, Mo, Pm leads to a strong upshift of the O2s2p band center of O<sub>surface</sub> atoms, whereas Ce, Mn, Nd, Ni, Ru, Ti, V result in a strong downshift of the band center.

Compared to the variations of the average O2s2p band center of  $O_{surface}$  atoms for the La<sub>2</sub>O<sub>3</sub>(0001) surfaces doped by various elements, the variations in the positions of O2s2p band centers of O<sub>i</sub> atoms (close to the doping site) are significantly shifted by by Cu, Er, Gd, Ti, V dopants. For the O<sub>ii</sub> atoms (far from the dopant site), more dopants lead to significant shifts in O2s2p band centers, including Ca, Cr, Er, Gd, Ho, Mg, Mo, Pm, Ti, V. Doping with Mn, Ru, Ce, Pm, Ho and Er leads to a large shift of the O2s2p band centers of both O<sub>i</sub> and O<sub>ii</sub> atoms, while other dopants only significantly affect the band center position of either O<sub>i</sub> or O<sub>ii</sub> atoms. The O2s2p band center position and, hence, the basicity of either O<sub>i</sub> or O<sub>ii</sub> is essentially unchanged by doping with Li, Na, and Co.



**Figure 2:** The O2s2p band centers of (a) the surface O atoms, and the single O atom located at (b)  $O_i$  site and (c)  $O_{ii}$  site on the regular doped La<sub>2</sub>O<sub>3</sub>(0001) surface for various doping elements. The horizontal line in the left diagram denotes O2s2p band centers of the corresponding O atoms on the undoped regular La<sub>2</sub>O<sub>3</sub>(0001) surface. (d) The right panel shows the labels of the analyzed surface La or O atoms on the generalized La<sub>2</sub>O<sub>3</sub>(0001) surface with an O vacancy. However, a regular La<sub>2</sub>O<sub>3</sub>(0001) surface has no O vacancies.

#### 3. NH<sub>3</sub> and CO<sub>2</sub> adsorption energy on the regular doped La<sub>2</sub>O<sub>3</sub>(0001) surface

The adsorption energies of NH<sub>3</sub> and CO<sub>2</sub> can serve as another, more direct indicator of the apparent Lewis acidity and basicity of the surface. They have been calculated for various doped surfaces and variations of the acidity/basicity due to dopants have been compared to the variation in the above-mentioned position of the O2s2p band center. The adsorption energy of  $NH_3$  (a basic probe molecule) can serve as a measure of Lewis acidity, where a more negative adsorption energy corresponds to a stronger Lewis acidity. As shown in Figure 3, Lai (close to the dopant) and La<sub>ii</sub> sites (far from the dopant) show similar Lewis acidity (La<sub>i</sub> being always slightly more acidic than La<sub>ii</sub>), while the dopant site in most cases shows a significantly different adsorption strength of  $NH_3$  for the various dopants. The adsorption strength of  $NH_3$  at the dopant site changes by more than 0.1 eV compared to Lai, Laii sites for most of the transition metals and alkali metals dopants, of which Fe, Ru, and V lead to most negative NH<sub>3</sub> adsorption energies at the dopant site and the largest difference to Lai, Lai sites. For alkaliearth metals and lanthanides (Ce, Er, Eu, Gd, Ho, Nd, Pm) as well as Mn, Ni, the adsorption energy of NH<sub>3</sub> molecule is not significantly dependent on the binding site. In most cases (except for Er), the adsorption energy of  $NH_3$  on the surface La<sub>i</sub> and La<sub>i</sub> sites is found between 0.6 and 0.8 eV, which shows that the dopants generally have little effect on the Lewis acidity of the adjacent surface La atoms. However, alkali metal dopants (Li and Na) and Ru induce a relatively large difference between the acidic properties of the Lai and Lai sites.

 $CO_2$  (an acidic probe molecule) can serve as a measure of Lewis basicity of the surface O atoms, where a more negative adsorption energy indicates a stronger surface Lewis basicity. As shown in Figure 4, the adsorption energies of  $CO_2$  on the  $O_i$  and  $O_{ii}$  sites differ significantly, which could be explained by a larger influence of the dopant on the adjacent  $O_i$  sites in comparison to the more distant  $O_{ii}$  sites. Ca, Co, Cu, Li, Na, Ru dopants result in a difference of the  $CO_2$  adsorption energy of > 0.2 eV between  $O_i$  and  $O_{ii}$  sites. The adsorption energy of  $CO_2$  on top of the surface O atoms of the undoped La<sub>2</sub>O<sub>3</sub>(0001) (where  $O_i$  and  $O_{ii}$  sites are indistinguishable) is 0.9 eV. After doping by various elements, the Lewis basicity of  $O_i$  and  $O_{ii}$ 



sites (reflected by the more negative adsorption energy of CO<sub>2</sub>) increases in most cases, except for the O<sub>i</sub> site on the La<sub>2</sub>O<sub>3</sub>(0001) surface doped by Co and Cr. In contrast to the small effect of dopants on the NH<sub>3</sub> adsorption energy at La<sub>i</sub> and La<sub>ii</sub> sites, the adsorption strength of CO<sub>2</sub> on O<sub>i</sub> and O<sub>ii</sub> sites is heavily affected by dopants. As seen in Figure 4, the variation of Lewis basicity of surface O<sub>i</sub> and O<sub>ii</sub> sites expressed in terms of the adsorption energy of CO<sub>2</sub> is not identical to that calculated in terms of the O2s2p band center. This is because the position of the O2s2p band center is only a rough indicator of the basicity. Futhermore, the CO<sub>2</sub> adsorption energy is not only affected by the surface Lewis basicity, but also depends on the CO<sub>2</sub> adsorption energy and the O2s2p band center.



**Figure 4:** Adsorption energy of CO<sub>2</sub> molecule and O2s2p band center of the (a) O<sub>i</sub> site, (b) O<sub>i</sub> site on the regular doped La<sub>2</sub>O<sub>3</sub>(0001) surface for various dopant elements. The CO<sub>2</sub> adsorption energy on the undoped surface is shown by the horizontal line. CO<sub>2</sub> adsorption energy is calculated:  $E_{ads} = E(surface) + E(CO_2) - E(adsorption complex)$ , where more positive adsorption energy indicates larger adsorption strength (favorable adsorption).



#### Outlook

The acidity-basicity property has been studied theoretically on the regular (without O vacancies)  $La_2O_3(0001)$  surfaces doped by various metal cations by a DFT method. Combined with the results on the defective (with O vacancies)  $La_2O_3(0001)$  surface calculated in the previous working phase, we have tried to build a relationship between the O2s2p band center and the oxygen vacancy formation energy. In the future, we will apply a similar approach to investigate the acidity-basicity property of the CeO<sub>2</sub>(111) surface, a representative reducible oxide surface.

#### Publications

- 1. S. Li, Y. Li, M. Bäumer, L.V. Moskaleva. Assessment of PBE+ U and HSE06 methods and determination of optimal parameter U for the structural and energetic properties of rare earth oxides. J. Chem. Phys. 2020, 153, 164710.
- 2. S. Li, Y. Li, M. Bäumer, L.V. Moskaleva. Insights into the correlation of Lewis aciditybasicity and oxygen vacancy formation in doped La<sub>2</sub>O<sub>3</sub> from DFT calculations. In preparation.

#### References

- [1] Z.-Q. Wang, D. Wang, X.-Q. Gong. Strategies To improve the activity while maintaining the selectivity of oxidative coupling of methane at La2O3: A density functional theory study, ACS Catal. 2019, 10(1), 586-594.
- [2] S. Wang, S. Li, D.A. Dixon. Mechanism of selective and complete oxidation in La2O3catalyzed oxidative coupling of methane, Catal. Sci. & Technol. 2020, 10(8), 2602-2614.
- [3] S.G. Podkolzin, E.E. Stangland, M.E. Jones, E. Peringer, J.A. Lercher. Methyl chloride production from methane over lanthanum-based catalysts, J. Am. Chem. Soc. 2007, 129(9), 2569-2576.



# 6.3 *hbc00030:* Dynamics of fluoride anions in all-silica and silicogermanate zeolites

HLRN Project ID:	hbc00030
Run time:	II/2018 – III/2021
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#### Overview

In this project, *ab-initio* molecular dynamics calculations were used to study the dynamic behavior of fluoride anions confined to small cages in zeolite structures. One part of the work done in the past year addressed the dynamics of fluoride anions in all-silica zeolites having different topologies, providing atomic-level insights into the origins of dynamic disorder. Another part of the project dealt with ITQ-13 silicogermanates, which are quite unique as two different fluoride environments coexist in the same structure.

#### Scientific background

Zeolites are a class of inorganic porous materials with important applications in ion exchange, gas and liquid separation, and catalysis.[1] Zeolite structures consist of a three-dimensional framework of tetrahedrally coordinated atoms connected by oxygen atoms. A rich variety of zeolite structures has been reported: To date, more than 250 distinct framework types have been recognized by the International Zeolite Association, which assigns three-letter framework type codes to each framework (*e.g.*, ITH for the framework of ITQ-13). Prototypical zeolites, such as zeolite minerals, possess an aluminosilicate framework whose negative charge is balanced by extra-framework cations. However, the development of sophisticated synthesis techniques has led to the discovery of zeolite-like materials having a neutral framework, among them all-silica zeolites (composition SiO<sub>2</sub>), germanates (GeO<sub>2</sub>), silicogermanates (Si<sub>x</sub>Ge<sub>1-x</sub>O<sub>2</sub>), and aluminophosphates (AIPO<sub>4</sub>).

The synthesis in the presence of fluoride anions ("fluoride route") is a particularly successful strategy to obtain neutral-framework zeotypes with very open frameworks and low defect concentrations.[2,3] In the as-synthesized zeolites, the fluoride anions occupy well-defined positions in the crystal structure, balancing the charge of the cationic organic structure directing agents (OSDAs) that are used to promote the formation of a particular framework. Broadly, two different fluoride environments can be distinguished in this context, which are illustrated in **Figure 1** for the case of ITQ-13: On the one hand, the fluoride anions can be located at the centre of double four-ring (d4r) cages. On the other hand, they can occupy other small cages in the structure. In these cases, they are covalently bonded to a silicon atom at one corner of the cage, forming trigonal-bipyramidal [SiO<sub>4</sub>F]<sup>-</sup> units. Disorder over two or more positions in one cage is observed in some zeolites containing these [SiO<sub>4</sub>F]<sup>-</sup> units, which can be of a static or dynamic nature.

In this project, the dynamics of fluoride anions confined to small cages in zeolite structures were studied using density functional theory (DFT) calculations and DFT-based *ab initio* 



molecular dynamics (AIMD) simulations, which cover a timescale of several picoseconds. These investigations were carried out in the context of the project "*Beyond tetrahedral coordination in zeolite-type materials - A computational approach*" (project no. 389577027, Fi1800/5-1), funded by the Deutsche Forschungsgemeinschaft (DFG - German Research Foundation) from May 2018 to September 2021.



**Figure 1: Left:** Crystal structure of the all-silica zeolite ITQ-13.[4] Yellow = silicon, red = oxygen, dark/light blue = fluoride in different building units. The positively charged OSDAs are omitted for clarity. **Middle and right:** Zoomed-in view of distinct fluoride environments in ITQ-13.

#### Results

#### 1. All-silica zeolites with different topologies

In this part of the project, the equilibrium positions of fluoride anions and their dynamic behavior were studied for five different all-silica zeolites having CHA, IFR, NON, STF, and STT topologies. For all these systems, experimental crystal structure determinations of the assynthesized forms (including OSDA molecules and fluoride anions) had been reported previously (see [5] for an overview). A DFT-based prediction of the energetically preferred fluoride positions delivered excellent agreement with the experimental sites for all zeolites except STF, where the experimental site was second-lowest in energy. In the most complex system, STT, the fluoride anions are disordered over three non-equivalent sites.[6] According to the DFT calculations, these three sites are energetically very close together, whereas other positions in the cage are significantly less stable (**Figure 2**). While these results show that the DFT calculations reliably reproduce the equilibrium positions of fluoride in all-silica zeolites, an in-depth analysis revealed that the energetically preferred site(s) are determined by a complex interplay of factors. Apart from a preference to locate in the proximity of four-membered rings, no other generally valid "rules" that would allow the prediction of the most probable fluoride sites without actual calculations could be established.

For all studied all-silica zeolites except CHA, nuclear magnetic resonance (NMR) spectroscopy investigations have delivered insights into the dynamic behavior of fluoride:[7] In IFR and STT, the fluoride anions are dynamically disordered, in other words, they move between different locations within the cage over time. In contrast, fluoride is statically disordered in NON, and there is no disorder at all in STF. In order to understand the reasons for the different behavior of these zeolites, AIMD simulations were performed for 25 °C, 100 °C, and 200 °C. The trajectories of the fluoride anions were then analyzed to determine the occurrence of a "hopping" of fluoride anions between different Si atoms. For room temperature, such jumps



were observed for IFR and STT, but not for the other three zeolites, in perfect agreement with experiment. The right panel of **Figure 2** shows an individual trajectory of a fluoride anion in STT, which, incidentally, visits all three experimental positions during the simulation. At elevated temperatures, dynamic disorder occurred in CHA and STF, but not in NON. When analyzing the differences among the five zeolites, it was found that the local environment determines the likelihood of dynamic jumps between different sites. Specifically, short contacts to "secondary" Si atoms enhance the probability of a dynamic motion, which involves a breaking of the primary F–Si bond. These secondary contacts are shortest in IFR and STT. Longer-range interactions with the OSDA molecules, which had been at the core of an earlier study,[8] play only a minor role in most zeolites, but they may suppress the dynamic disorder in specific cases. Although such detailed insights into the structure and dynamics of fluoride-containing zeolites are primarily of fundamental interest, they might also aid the development of improved synthesis routes.**[P1]** 



**Figure 2:** Visualization of the fluoride-containing cage in the STT-type zeolite SSZ-23. **Left:** Fluoride positions from the crystal structure. [6] **Middle:** Summary of DFT results, with fluoride locations colored according to their total energy (cyan/light blue = energetically favorable; dark blue/black = unfavorable). **Right:** Representative trajectory of a single fluoride anion during an AIMD simulation.

#### 2. Ge distribution and fluoride dynamics in ITQ-13 silicogermanates

The zeolite ITQ-13 (ITH topology) can be synthesized in all-silica form and as silicogermanate with Si/Ge ratios as low as ~3.[9] In addition to being a promising material for catalytic applications, especially in hydrocarbon conversions, ITQ-13 is also interesting from a fundamental point of view, as two different fluoride environments coexist in the structure (Figure 1). In ITQ-13 silicogermanates, a lack of long-range order of the Ge atoms precludes an unambiguous determination of the distribution of Ge in the structure. It was, however, inferred from NMR experiments that the Ge atoms preferentially occupy the corners of the d4r cages and the basal four-membered rings of the [4.5<sup>6</sup>] cages (middle and right panel of **Figure** 1).[10] This preference was corroborated in DFT optimizations of ITQ-13 models with one Ge atom per unit cell (u.c.). In further calculations, between 2 and 8 Ge atoms/u.c. were incorporated. While considering only the positions associated with d4r units and basal planes of the [4.56] cages, different possible distributions among them, as well as different local arrangements were included (between 18 and 48 models for a given Ge content). The total energies were then evaluated to determine the most probable arrangements. Up to a Ge content of about 4 atoms/u.c., a tendency to distribute the Ge atoms relatively evenly among the available cages was observed. This agrees with the fast decline of <sup>19</sup>F-NMR resonances associated with purely siliceous building units upon increasing Ge content.[9,10] At higher Ge



contents, the calculations pointed to a coexistence of a multitude of different local environments, *i.e.*, of cages having different numbers and/or arrangements of Ge atoms at the corners.

For the highest Ge content considered, the calculations predicted the stability of  $[4 \cdot 5^6]$  cages having two Ge atoms at adjacent corners (**Figure 3 c**). Previous assignments of <sup>19</sup>F-NMR resonances had not considered such building units, and there is no unaccounted peak in the experimental spectra. DFT calculations of the <sup>19</sup>F chemical shifts pointed to an overlap of the resonance stemming from these  $[4 \cdot 5^6]_{2Ge}$  cages with peaks from Ge-rich *d4r* units. Therefore, they may have been overlooked in prior experimental work. AIMD simulations to investigate the dynamic behavior of the fluoride anions delivered no evidence for dynamic disorder at room temperature. Dynamic jumps between Si sites were predicted to occur at the temperature of zeolite synthesis (135 °C). As shown in **Figure 3**, the dynamic behavior varies depending on the local distribution of Si and Ge.**[P2]** 



**Figure 3:** Dynamic behavior of fluoride anions in different  $[4 \cdot 5^6]$  cages of ITQ-13 at 135 °C. **a)** Dynamic jumps between different Si atoms in all-silica cage. **b)** Short-lived displacements from Ge atom (green) towards Si atom. **c)** Oscillation between two Ge atoms without distinct dynamic jumps.

#### **Project-related publications**

- **P1** M. Fischer, Fluoride Anions in All-Silica Zeolites: Studying Preferred Fluoride Sites and Dynamic Disorder with Density Functional Theory Calculations, J. Phys. Chem. C 125, 8825–8839 (2021)
- **P2** M. Fischer, C. Bornes, L. Mafra, J. Rocha, *Elucidating the germanium distribution in ITQ-*13 zeolites by density functional theory, Chem. Eur. J., accepted manuscript (2022); https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/chem.202104298

#### **Project-related presentations**

- P3 M. Fischer, Dynamic disorder of fluoride anions in all-silica zeolites: Enhancing understanding with DFT-based molecular dynamics simulations, talk at the 29<sup>th</sup> Annual Meeting of the German Crystallographic Society (online), March 2021
- P4 M. Fischer, DFT-based molecular dynamics elucidate the dynamic behaviour of fluoride anions in all-silica zeolites, talk at the 8<sup>th</sup> Conference of the Federation of European Zeolite Associations FEZA 2021 (online), July 2021



#### References

- [1] A. F. Masters, T. Maschmeyer, Microporous Mesoporous Mater. 142, 423–438 (2011)
- [2] M. A. Camblor, L. A. Villaescusa, M.-J. Díaz-Cabañas, Top. Catal. 9, 59–76 (1999)
- [3] P. Caullet, J. Paillaud, A. Simon-Masseron et al., Comptes Rendus Chim. 8, 245–266 (2005)
- [4] A. Corma, M. Puche, F. Rey et al., Angew. Chem. Int. Ed. 42, 1156–1159 (2003)
- [5] D. S. Wragg, R. E. Morris, A. W. Burton, Chem. Mater. 20, 1561–1570 (2008)
- [6] M. A. Camblor, M.-J. Díaz-Cabañas, J. Perez-Pariente et al., Angew. Chem. Int. Ed. 37, 2122–2126 (1998)
- [7] H. Koller, A. Wölker, L. A. Villaescusa et al., J. Am. Chem. Soc. 121, 3368–3376 (1999)
- [8] M. Fischer, J. Phys. Chem. C 124, 5690–5701 (2020)
- [9] X. Liu, U. Ravon, A. Tuel, Chem. Mater. 23, 5052-5057 (2011)
- [10] J. A. Vidal-Moya, T. Blasco, F. Rey et al. Chem. Mater. 15, 3961–3963 (2003)



#### 6.4 hbc00045: Rupturing Materials in Electric Fields

HLRN Project ID:	hbc00045
Run time:	II/2020 – III/2022
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#### Overview

In mechanochemistry, forces are applied to initiate chemical reactions. This approach can be used in the production of mechanochromic materials, which change their color when a threshold stretching force is applied. In the case of a polymer, for example, a molecular subunit, the so-called mechanophore, is embedded in the polymer backbone. Upon application of stretching forces, the mechanophore changes its structure, e.g., via bond-rupture or cis/trans-isomerization, which can be accompanied by color changes. The applications of this approach are immense, including optical strain detection in the construction industry, tamper-proof packaging, and self-healing materials.

Oriented external electric fields (OEEFs) have been used to catalyze a number of reactions by lowering the energy of a transition state if a zwitterionic resonance structure, which is favored in an OEEF, is present in the transition state (cf. Figure 1). Examples of reactions induced by OEEFs include enzymatic processes, isomerizations and Diels-Alder reactions. Moreover, it has been demonstrated that OEEFs reduce the bond dissociation energy of  $\sigma$ - and  $\pi$ -bonds and allow the switching of typically homolytic to heterolytic bond rupture processes.

In this project, mechanochemistry is coupled to the application of OEEFs in order to reduce the rupture forces of mechanophores in mechanochromic materials. While it is far from straightforward to conduct mechanochemical experiments in OEEFs due to the difficulty of controlling the relative orientation of the substrate and the electric field, computational chemistry offers the opportunity to rapidly screen a variety of mechanochemical reactions in OEEFs. The focus in this project lies on determining the rupture forces required to achieve the color switching process, using state-of-the-art computational methods.



**Figure 1:** Schematic representation of the resonance structures in the transition state of a Diels-Alder reaction, which can be energetically favored in an oriented external electric field (OEEF).



#### Results

At the beginning of this project, one focal point was a thorough benchmark of electronic structure methods that allow an accurate reproduction of energies and geometries of different molecules in OEEFs of various strengths. Reference data was provided by gold standard CCSD[T] calculations extrapolated to the complete basis set limit. Several wavefunction-based quantum chemical methods and a large number of density functionals were tested. It was found that, surprisingly, the accuracy with which a given density functional reproduces CCSD[T] energies and geometries in OEEFs of various strength does not correlate with the rung of this functional on Jacob's ladder (Figure 2). In other words, newer, more sophisticated and computationally more demanding density functionals do not necessarily deliver more reliable results than more traditional functionals. For instance, well-known functionals such as B97 and PBE perform remarkably well when treating molecules in OEEFs. This finding is important for scientists working in various branches of chemistry in which electric fields are present, and not only in mechano-electrochemistry. The results from this study will be published shortly in a thorough benchmark paper, which will also constitute the basis for our further investigations by providing a justification for the choice of the density functional.



**Figure 2**: Benchmark of electronic structure methods for the deviation of bond lengths in a test set of 20 organic and inorganic molecules in external electric fields, calculated with various density functionals. Reference data is provided by CCSD[T]/cc-pVQZ.

Moreover, a proof-of-principle study on the behavior of a mechanophore in an OEEF was conducted. It was found that, in agreement with our hypothesis, the rupture force of a model mechanophore can be reduced significantly if an OEEF is present (Figure 3). Not surprisingly, the degree of this reduction is strongly dependent on the strength of the OEEF and its orientation relative to the scissile bond in the mechanophore. Preliminary results suggest that the influence of an OEEF on the mechanical properties of a mechanophore becomes more complex with increasing complexity of the mechanophore. We are currently working on completing the calculations and analyses, with the aim of publishing our results shortly.

#### Outlook

While the aforementioned observations have important implications for the design of mechanophores, it is only the starting point for further investigations. Crucially, we are currently in the process of iteratively determining the rupture forces of various mechanophores in OEEFs of different strengths and orientations with high resolution, which requires iterative two-





**Figure 3:** Rupture forces of a model mechanophore in OEEFs of various strengths, calculated with the quantum chemical EFEI method to apply mechanical forces.

dimensional scans. Moreover, the propagation of the fragments needs to be investigated in great detail by using multireference methods. Finally, the roles of the relative orientation of the mechanophore and the external force, the chemical composition of the mechanophore itself and the linkers to the polymers as well as local topological factors shall be considered and their influence on the rupture forces shall be determined. This will allow us to tune the rupture forces in mechanophore and its surrounding.

Turning to applications, various known (mechano)chemical transformations will be scrutinized as to their applicability in OEEFs. Cycloreversions and Retro-Diels-Alder reactions will be tested as well as the rupture of sulfur-sulfur bonds, which traditionally proceeds homolytically. It can be assumed that this is switched to a heterolytic process if the OEEF is strong enough. Another test case is provided by flex-activated mechanophores, in which bond angle bendings in the main polymer chain leads to rupture of chemical bonds perpendicular to it and to the release of small molecules. This can potentially be used for self-healing purposes and for the delivery of medical drugs.

All mechanochemical transformations in OEEFs will be understood in terms of the strain generated by the combined application of mechanical forces and OEEFs, by using the previously developed Judgement of Energy DIstribution (JEDI) analysis. This will allow an indepth analysis of the molecular basis for mechanochemical bond rupture in OEEFs and the subsequent optimization of this process by specifically targeting those bonds that are most susceptible to stretching forces in a given setup.

For the major part of the remaining calculations conducted in the course of this project the Q-Chem program package will be used, since it includes a wide variety of density functionals, the External Force is Explicitly Included (EFEI) method for geometry optimzations under external forces, the straightforward application of electric fields and an interface to the JEDI analysis, which allows the determination of the force-bearing scaffold of a mechanically deformed molecule and the subsequent optimization of the mechanochemical response.

In summary, the combination of strong electric fields and mechanochemistry offers the possibility of tuning the rupture forces and consequently the color response of mechanochromic materials with unprecedented precision. State-of-the-art computational methods are applied to model both effects simultaneously, thus paving the way for experimental verification.



# 6.5 *hbc00046:* Towards an atomistic picture of phage display: the case of TiO<sub>2</sub> binding peptides

HLRN Project ID:	hbc00046
Run time:	II/2020 – I/2021
Project Leader:	Dr. Massimo Delle Piane
Project Scientists:	Dr. Monika Michaelis
Affiliation:	Bremen Centre for Computational Materials Science (BCCMS) and Hybrid Materials Interfaces (HMI) group, Faculty of Production Engineering, University of Bremen

#### Overview

The identification of the primary structure (amino acid sequence) of a peptide which possesses the property to bind selectively and/or specifically to a substrate of interest is referred to as genetically engineered polypeptides for inorganics (GEPI). Within this framework, combinatorial biological protocols like for instance phage display (PD), are applied to identify peptide sequences to allow for faster, rational design. Additionally, these display techniques enable the identification of the genotype of the peptide that binds to the targeted material without requiring a detailed knowledge of the system. For this purpose, randomized peptide libraries with up to 10<sup>9</sup> variations of sequences encoding peptides of fixed lengths are inserted into the capsid genome of the phage. An unrivaled property of these viruses is the direct relation of its genotype and its phenotype as, for example, chimeric peptides are directly expressed on the surface of the coat protein pIII *via* a linking sequence displayed at one end of the bacteriophage (cf. Figure 1a). Another outstanding property of the bacteriophages is their ability to infect bacteria and replicate within them, which leads to their quick reproduction.



**Figure 1**: Overview of Phage display. a) Phage M13 in schematic representation with a zoom in revealing the atomistic setup and the subunits. b) Process of biopanning in Phage display on the material of interest.



The affinity selection is performed by a process known as biopanning (Figure 1.b). Briefly, the phage library and substrate are brought into contact and incubated in an appropriate solvent allowing the phages displaying the chimeric peptides to bind to the substrate. After the incubation time, unbound or weakly bound bacteriophages are removed by a washing step with a suitable detergent-containing solution. The phages that are still bound to the target material after this step, and therefore have a potential high binding affinity, are eluted. The obtained phages with the desired peptide sequences are replicated by infection of *Escherichia coli*. Gene sequencing of individual phage clones is performed to identify the peptides that can specifically and strongly bind to the target material.

Since the adaptation of phage display for the identification of specifically binding peptides to materials, a huge variety of sequences for different materials could be identified. The limited understanding of how to exploit the relationship between peptide sequences identified during phage display and their corresponding materials-binding affinity as well as their specificity of interaction is so far a significant obstacle towards reliable peptide-based strategies for the generation and organization/activation of (nanostructured) inorganic materials.

In this project, we focus on TiO<sub>2</sub> (Titania), which is an attractive material used in medical and environmental applications based on its optical, adsorbent, and catalytic properties as well as its use in biomedical implant materials. We chose two 12mer peptides for our investigation, which were originally identified via Phage display against 100 nm titanium nanoparticles. It was revealed that although these peptides have very similar binding affinities towards Titania, their binding shows profoundly different modes of surface interaction.

A fundamental understanding of the atomistic aspects of peptide-materials recognition during phage display in comparison to peptide binding in their intended application is absolutely necessary to advance peptide-based generation and organization of nanostructured inorganic materials. Therefore, the general question we aim at answering during the project is: How does the attachment to a phage, as happens in widespread phage display binding assays, influence the conformation and bio-material interaction behavior of titania binding peptides?

#### Results

As a first step we investigated the conformational ensemble of the selected titania binding peptides, to use as a reference to identify the perturbation induced by the phage linkage. The sequences of the two selected peptides, obtained via phage display assay, are: QPYLFATDSLIK (Ti-1) and GHTHYHAVRTQT (Ti-2). Based on quartz-crystal microbalance with dissipation (QCM-D) preliminary studies, we focused also on the two 6-mer halves of each peptide. We generated starting conformations based on the known sequences, using de novo secondary structure prediction tools. The REMD method was used to identify molecular equilibrium structures of the peptide strands. 16 replicas of each strand with initial random configuration were simulated at temperatures between 300 and 800K to ensure sampling of the entire conformational space. The simulations were carried out using the CHARMM force field. REMD was run for 10 ns /sample (total of 160 ns) and the temperatures exchanged every 0.2 ps. Statistical analysis was performed using the MMTSB toolbox, with a k-means clustering algorithm. Representative final ensemble structures were chosen from the lowest temperature replica (300 K). The higher temperatures were used for fast conformational search and overcoming kinetic trapping in the REMD scheme. The center of the most populated cluster. meaning the structure with minimum RMSD, was exported for analysis. The secondary structure of each structure is determined using the STRIDE toolset and VMD.

After the equilibration, the individual structures were arranged in a circle with diameter 3 nm, representing a phage display. The structures were then equilibrated for 50ns in explicit solvent with ions present and the final structure was determined. A second set of computational experiments was performed where the peptides are equilibrated in explicit solvent with ions as part of a larger protein structure. The peptides were built in random conformation onto that



structure (1TOL.pdb). Exposed amino acids were identified (parts of the sequence that were "sticking out") that could potentially interact with an abiotic surface.

Estimating the free energy of adsorption of materials-binding peptides is fundamental to quantifying their interactions across bio/inorganic interfaces. Among experimental methods that can be used to estimate this quantity, QCM-D has been already performed in our group on the selected peptides. As a second step in this project, we decided to couple the experiment with the accurate calculation of the free energy of adsorption by means of Replica Exchange with Solute Tempering augmented with metadynamics (RESTmetaD) simulations, performed on the interaction of the peptides with a model amorphous titania surface in pure water. However, both during this project and during the parallel investigation of the adsorption of peptides on a zinc oxide (ZnO) surface, we have encountered some issues in this approach. hindering convergence and the quality of the computed free energies of adsorption. This was due to a deficient sampling of the area in proximity to the surface. Indeed, metaD has been shown to very poorly converge in the case of molecules interacting with material surfaces with high solvent affinity, due to the inherent difficulty of displacing solvent molecules within the strongly adsorbed solvent layer. In our case distinct solvent rearrangements induced by the surface created entropic barriers to the adsorption process. We would like to note that this is not necessarily due to a high free-energy barrier along the free energy profile, but to the narrowness of the adsorption pathway that can lead to successful displacement of the chemisorbed water layer by the amino acids. After several trials and methods' benchmarking, we found that convergence and agreement with experiment can only be achieved by explicitly biasing the surface/solvent interactions, in a novel extension to the standard RESTmetaD approach, that we published.[1] Figure 2 reports a comparison between three methods for the adsorption of an amino acid on the oxide surface, to demonstrate this point.



**Figure 2**: Comparison in performance between different enhanced sampling methods for the adsorption of histidine on the oxide surface. metaD: standard metadynamics with CV set as the height of the amino acid's center of mass with respect to the surface. REST-metaD: metadynamics augmented with Replica Exchange with Solute Tempering (solute = amino acid). RES(S)T-metaD: metadynamics augmented with Replica Exchange with Solute and Surface Tempering. Top: evolution of the free energy profiles profiles during the simulations, according to the color scale on the right. The zero of the free energies is set at the minimum value. Bottom: value of the CV along the simulations.



We are currently employing this method to extract binding free energies of out titania binding peptides. Promising data is coming again from the ZnO system, as reported in Figure 3, where an excellent agreement wity experimental binding energies is shown, bot for amino acids and a binding peptide.



**Figure 3**: (a) Adsorption free energy for the selected amino acids in methanol, in comparison with the experimental O-IDA values.[1] (b) Enhanced sampling results for ZnOBP1 on ZnO (10-10): convergence of the free energy of adsorption during the simulation and comparison with O-IDA and SMFS experimental results.

#### Outlook

The next step will be to compare the interaction of the peptides with titania as free in solution as opposed to linked to a phage, understanding how the additional structural constraint influences the way these biomolecules approach and interact with the inorganic material. We will therefore investigate the interaction of the "minimal phage" system with our titania surface. We plan to perform only a qualitative investigation of the interaction by simulating the phage approach to the material surface via slow steered molecular dynamics simulations, followed by long standard MD simulations to investigate the equilibrium ensemble of the system at the surface interface.

We believe that the obtained results, although obtained for titania binders, will be of general interest within the larger (bio)material community, adding caveats to the extrapolation of results from phage display assays and providing a better atomistic understanding of the biomolecular recognition of inorganic material surfaces.

#### References

[1] Monika Michaelis, Massimo Delle Piane, Dirk Rothenstein, Carole C. Perry, and Lucio Colombi Ciacchi *Journal of Chemical Theory and Computation* **2021** *17* (7), 4420-4434 DOI: 10.1021/acs.jctc.1c00165



# 6.6 *hbc00048:* Antimicrobial peptides: structure-activity relationships and antimicrobial mechanisms

HLRN Project ID:	hbc00048
Run time:	III/2020 – II/2021
Project Leader:	Dr. Monika Michaelis
Project Scientists:	Dr. Massimo Delle Piane, Prof. Lucio Colombi Ciacchi
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#### Overview

Infections are a major concern in global healthcare, especially from bacteria that form biofilms. Their presence can for instance lead to the establishment of chronic wounds, which cause persistent inflammation and damage and can ultimately result in death. In particular, multidrug-resistant bacteria, that are difficult or even impossible to treat, have evolved increasingly into a global health threat, with special emphasis on strains that belong to the so-called ESKAPE panel. According to the WHO priority list, future development strategies should therefore focus on antibiotics and their alternatives that are active against 'critical-priority' bacteria, especially multidrug-resistant and Gram-negative bacteria. It was recently shown that antibiotic resistant bacteria have a high propensity towards a collateral sensitivity against so-called Antimicrobial Peptides (AMPs). AMPs are short-chain, cationic peptides that evolved as a host-defense mechanism and are conserved in all kingdoms of life. AMPs are excellent candidates for the functionalization of biomaterials and medical devices. However, despite their advantages, few AMPs have been advanced to date for clinical use and/or passed clinical trials.

Understanding the mechanisms behind AMP antimicrobial action is crucial for their application. A complex interplay of physicochemical and structural parameters mediates the antimicrobial performance of such peptides. It was previously shown that antimicrobial activity is strongly correlated to peptide conformation (structure activity relationship) or, more precisely, to their induced amphipathic conformation upon membrane interaction. A promising candidate for computer-assisted AMP design is the synthetic oligopeptide SAAP-148. Developed from human peptide LL-37, SAAP-148 shows enhanced antimicrobial and antibiofilm activity under physiological conditions. However, its structure and the precise mechanism of action are unknown.

Within this project we want to understand the atomistic details of the conformational ensemble of SAAP-148 in solution and upon interaction with the membrane. Based on these results we want to identify potential interaction mechanisms. We focus on the application of enhanced sampling methods to overcome the timescale problems described in previous approaches. The general question we aim at answering during the proposed project is: How do the conformational ensemble and the membrane-induced conformational changes influence the antimicrobial action of an antimicrobial peptide?

#### Results

In a first step we used *de novo* secondary structure prediction (Pep-Fold3) to provide an initial "educated guess" about the intrinsic propensities to form either well-defined or unordered secondary structures for both LL-37 and SAAP-148. With this structure prediction we obtained

a first impression on the variability within the conformational ensemble. As expected, structure prediction resulted in a high degree of helicity for both peptides.

Based on these structure predictions we chose the alpha-beta collective variable to thoroughly explore the peptides' conformational space in solution, using Replica Exchange with Solute Tempering (REST) simulations coupled with Metadynamics (RESTMetaD). Figure 1 reports the free energy landscapes for LL-37 and SAAP-148 in solution, plotted based on the alphabeta collective variable. At variance from secondary structure predictions, the free energy profiles do not show a global minimum close to 100% helicity, but a more variable conformational landscape is found, with global minima around 50%. Indeed, these peptides are expected to gain helicity only when in contact with the bacterial membrane



**Figure 1:** Free energy profiles for LL-37 and SAAP-148 in solution, plotted based on the alpha-beta collective variable. The evolution of the profiles during the REST-MetaD simulations is reported, according to the color scale on the right. The zero of the free energies is set at the minimum value.

The construction of accurate atomistic models for bacterial membranes is an important part of our project. The cell envelope of Gram-negative bacteria consists of two separated membranes. The outer membrane is asymmetric, and the outer leaflet is composed of lipopolysaccaride (LPS), while the inner leaflet contains a mixture of zwitterionic and anionic phospholipids. This asymmetry is important to rationalize the first membrane/peptide interactions and was taken into account. The inner membrane contains a symmetric arrangement of phospholipids including zwitterionic (phosphatidyl-ethanolamine) and anionic (cardiolipin and phosphatidylglycerol) phospholipids (similar to the membrane of Gram-positive bacteria). The parameter set CHARMM36 was used to reproduce the realistic lipid properties as closely as possible.

For the outer membrane of *Pseudomonas Aeruginosa*, the upper leaflet consists of the pentaacyl Lipid A domain of *P. aeruginosa* LPS which contains  $\beta$  (1-6)-linked D-glucosamine disaccharides decorated with two negatively charged phosphates at 1 and 4' position and five symmetrically distributed fatty acids. The inner leaflet has combinations of head and tail groups with 60% PE, 30% PG and 10% PC with 59% DP and 41% DO. We focused on symmetric acyl chains with the same levels of acyl chains in both leaflets. The system was built with the CHARMM-GUI Membrane Builder, which enables us to include all relevant components. 150 mM NaCl with Ca ions were added to balance the charge of the sugar coating. We have confirmed the correct description of the physicochemical properties of the membranes, in particular the lipid density per surface area, the lateral diffusion coefficient of individual molecules within the membrane and the overall membrane stability in long MD runs at at 37°C within the NPT ensemble (Figure 2).





**Figure 2**: a) representative snapshot of the equilibrated membrane, b) area per lipid of inner lipids and LPA and c) mass density profiles of selected functional groups across the membrane (averaged from the last 100ns).

At this point, however, it became clear that a full atomistic description of this membrane could potentially hinder the project, due to the elevated computational cost. For this reason, we deviated from the original plan and decided to collaborate with the group of Prof. Pavan at Politecnico di Torino, Italy. This group has recently developed Swarm-CG, a versatile software for the automatic iterative parametrization of bonded parameters in coarse-grained (CG) models, ideal in combination with popular CG force fields such as MARTINI.[1] We are currently using this method to parametrize a CG model for our membranes, combining the speed of this approach and the accuracy coming from our all-atom simulations.

#### Outlook

In the next step of the project, apart from continuing this parametrization process, we are currently identifying the preferential binding configuration of SAAP-148 and LL-37 on the membrane. This step is the most computationally demanding, due to the combination of system size, necessity of multiple replicas and expected slow convergence of the profiles. From the simulations, we will be able to compute an accurate estimation of the free energy of adsorption and we will determine the predicted dominant structures of the peptides in the adsorbed states.

Finally, we want to provide insight into the mechanisms of antimicrobial activity using either state-of-the-art, unbiased and long MD simulation with increased temperature or steered MD simulations of the peptide across the membrane.

We believe that the obtained results, although obtained for a selected peptide and an exemplary outer and inner membrane composition of a gram-negative bacteria, will be of general interest within the larger microbiological and (bio)material community, adding caveats to the extrapolation of results from experimental assays and providing a better atomistic understanding of the antimicrobial mechanisms of AMPs.

#### References

[1] Charly Empereur-Mot, Luca Pesce, Giovanni Doni, Davide Bochicchio, Riccardo Capelli, Claudio Perego, and Giovanni M. Pavan *ACS Omega* **2020** *5* (50), 32823-32843 DOI: 10.1021/acsomega.0c05469



# 6.7 *hbc00049:* Toward Computational Design of Photocatalysts for deNOx Reaction through High-dimensional Reaction Potential Surface

HLRN Project ID:	hbc00049
Run time:	II/2021 – IV /2021
Project Leader:	Prof.Dr. Thomas Frauenheim
Project Scientists:	Pu Guo
Affiliation:	Bremen Center for Computational Materials Science

#### Overview

NOx emission heavily affects our environment and human health. Photo-catalytic denitrification (deNOx) attracted much attention because it is low-cost and nonpolluting, but undesired nitrite and nitrate were produced in reality, instead of harmless N<sub>2</sub>. Unveiling the active sites and the photocatalytic mechanism is very important to improve the process. Herein, we have employed a combinational scenario to investigate the reaction mechanism of  $NO_2$  and  $H_2O$  on anatase TiO<sub>2</sub>(101). On the one hand, a polaron-corrected GGA functional (GGA + Lany-Zunger) was applied to improve the description of electronic states in photoassisted processes. On the other hand, a reaction phase diagram (RPD) was established to understand the (quasi) activity trend over both perfect and defective surfaces. It was found that a perfect surface is more active via the Elev-Rideal mechanism without NO2 adsorption, while the activity on defective surfaces is limited by the sluggish recombinative desorption. A photogenerated hole can weaken the OH\* adsorption energies and circumvents the scaling relation of the dark reaction, eventually enhancing the deNOx activity significantly. The insights gained from our work indicate that tuning the reactivity by illumination-induced localized charge and diverse reaction pathways are two methods for improving adsorption, dissociation, and desorption processes to go beyond the conventional activity volcano plot limit of dark conditions.



**Figure 1**: (a) The complete  $deNO_2$  reaction network with stable intermediates marked and transition states unmarked. (b) The algorithm of determining the pathways from global energy optimization, and (c) the optimal reaction pathway for  $deNO_2$  over the perfect anatase  $TiO_2(101)$  surface (blue,  $NO_2$  evolutional paths; red,  $H_2O$  evolutional paths).



#### Results

In this work, we considered 22 elementarty steps and obtained a total of 529 possible reaction pathways. The established reaction network is as shown in the Figure 1. We could select the optimal reation mechanism from the complex the reaction networks. The calculated adsorption free energies of all intermediates were correlated with two descriptors (G<sub>ad</sub>OH(Ti)\* and  $G_{ad}N(Ti)^*$ ), to reduce the dimensionality in the mechanism analysis.  $G_{ad}OH(Ti)^*$  is the adsorption free energy of OH\* on a Ti atom. The nomenclature is the same here for all intermediates, unless otherwise stated. The scaling relation is consistent with that found in our previous work, where we have also observed the scaling relations of a set of adsorption energies over different active sites for one oxide catalyst.<sup>1</sup> This is reasonable for the surface/ sites with large electronic contributions and small geometric effects. The  $\Delta G_{RPD}$ -limiting steps and energies, which are the reaction-determining steps deduced from the reaction phase diagram (RPD) analysis. The  $\Delta G_{RPD}$ -limiting energies over all active sites were used to determine the (quasi) activity trend and mechanism variation under dark and illuminated conditions. Kinetic barrier calculations were then performed for confirmation. More details of our algorithm were described in our previous work.<sup>2</sup> We have employed an improved scheme to study the mechanisms of photoassisted deNO<sub>2</sub> reactions on the active sites of the anatase TiO2(101) surface. The electronic structures and energies were calculated by using a GGA + LZ functional, which significantly improved the accuracy (comparable to calculations with the hybrid HSE06 functional) while maintaining the efficiency of normal GGA calculations. In addition, a novel algorithm was applied to study all possible reaction pathways and to obtain a global optimization of the limiting energies. It was found that the activity on the perfect surface is higher than on a defective one, because the strong OH\* adsorption inhibits its combination with NO2. We found the photogenerated hole to be more important for the perfect surface in tuning the reactivity. Because the hole is trapped by a reduced Ti on the defective surface, it has no effect on the adsorption energy of OH\* species on the oxygen vacancy. In contrast, the OH\* adsorption energy on a perfect surface can be weakened in the presence of the photogenerated hole, resulting in enhanced OH\* conversion. We have proved the concept that the tunable reactivity in a charge-assisted process and diverse reaction pathways in photocatalysis are two methods that break the conventional scaling relation and the activity volcano plot limit under dark conditions, which is a guite critical insight for the design of photocatalysts.

#### **Publications**

 Guo, P.; Fu, X.; Deák, P.; Frauenheim, T.; Xiao, J. Activity and Mechanism Mapping of Photocatalytic NO<sub>2</sub> Conversion on the Anatase TiO<sub>2</sub> (101) Surface. *J. Phys. Chem. Lett.* **2021**, *12* (32), 7708–7716.

#### References

- (1) Shi, Y.; Ji, Y.; Long, J.; Liang, Y.; Liu, Y.; Yu, Y.; Xiao, J.; Zhang, B. Unveiling Hydrocerussite as an Electrochemically Stable Active Phase for Efficient Carbon Dioxide Electroreduction to Formate. *Nat. Commun.* **2020**, 11, 3415.
- (2) Guo, C.; Fu, X.; Long, J.; Li, H.; Qin, G.; Cao, A.; Jing, H.; Xiao, J. Toward Computational Design of Chemical Reactions with Reaction Phase Diagram. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2021**, 11, e1514.
# 6.8 *hbc00051:* Investigations of Defects and Luminescent Origins in Zinc Sulfide and Doped Zinc Sulfide Materials utilizing Optimized Hybrid Functionals

HLRN Project ID:	hbc00051
Run time:	I/2021 – XII /2021
Project Leader:	Dr. Quoc Duy Ho
Project Scientists:	Dr. Martin Catillo
Affiliation:	ZARM – Bremen Univesity

# Overview

The general work herein aims at understanding and improving the energy efficiency of electroluminescent zinc sulfide (ZnS) doped materials there are 2 parts in our work. In the experimental part, ZnS and ZnS doped materials are synthesized at the Center of Applied Space Technology and Microgravity (Zentrum für angewandte Raumfahrttechnologie und Mikrogravitation, ZARM) drop tower. Unfortunately, characterization of these synthesized materials alone is insufficient in the identification of specific defects and in the explanation of electroluminescent origins in semiconductor materials. It is necessary to perform theoretical part parallel with the characterization of the synthesized materials in order to identify intrinsic and extrinsic defects. The operation of semiconductors-based devices is related to defects. which control electronic and optical behavior. The commonly used approximation, density functional theory (DFT) with local density approximation (LDA) or generalized gradient approximation (GGA) exchange, often fail completely in describing defects in wide band gap semiconductors. In recent years, screened hybrid functionals (like HSE06) have emerged as a useful alternative. This project will deal with the possible refinement, extension and application of the HSE-type functionals for defects in sphalerite and wurtzite ZnS. We look for optimized hybrid functional parameters for zinc blende and wurtzite ZnS materials, we will then study intrinsic and impurities defects charge transition levels, hyperfine interaction, and luminescent origins in ZnS at the aims of explaining origins and improving electroluminescent ZnS-based devices.

## Results

The 320 kNPL for the project hbc00051 was extremely useful to begin calculations and was highly appreciated. With this 320 kNPL have accomplished the optimized HSE-parameters for zinc blende and wurtzite phase of ZnS. The entire band structure calculated from the optimized hybrid functional (Fig. 1a and 1b.) agree very well to the GW results [1,2], and the total energy from a Zn defect vacancy is a linear function of fractional occupation numbers.





Figure 1: Band structure of ZnS in a) the zinc blende phase and b) wurtzite phase

The charge transition levels of intrinsic and extrinsic defects in zinc blende and wurtzite ZnS are studied with the new optimized hybrid functional. By using the new parameters, the origin of UV luminescence in zinc blende phase is also explained for the first time. Our calculated results are in agreement with the experimental results and under preparing for publications.

## Outlook

#### HSE-type functionals for defect calculations ZnS semiconductors.

Like other researchers in the field of defect calculations, we use the supercell model for all defect calculations. We will then apply the same size of supercell, 64 atoms for sphalerite and 128 atoms for wurtzite, which are equal or larger than the supercells that were used in the previous research [3,4]. The next symmetric multiplication, one would use 216 atoms for sphalerite and 300 atoms for wurtzite. It should be significantly noted that we would not take this next step, as this is unnecessary and would drastically lead to over usage of computational time for hybrid functional calculations. In the case of the Coulomb interaction between charged defects that cannot be neglected at any realistic supercell size. Therefore, the artificial interaction of charge defects should be considered by applying a charge correction method. In our calculations, we use the scheme of Freysoldt et al. [19] to compensate the spurious periodic Coulomb interaction of charged defects.

We have begun this work with the optimization of the HSE-type Hybrid Functional for sphalerite ZnS. We ran defects calculations with the obtained optimized hybrid functional, implemented in the VASP package. We have performed the calculations of copper substitutions at the zinc site in sphalerite phase and sulfide vacancy in the wurtzite phase. From these calculations we found that a full self-consistent field (SCF) cycle takes around ~40 steps, a defect geometry optimization usually reaches the convergence conditions after ~50 SCF. This is again a demonstration that this methodology can be performed without over consuming wasteful amounts of computational time.

#### Identification of defects in ZnS for determination the electrical activity

The UV luminescent center in zinc blende phase is identified by using the new parameters of hybrid functional, in the next step, we will study other defects in different conditions (temperature, carrier concentration, doping etc.) to identify other luminescent centers in both zinc blende and wurtzite.

Copper, aluminum, and chlorine are often observed in ZnS as dopants and/or unintentional impurities [5-7]. In theoretical research, recently, a number of reports about intrinsic and extrinsic defects have been published, but information about the defects in ZnS are still very limited or missing. For example, the origin of luminescence of Cu-doped sample at around



2.76 eV is often assigned to Cu at Zn site [8,9]. However, other studies show that an intrinsic defect or a complex one can be the source of that radiation [5,10]. That has shown the complication of a luminescent origin identification procedure. To identify a source of luminescence, a stable defect should be identified at a specific Fermi-level, but in semiconductor, there can be multiple defects, (intrinsic extrinsic and complex) can be present at a fermi-level. Thus, many possible defects should be studied to find out the origin of luminescence. The procedure has been shown in a previous report of Quoc Duy Ho et al. [11]. In the first round, Zn, S vacancies, Znvac + Svac complex vacancy, Zn, S interstitial, Zn at S site, and S at Zn will be studied. In the next round, we will consider extrinsic defects us a Mn, Pr (for wurtzite), Er, Eu, Al, Fe, Cl, O, C, H, as well as the complex of defects. In each case, the equilibrium geometry of defect must be found in all possible charge states. The relative charge transition levels of defect will be calculated and compared to the experimental results.

#### Identification paramagnetic resonance (EPR) centers

This step is very important in our project, the calculated results can be compared directly with the experimental results. The success of optimized hybrid functional is shown exactly here, because hyperfine interaction is very sensitive to the localization of defect and the defect distance to neighbors, the calculated results from an optimized HSE for  $\beta$ -Ga2O3 has shown very good agreement to experimental results [12,13]. The hyperfine tensor that describes the interactions between a nuclear spin and the electronic spin distribution consists of the isotropic Fermi-contact and anisotropic dipolar term. The Fermi-contact requires calculating the spin density at the nuclear sites that carry a nuclear spin. This interaction occurs when the electron is inside the nucleus, where electrons in the s orbital exhibit this kind of interaction. After a paramagnetic defect state had been relaxed, the hyperfine tensor will be calculated with the electron spin density from the previous calculation.

#### Publications

We are preparing a paper which we will submit to Physical review B journal.

#### References

- (1) P. Rinke.; A. Qteish.; J. Neugebauer.; C. Freysoldt, and M. Scheffler, New Journal of Physics 7, 126 (2005).
- (2) O. Zakharov.; A. Rubio.; X. Blasé.; M. L. Cohen and S. G. Louie, Physical Review B 50, 10780 (1994).
- (3) K. Hoang.; C. Latouche and S. Jobic, Computational Materials Science 163, 63 (2019).
- (4) J. B. Varley and V. Lordi.; Applied Physics Letters 103, 102103 (2013).
- (5) C. Corrado.; Y. Jiang.; F. Oba.; M. Kozina.; F. Bridges and J. Z. Zhang, The Journal of Physical Chemistry A 113, 3830 (2009).
- (6) S. Sambasivam.; B. Sathyaseelan.; D. Raja Reddy.; B. K. Reddy and C. K. Jayasankar, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 71, 1503 (2008).
- (7) A. A. Bol.; J. Ferwerda.; J. A. Bergwerff and A. Meijerink, Journal of Luminescence 99, 325 (2002).
- (8) S. Ummartyotin.; N. Bunnak.; J. Juntaro.; M. Sain and H. Manuspiya, Solid State Sciences 14, 299 (2012).
- (9) S. J. Xu.; S. J. Chua.; B. Liu.; L. M. Gan.; C. H. Chew and G. Q. Xu, Applied Physics Letters 73, 478 (1998).
- (10) J. Dong.; X. Zeng.; W. Xia.; X. Zhang.; M. Zhou and C. Wang, RSC Advances 7, 20874 (2017).
- (11) Q. D. Ho, T. Frauenheim and P. Deák, Physical Review B 97, 115163 (2018).
- (12) N. T. Son.; Q. D. Ho.; K. Goto.; H. Abe.; T. Ohshima.; B. Monemar.; Y. Kumagai., T. Frauenheim and P. Deák, Applied Physics Letters 117, 032101 (2020).
- (13) Q. D. Ho.; T. Frauenheim and P. Deák, Journal of Applied Physics 124, 145702 (2018).



# 6.9 *hbc00053:* A solid theory for solid battery materials: Calculation of self-consistent DFT+U+V Hubbard parameters and their application for electrochemical purposes

HLRN Project ID:	hbc00053
Run time:	III/2021 – II/2022
Project Leader:	Prof. Dr. Lucio Colombi Ciacchi
Project Scientists:	M.Sc. Eric Macke, M.Sc. Lorenzo Bastonero
Affiliation:	Hybrid Materials Interfaces Group, Faculty of Production Engineering and Bremen Center of Computational Materials Science, University of Bremen

## Overview

On the quest for novel, efficient, safe and inexpensive battery materials, a reliable yet affordable computational technique with the ability to predict and understand electrochemical properties from first principles is indispensable. Various members of the diverse family of Prussian Blue Analogues (PBAs) for example, have shown to be attractive candidates for grid energy storage solutions, but the knowledge about mechanisms such as cation diffusion in these materials remained very limited.

At least partly, this lack of theoretical studies is owing to an inherent deficiency of Density Functional Theory (DFT), which represents the traditional "workhorse" for routine calculations on the quantum mechanical level. In spite of being a powerful and often sufficiently accurate method, DFT fails to capture the electronic structure of strongly correlated materials and precludes it from being used to compute PBAs. However, many electronic features of strongly correlated materials can be restored in DFT by using so-called on-site and inter-site Hubbard corrections to DFT (DFT+U and DFT+U+V, respectively) [1]. They represent computationally lightweight alternatives to more exact but also far more expensive techniques such as coupled cluster approaches and hybrid DFT. However, in order to achieve quantitative accuracy with Hubbard corrections, it is imperative that a consistent and physically justified method is employed from which U and V parameters can be derived [2].

HLRN project hbc00053 was therefore proposed to derive self-consistent Hubbard U and V parameters for a variety of Prussian Blue Analogues solely from first-principle calculations. In a second step, it was planned to benchmark those Hubbard corrected DFT simulations against the computationally more demanding hybrid DFT approach with respect to observables including intercalation potentials, lattice parameters and electronic structures.

While the calculation of Hubbard U and V parameters for Prussian Blue Analogues using density functional perturbation theory (DFPT) succeeded, it became apparent that traditional Hubbard corrections alone could do not suffice to obtain neither correct intercalation potentials nor realistic electronic structures for some of the compounds. In an attempt to get to the bottom of the theoretical failure, the purpose of hbc00053 was shifted from a production-oriented to a more method-oriented approach.

Since the development of new methods typically consumes less computational resources than pure production runs, we decided to repurpose a part of the allocations for the calculation of absorption spectra using the same method of self-consistently obtained *ab initio* Hubbard parameters in combination with the finite differences approach. This was possible because the



minerals investigated in this study did not suffer from the same theoretical failure that impeded the successful work on Prussian Blue Analogues.

## Results

By carrying out DFPT calculations using QuantumEspresso's *hp.x* binary, on-site Hubbard U and inter-site Hubbard V parameters were established and brought to self-consistency in a multi-step procedure. In principle, Hubbard parameters are obtained from perturbation theory, which are then employed to (re-)relax the ionic structures of the material using DFT+U+V. This is repeated until both the self-consistent Hubbard parameters and the material's ionic structure stop changing by more than a predefined threshold.

It was the author's hope that this procedure, being conceptually straightforward, would finally deliver a rational set of Hubbard parameters that allows for good estimates of important material properties such as the lattice parameters or the intercalation potential. In fact, during the investigation we have observed that this assumption does not hold true and worse, that Prussian Blue Analogues in general are erroneously described by traditional DFT+Hubbard methods, even when the more elaborate inter-site V terms are applied.

Figure 1 exhibits one the most pronounced failures, here shown for the compound Fe[Fe(CN)<sub>6</sub>] (Berlin Green). The projected density of states shows a significant discrepancy between the DFT+U+V ground state and the more correct hybrid DFT ground state (HSEsol06 exchange correlation functional). In the DFT+U+V ground state, Berlin Green is a semi-metal, but it is known to be an insulator. Furthermore, it is not expected that carbon and nitrogen states dominate the highest occupied molecular orbital (HOMO). The erroneous DFT+U+V ground



state then manifests in overestimated lattice parameters (for Berlin Green, DFT+U+V yields 10.35Å compared to exp. 10.20Å) as well as strongly underestimated intercalation potentials.

After a long process of analysis and literature research, the fundamental flaw of Hubbard corrected DFT applied to PBAs was tracked down to the presence of strong ligand fields, induced by the C≡N linkers that connect the transition metal centres in the crystal. Strong ligand fields push electron density from their occupied σ-orbitals into the unoccupied  $e_{\alpha}$  orbitals of the transition metal centre. However, this electron density, correctly predicted by density functional theory, will inevitably lead to an increase in d-orbital occupation numbers.

**Figure 1:** Projected density of states (PDOS) for the PBA  $Fe[Fe(CN)_6]$ , calculated with a hybrid XC-functional (top) and the PBEsol+U+V method (bottom). Note the drastic dissimilarity below the HOMO level at 0 eV.



The conflict arises when this occupation number *n* reaches a value  $\approx 0.5$ , because then the Hubbard energy term

$$E_U = \sum_{\sigma, I} \frac{U^I}{2} \mathrm{Tr}[n^{I\sigma}(1 - n^{I\sigma})]$$

is maximized. We emphasize that Hubbard corrections can be understood as a means of counteracting the self-interaction error in DFT which ultimately leads to an unphysical delocalization, particularly of d-shell electrons. However, we argue that if the occupation of a magnetic (spin-) orbital is dominated by the effect of hybridization with a ligand, Hubbard corrections should **not** be applied in the same way as for unaffected orbitals.

To account for such inhomogeneous bonding regimes, we propose a more flexible scheme that enables the use of distinct Hubbard parameters U(m) for the different magnetic orbitals m that belong to the same species, computable by means of the same *ab initio* methods as "traditional" Hubbard parameters.

#### Conclusion on hbc00053 and Outlook

Despite the unexpected outcome of this HLRN project, a new perspective on an established theory paved the way for future improvements in the field of DFT simulations of strongly correlated materials. We are currently working on an efficient implementation of the proposed DFT+U(m) method for QuantumEspresso. The extensive resources provided by the HLRN facility will continue to play a crucial role in this project, especially when parameters for the new method need to be computed from first principles or when further benchmark calculations with expensive hybrid exchange correlation functionals are required.

#### Allocations repurposed for the calculation of absorbtion spectra

L. Bastonero has used the allocations to compute Raman and infra-red spectra of the olivine solid solution series ( $M_2SiO_4$ , M=Mg,Fe,Mn), one of the most common minerals on rocky planets.

Theoretical investigation of Raman spectra of the more complex transition metal endmembers had never been attempted. The reason being, as in the case of PBAs, that the electronic structure is badly described by pure local and semi-local functionals. Theoretical prediction of vibrational spectra is computationally demanding, since the prediction of the intensities and the peak positions requires the evaluation of high order derivatives of the total energy with respect to atomic displacements and electric fields.

To contain the computational cost, but especially to make these simulations feasible, selfconsistent Hubbard corrections were the method of choice in this project, too. Nevertheless, current DFT codes based on plane waves basis sets allows the evaluation of the needed derivatives through efficient perturbation techniques only for local functionals.

Therefore, we developed a powerful workflow in the AiiDA framework [3] capable of evaluating the needed derivatives through finite differences techniques, thus allowing for the use of any functional for the prediction of these spectra in the simulation. The workflow efficiently parallelizes the calculations over multiple runs, each containing a finite displacement or field, thus exploiting the massive number of nodes of the HLRN facilities.

Comparing the results of the simulated optimized structures with experimental and simulated values from the literature, it was observed that the use of PBEsol and Hubbard corrections for transition metals provides the best agreement with experiments, even outperforming costly hybrid functional calculations. The Raman spectra have been computed for forsterite, the magnesium endmember of the olivines. We reported the results in Fig. 2, where we compare the measurements with experiments.





**Figure 2:** Comparison of Raman spectra of Forsterite (Mg<sub>2</sub>SiO<sub>4</sub>) computed from DFT using LDA and PBEsol with the experimental measument on a powder sample. The (\*) indicates that the susceptibility derivatives of LDA have been taken from the PBEsol ones.

#### Literature

- [1] V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein. First-principles calculations of the electronic structure and spectra of strongly correlated systems: the LDA+U method. Journal of Physics: Condensed Matter, 9(4):767–808, 1 1997
- [2] Iurii Timrov, Nicola Marzari, and Matteo Cococcioni. Hubbard parameters from densityfunctional perturbation theory. Physical Review B, 98(8):085127, August 2018.
- [3] Giovanni Pizzi, Andrea Cepellotti, Riccardo Sabatini, Nicola Marzari, and Boris Kozinsky. AiiDA: automated interactive infrastructure and database for computational science. Computational Materials Science, 111:218 – 230, 2016



# 6.10 *hbc00056:* Towards an atomic-level understanding of the interaction of probe molecules with acid sites in zeolites

HLRN Project ID:	hbc00056
Run time:	III/2021 – II/2022
Project Leader:	Dr. Michael Fischer
Project Scientists:	Dr. Michael Fischer, Carlos Bornes
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# Overview

The adsorption of probe molecules like ammonia, pyridine, or trimethylphosphine oxide is a common technique to characterize protonated zeolites, which are important solid acid catalysts. However, recent work has shown that the interpretation of experimental results is less straightforward than commonly assumed because more than one probe molecule can interact with a single acid site. In this project, electronic structure calculations in the framework of density functional theory (DFT) and DFT-based molecular dynamics simulations are performed to shed light on the interaction between protonated zeolites and probe molecules. The calculations are carried out in close collaboration with experimental partners, who employ advanced nuclear magnetic resonance (NMR) experiments to investigate these systems.

## Scientific background

Zeolites are inorganic tetrahedral frameworks exhibiting an intrinsic porosity. In addition to applications in ion exchange and separation, they are used as solid acid catalysts in several industrial processes, where they constitute a safer alternative to harmful and corrosive liquid catalysts.[1,2] The economically most significant application is the fluid catalytic cracking of heavy hydrocarbons into lighter fractions, a key step in the production of fuels and feedstocks from crude oil. Highly siliceous zeolites, which are the most important zeolite catalysts, contain relatively small amounts of tetrahedrally coordinated aluminium atoms, the remainder of the tetrahedral sites being occupied by silicon. The negative charge of the framework is balanced through protons, which are bonded to one of the oxygen atoms of the  $AIO_4$  tetrahedra. The overall catalytic activity of these zeolites strongly depends on the location, amount, and acid strength of the framework protons, which act as Brønsted acid sites. For that reason, a comprehensive characterization of the acid site properties is pivotal to develop increasingly active and selective catalysts.[3,4] Probe molecules, such as ammonia, pyridine, and trimethylphosphine oxide (TMPO), have been widely used to study the acid properties of zeolites, as they can provide information about acid-base interaction and accessibility of the acid sites. Studies employing probe molecules typically identified several vibration modes (in vibrational spectroscopy) or distinct chemical shifts (in NMR spectroscopy), which are commonly assigned to probe molecules interacting with Brønsted acid sites having different acid strength.[3,4] However, computational studies have shown consistently that the deprotonation energy of zeolites, often considered as the "true" measure of acid strength, is homogeneous and largely independent of the acid site location and the zeolite framework.[5,6]



This project aims to enhance the atomic-level understanding of the interaction of protonated zeolites with the commonly used probe molecules ammonia, pyridine, and TMPO through DFT calculations. In order to study the impact of the local environment on the interaction strength, two zeolites with channels of different size are included in the investigation (**Figure 1**), and different positions of framework AI atoms and charge-balancing protons are considered for each of them. In addition to DFT structure optimizations, which deliver local energy minima and adsorption energies in the absence of any thermal motion, DFT-based *ab initio* molecular dynamics (AIMD) simulations are performed to include temperature effects, which are of importance in any real-world application. The calculations are performed in close conjunction with advanced NMR experiments, which are carried out by the collaboration partners at **CICECO**, **Aveiro Institute of Materials**, **Portugal** (Carlos Bornes, Dr. Luís Mafra, Prof. Dr. João Rocha). Funding of the project scientists is provided through a DFG Heisenberg grant to Dr. Michael Fischer (Deutsche Forschungsgemeinschaft project no. 455871835, Fi1800/6-1), and through a PhD scholarship from the Portuguese Fundação para a Ciência e Tecnologia (FCT) to Carlos Bornes (ref. PD/BD/142849/2018).



**Figure 1:** Zeolites and probe molecules considered in this investigation. **Top:** MFI-type ZSM-5 contains a two-dimensional system of channels formed by ten-membered rings of TO<sub>4</sub> tetrahedra (10MRs), mordenite contains a one-dimensional system of 12MR channels. Yellow = silicon, turquoise = aluminium, red = oxygen, white = hydrogen. Positions of the framework protons are emphasized by arrows. **Bottom:** Probe molecules. Blue = nitrogen, grey = carbon, purple = phosphorus. Note that probe molecules are not shown on the same scale as the zeolite crystal structures.

## Preliminary investigation and first project results

In a preliminary investigation, the results of <sup>1</sup>H-<sup>31</sup>P heteronuclear correlation NMR experiments on TMPO-loaded ZSM-5, performed at CICECO Aveiro, were complemented by a computational prediction of NMR shifts.**[P1]** The structures that were taken as starting point for these NMR shift calculations had been obtained from DFT structure optimizations and, in some instances, AIMD simulations that were carried out using the HLRN facilities. The analysis showed that higher-order complexes, *i.e.*, complexes involving more than one probe molecule per acid site, can form in ZSM-5 upon adsorption of moderate amounts of TMPO, because only the presence of 2:1 complexes (dimers) can explain the U-shaped correlation peak



observed experimentally (**Figure 2**). The formation of such dimers means that any quantification of acid sites based on probe molecule adsorption that does not take the extent of dimerization into account will inevitably lead to an overestimation of the amount of acid sites. On the basis of these findings, it was concluded that the use of NMR experiments on TMPO-loaded zeolites to measure Brønsted acidity has limitations and may result in erroneous conclusions. Although there are some previous works suggesting the formation of high-order complexes in ammonia- and pyridine-loaded zeolites,[7,8] the large majority of studies have ignored the possible occurrence of such species. Moreover, little is known about the mechanism of dimer (or trimer, tetramer...) formation, and about the dynamic behavior of the species that form in the vicinity of the acid site.



**Figure 2**: <sup>1</sup>H-<sup>31</sup>P heteronuclear correlation NMR spectrum of a ZSM-5 sample loaded with approximately 0.75 TMPO molecules per acid site. Whereas <sup>31</sup>P resonances above ~63 ppm (orange line) can be explained as being due to 1:1 complexes (one TMPO per acid site), those below this value are indicative for the formation of 2:1 complexes. As a consequence, these resonances are absent at low TMPO loadings (see **[P1]**).

As the project aims at a systematic study of two different zeolites (**Figure 1**), considering different AI and proton locations for each of them, the initial calculations focussed on the bare zeolites. In addition to DFT structure optimizations, AIMD simulations for temperatures of 25 °C and 500 °C were run in order to assess whether any structural rearrangements occur under relevant conditions. Ongoing calculations are now addressing 1:1 adsorption complexes of ammonia, pyridine, and TMPO in these systems. As an abstraction of the framework proton will occur upon interaction with these strong bases, AIMD simulations for temperatures of 25 °C and 150 °C (a typical temperature of adsorption experiments) are being performed to investigate whether the probe molecules remain confined to the direct proximity of the framework AI atoms, or whether an appreciable diffusion through the channels may occur. Due to the sensitivity of the NMR chemical shifts to the local environment, such a motion away from the framework AI atoms should result in measurable changes in the NMR spectra.

## Outlook

After finishing the calculations for 1:1 adsorption complexes, the relevant NMR shifts will be predicted computationally, and compared to experimental results. Further work will then address the formation of 2:1 adsorption complexes of ammonia, pyridine, and TMPO in the



channels of ZSM-5 and mordenite (the channels of both zeolites are spacious enough to allow for a formation of dimers), considering zeolite models with a low amount of acid sites as shown in **Figure 1**. In the final part, the role of the concentration of acid sites will be evaluated, studying zeolites with two acid sites in relatively close proximity. For such systems, a competition between the formation of two separate 1:1 complexes at both sites and a formation of a single 2:1 complex can be expected, and it will be evaluated which of these scenarios will dominate.

#### **Project-related publications**

Results from preparatory calculations carried out prior to submission of the project proposal were included in the following publication:

**P1** C. Bornes, M. Fischer, J. A. Amelse, C. F. G. C. Geraldes, J. Rocha, L. Mafra, *What Is Being Measured with P-Bearing NMR Probe Molecules Adsorbed on Zeolites?*, J. Am. Chem. Soc. 143, 13616–13623 (2021)

#### **Project-related presentations**

**P2** C. Bornes, *Atomic-level description of* <sup>31</sup>*P-bearing NMR probe molecules adsorbed on zeolites,* talk at the Portuguese National Meeting on Catalysis and Porous Materials (online), December 2021

#### References

- [1] G. Busca, Chem. Rev. 107, 5366–5410 (2007)
- [2] A. Primo, H. Garcia, Chem. Soc Rev. 43, 7548-7561 (2014)
- [3] L. E. Sandoval-Diaz, J. A. González-Amaya, C. A. Trujillo, Microporous Mesoporous Mater. 215, 229–243 (2015)
- [4] G. Busca, Microporous Mesoporous Mater. 254, 3-16 (2017)
- [5] A. J. Jones, E. Iglesia, ACS Catal. 5, 5741-5755 (2015)
- [6] P. Deshlara, E. Iglesia, Chem. Commun. 56, 7371–7398 (2020)
- [7] F. Lonyi, J. Valyon, Microporous Mesoporous Mater. 47, 293–301 (2000)
- [8] F. Jin, Y. Li, Catal. Today 145, 101-107 (2009)



# 6.11 *hbc00057:* Towards a molecular description of the conformational ensemble of miRNA

HLRN Project ID:	hbc00057
Run time:	III/2021 – II/2022
Project Leader:	Dr. Massimo Delle Piane
Project Scientists:	Dr. Monika Michaelis, Prof. Lucio Colombi Ciacchi
Affiliation:	Bremen Centre for Computational Materials Science (BCCMS) and Hybrid Materials Interfaces (HMI) group, Faculty of Production Engineering, University of Bremen

#### **Overview**

Errors in cell signaling, which cause an uncontrolled cell proliferation, can develop from misexpressions or dysfunctions of microRNA (miRNA). MicroRNAs are small endogenous RNAs, approximately 22 nucleotides in length, which regulate eukaryotic gene expression on the post-transcriptional level. They work as a guidance for mRNA, to prevent it from expressing the wrong proteins. Gene therapy is a kind of targeted therapy, that uses genetic material to modify the signaling pathways and thereby the gene expression within cells. The introduction of miRNAs into human cells could provide an efficacious therapeutic approach to inhibit tumour progression. The delivery of miRNAs has been tested with functionalized gold nanoparticles, combined with either the stem-loop or hairpin structure of a miRNA. More recently chitosan-miRNA (CS-miRNA) complexes have been proposed as delivery systems, and their structure-function relationship has been investigated.

MicroRNA 145 is known to be dysregulated in endometriosis. Delivered to the cells, it has been found to inhibit breast cancer and endometriotic cell invasiveness, marking this reagent as a potential candidate for novel antimetastatic therapeutic applications. To this purpose, the cell-relevant part of this miRNA is considered for delivery. One strand (hsa-miR-145-5p) is the one having medical effectiveness. To increase stability, it is delivered together with its stabilizing partner (hsa-miR-145-3p), forming a duplex. Determining the stability and structure of both the individual components and their duplex is therefore of paramount importance to advance the therapeutic applications of this miRNA.

The structure of RNA plays a crucial role for its functionality in biological systems as well as for the functionality of the cell-relevant components. Among solution-based methods, electronic Circular Dichroism (CD) spectroscopy is widely used for identifying and quantifying the secondary structures of solvated biomolecules, including nucleic acids. Interpretation is however not straightforward due to a lack of atomistic information on the conformational origin of the specific signals. Molecular dynamics (MD) simulations in principle provide a powerful tool to access RNA dynamics at virtually unlimited space and time resolution, and can be performed in an environment very similar to that used in CD. However, their result is often not satisfactory mostly due to the short accessible time-scales and the inaccuracy of the employed force fields. The former issue can be tackled using enhanced sampling methods.

In this project, due to its importance for the functionality of cancer treatment, hsa-miR-145, and its components will be analyzed in greater depth combining our Circular Dichroism spectroscopy experiments with enhanced sampling MD. The calculations of CD spectra from simulated ensembles, will be used to gain novel understanding on the origin of the spectral changes with increasing temperature for miRNA.



Particularly, the general question we aim at answering during the proposed project is: What is the undelaying conformational variability of miRNAs structures and how does it impact the structural/CD spectra relationship?

# Results

Starting from secondary-structure information available in the miRBase databank, we used the make-na web server to obtain an associated 3D model of the cell-relevant duplex of miRNA-145 and the Rosetta Online Server for the structural prediction of the individual 3p and 5p strands. We characterized these predicted models, by employing temperature ramping simulations, ranging from 300K to 700K, to characterize the thermal stability (Figure 1). We followed the denaturation, by following structural parameters, such as the number of base-base hydrogen bonds and the distribution of the backbone characteristic angles. The melting pattern of nucleic acids, and the corresponding characteristic melting temperature Tm, can give important information on their conformation and stability, and key features or properties of their folding landscape. Based on these results, we calculated the CD spectra with DichroCalc and compared the simulated CD spectra to our experimental data of melting. This acted both as validation of the model and as an atomistic understanding of the measured spectra.



**Figure 3**: Simulation of the denaturation of the cell relevant component of miRNA-145 from 300 to 700 K. (top, left) Simulated CD spectra at different temperatures. (top, right) Variation with temperature of the CD intensity at 260 nm. (bottom, left) Variation with temperature of the number of inter-strand hydrogen bonds. (bottom, right) Correlation between CD intensity at 260 nm and number of inter-strand hydrogen bonds.

As a subsequent step, we probed the conformational landscape of hydrogen-bonded duplex resulting from the hybridization of the cell-relevant parts of miRNA 145, hsa-miR-145-5p and hsa-miR-145-3p. We used Replica Exchange with Solute Tempering (REST2) simulations to allow a sampling of the conformational phase space. With this approach, we did not explicitly bias specific conformational degrees of freedom, to gain a sampling as complete as possible with respect to structure. Aware that the size of the investigated strands is well above the current state of the art in RNA folding simulations, and that convergence could not be achieved also with the simulation length made available by HLRN, these costly enhanced sampling simulations still provided a never before achieved qualitative overview of the conformational



variability of these molecules. We studied structural variability by following metrics, such as base-base hydrogen bonds, RMSD, *c*RMSD24, backbone torsional and pseudotorsional angles (Figure 2).



**Figure 2**: REST2 simulation of the conformational phase space of the miRNA 145 duplex (a) Temperature position of each replica as the REST simulation progresses. (b) Number of inter-strand hydrogen bonds across the temperature replicas, showing a denaturation pattern.

## Outlook

We will calculate the CD spectra with DichroCalc on all structures in the simulated ensemble and compare the simulated CD results to our experimental CD spectra. By doing this we will be able to determine how the structural variability impacts the spectral variability and we will use this comparison to pinpoint the most probable conformations of the single strands in solution. Finally, we will also probe the conformational landscape of the cell-relevant parts of miRNA 145, namely hsa-miR-145-5p.

We believe that the obtained results, although obtained for a selected miRNA duplex and its single strands, will be of general interest within the larger cancer research and drug delivery communities, adding atomistic understanding to experimental results. This will provide essential information for the progress of miRNA-based therapeutics from laboratory research to further stages in pharmaceutical design and production.



# 6.12 *hbi00036:* Fluiddynamische Untersuchung der Stressbeanspruchungen proteinstabilisierter o/w-Phasengrenzflächen beim Premix-Membranemulgieren

HLRN-Projektkennung:	hbi00036
Laufzeit:	III/2021 – II/2022
Projektleiter:	Prof. Dr. Udo Fritsching
Projektbearbeiter.	A. Kyrloglou, P. Giefer
Institut / Einrichtung:	Fachgebiet Mechanische Verfahrenstechnik Universität Bremen

# Überblick

In der Verfahrens- und Prozesstechnik finden Dispersionen, also flüssig / flüssig Systeme eine breite Anwendung. In der Prozessierung von Lebensmitteln, sowie pharmazeutischen Anwendungen, spielen Emulsionen entscheidene eine Rolle. Das Premix-Membranemulgieren ist ein Verfahren, bei dem grobdisperse Voremulsionen mittels Dispergierung durch eine poröse Membran, in eine Feinemulsion bzw. Dispersion überführt werden. Ein Schlüsselparameter der Emulsionsqualität ist die Tropfengrößenverteilung, die maßgeblich durch das Stress-Verweilzeitverhalten beeinflusst wird. Bei der Einbindung von schersensitiven Medien, in diesem Fall Proteinen, ist die genaue Charakterisierung von besonderer Relevanz und bedarf wissenschaftlicher Klärung. Daraus können mechanistische Schädigungsmodelle abgeleitet werden.

Um einen genauen Einblick in das Aufbruchphänomen zu bekommen, konzentriert sich das Forschungsvorhaben auf die Beschreibung der mehrphasigen Strömung in porösen und idealisierten Strukturen. Um die Scher- und Dehnkräfte an den Phasengrenzflächen analysieren zu können, wurde ein Modell entwickelt und in die Open Source Software OpenFOAM implementiert. Da die, im Prozess eingebundenen Proteine an den Phasengrenzen adsorbieren, ist dies von besonderem Interesse. Ziel des Projektes ist es, die Kriterien für die Tropfendeformation und den Tropfenaufbruch anhand dieser Belastungen zu quantifizieren.

## Ergebnisse

## Tropfendruckverlust in idealisierte poröse Systeme

Ein anderer Teil der Arbeit in der letzten Förderperiode war die Analyse des Druckverlusts eines Tropfens beim Poren Eintritt. Abbildung 2 unten zeigt den Tropfen in der Simulation mit einem charakteristischen Druckprofil, das qualitativ gut mit der analytischen Lösung übereinstimmt (Zhang et al., 2018). Das Druckprofil zeigt sechs lineare Abschnitte. Am Anfang bleibt der Druck im Eingangsbereich konstant. Genau an der Grenzfläche steigt der Druck und bleibt noch mal fast konstant über den Tropfenradius. Ein geringer Druckverlust innerhalb des Tropfens ist sichtbar, in dem Bereich des Eintritts in die Pore. An der anderen Grenzfläche sinkt der Druck noch mal bis nahe des Auslassdrucks.





**Abbildung 1**: Tropfen in idealisierter poröser Struktur mit parallelen Kanälen. Der weiße Strich von 0 bis 0.007 m zeigt das Druckprofil in Abbildung 2.



**Abbildung 2:** Tropfendruckverlust beim Poren Eintritt bei drei verschiedenen Eingangsgeschwindigkeiten (0.3 m/s bis 0.5 m/s).

#### Tropfenaufbruch in komplexen Membranstrukturen

Die Ergebnisse wurden im Detail in (Wollborn et al., 2019) veröffentlicht. Neben den Ergebnissen zu Modellstrukturen wurden auch Simulationen in komplexen Geometrien durchgeführt. Diese zeigen den Tropfenaufbruch in einer Membran. Weiterführende Simulationen zur genauen Auswertung und Einordnung der Ergebnisse sind nötig wie z.B. in der Abbildung 3 (Wollborn et al., 2021).





**Abbildung 3:** Visualisierung der Tropfendispersion bei unterschiedlichen Kapillarzahlen (Ca, A-D) bei ähnlichem Dispersionsfortschritt. Die Färbung des Tropfens zeigt die Grenzflächen-Schubspannung in einer logarithmischen Skala an. (Wollborn et al., 2021).

#### Validierung des Viskolastischen Solvers

Zur Untersuchung komplexer mehrphasiger Fluide wurde ein zweiphasiger viskoleastischer Solver entwickelt. Dieser Solver basiert auf viscoelasticFluidFoam in OpenFoamExt 4.1 und interFoam von OpenFoam 6 und 7, der neue viscoInterFoam Solver wird auch zur Quantifizierung und Untersuchung der Scherspannung auf die Flüssig-Flüssig und Flüssig-Wand Grenzflächen eingesetzt. In der letzten Förderperiode wurde dieser Solver validiert.

In Abbildung 4 sieht man ein Simulationsergebnis des Weisenberg Effekts zur Validierung des Solvers. In dieser Simulation eines viskoleastischen Polymers steigt die Flüssigkeit an einem rotierenden Stab.



Abbildung 4: Weissenberg-Effekt Simulation zur Validierung des viskoelastischen Solvers.





**Abbildung 5:** Validierungsgrafik im Vergleich mit veröffentlichten Daten. h/R ist die Steighöhe des Polymers.

## Ausblick

In der neuen Förderperiode wird das Projekt in insgesamt vier Abschnitte gegliedert. Im ersten Arbeitspaket wird die Modellvalidierung der Kontaktwinkelmodelle durch die idealisierten Geometrien behandelt in Verbindung mit dem viskoelastischen Solver. Im zweiten Teil werden idealisierte poröse Strukturen berechnet. Im letzten Abschnitt werden reale Strukturen mittels CTs sowie zufällig generierte Kugelschüttungen betrachtet. Es erfolgt auch hier die Variation von Kontaktwinkel, Kapillarzahl und anderen Stoff- und Prozess-parametern.

## Publikationen

- 1. Wollborn, T., Luhede, L., & Fritsching, U. (2019). *Evaluating interfacial shear and strain stress during droplet deformation in micro-pores*. Physics of Fluids, 31(1), 012109.
- 2. Wollborn, T., et al. (2021) Investigation of local and temporal interfacial shear stress distribution during membrane emulsification. Can. J. Chem. Eng.

## Vorträge / Poster

1. Kyrloglou A., Poster ProcessNet MPH 2022, Web Conference



# 6.13 *hbi00037:* Molekulardynamische Untersuchung der Stressbeanspruchungen auf Proteine an der Phasengrenzfläche beim Premix-Membranemulgieren

HLRN-Projektkennung:	hbi00037
Laufzeit:	II/2019 – I/2023
Projektleiter:	Prof. Dr. U. Fritsching
Projektbearbeiter.	P. Giefer
Institut / Einrichtung:	Fachgebiet Mechanische Verfahrenstechnik, Universität Bremen

# Überblick

Emulsionen finden eine große industrielle Anwendung in der Lebensmittel-, Kosmetik- und Pharmazeutischen Industrie. Dabei werden unter anderem biologische Systeme zum Stabilisieren der Emulsionen eingesetzt. Bei der Prozessierung, wie zum Beispiel der Homogenisierung von Emulsionen werden grobdisperse Voremulsionen mittels Druckgradienten durch poröse Membranen in Feinemulsionen überführt. Der einwirkende Scherstress bedingt die Fragmentierung des dispersen Mediums innerhalb der Membranen. Dieser Stress wirkt auf die Phasengrenzfläche und folglich auch auf die adsorbierten, stabilisierenden biologischen Systeme. Insbesondere das Stress-Verweilzeitverhalten ist dabei von besonderer Bedeutung und bedarf vertiefter wissenschaftlicher Klärung. Daraus können mechanistische Schädigungsmodelle abgeleitet werden.

Um den Einfluss des Premix-Emulgierverfahrens und den dabei auftretenden Stress-Verweilzeit-Belastungen auf die Proteine an den Phasengrenzflächen zu untersuchen, werden molekulardynamische Simulationen durchgeführt. Dabei soll gezeigt werden, wie Proteinstrukturen an Phasengrenzflächen adsorbieren, sich durch Adsorption aktivieren und schlussendlich geschädigt werden. Aus dieser Erkenntnis können Emulgierverfahren entwickelt werden, die besonders schonend sind.

Zielsetzung des vorhergegangenen Projektzeitraumes war die Untersuchung von rekombinanten Beta Lactoglobulin und die Untersuchung von Lipase, einem Enzym welches sich an Grenzflächen aktiviert. Im Fall der Lipase wurde das Enzym an Öl/Wasser Grenzflächen und Wasser/SIO2 Grenzflächen betrachtet. Diese umfangreichen Simulationen konnten nur unter Bereitstellung von Rechenkapazität durch den HLRN realisiert werden.

Eine Betrachtung von Lipase erweitert das Bild der molekulardynamischen Betrachtung stresssensitiver Proteine an Grenzflächen, da mit der Lipase ein komplexeres Protein eingeführt wird. Das Besondere ist, dass Lipasen durch die Adsorption an Grenzflächen im Zuge struktureller Änderungen aktiviert werden. Dazu verfügen Lipasen über eine Lid Struktur, welche im Zuge der Aktivierung das katalytische Zentrum frei legen. Dies ermöglicht es, experimentell Schädigungsmechanismen und den eventuellen Aktivitätsverlust auf bereits adsorbierte Proteine zurückzuführen. Ziel war es, Lipase an Öl/Wasser und SIO2/Wasser Grenzflächen zu modellieren und Adsorptionskonfigurationen zu analysieren.

## Ergebnisse

Abbildung 1 ist zu entnehmen, dass sich die Adsoptionskonfiguration an festen und flüssigen hydrophoben Grenzflächen maßgeblich unterscheiden. Zu verdeutlichen ist dies, an der



a)

Position und Orientierung der in lila hervorgehobenen Lid Residuen. Im Falle der Adsorption an einer Öl/Wasser Grenzfläche orientiert sich das Enzym mit dem Eingang zum katalytischen Zentrum zur Grenzfläche, was eine mögliche katalytische Reaktion mit den Triglyceriden räumlich ermöglicht. Im Falle der Adsorption an einer SIO2/Wasser Grenzfläche sind die Lid Residuen in ihrer räumlichen Anordnung um 180° gedreht. Das heißt, der Eingang zum katalytischen Zentrum zeigt in Richtung des Wassers und nicht in Richtung der Grenzfläche. Die Zugänglichkeit zum katalytischen Zentrum bleibt damit erhalten

b)

**Abbildung 1:** Adsorptionskonfiguration von Lipase (1CRL) an MCT/Wasser Interface (a) und SIO2/Wasser interface (b), Lid Residuen in Iila ball Representation

Insbesondere die Adsorption von Lipase an festen Grenzflächen ist von besonderer Bedeutung, da die Immobilisierung von Lipase auf großes Interesse in industrieller Anwendung trifft. Die Immobilisierung machen Proteine handhabbarer und eine Aktivitätssteigerung ist zu erwarten.

Abbildung 2 ist zu entnehmen, dass sich die Position der Lid Residuen im Fall der aktiven Lipase (a und b) im Verlauf der Simulation signifikant verändern. Es ist anzumerken, dass sich die Lid Residuen näher zum aktiven Zentrum bewegen, jedoch nicht der inaktiven Konfiguration (b und c) vorliegen. Zur Verdeutlichung sind in Abbildung 2 die Distanzen der einzelnen Lid Residuen zueinander aufgetragen. Es ist zu erkennen, dass im Falle der inaktiven Lipase (Abbildung 2(f)) keine signifikanten Änderungen im Lid zu verzeichnen sind. Wohingegen das Lid im Falle der aktiven Lipase nach rund 250 ns in Bewegung gerät.

Zur Klärung der Aktivität der adsorbierten Proteine wurden numerisch zwei Möglichkeiten in Betracht gezogen, welche Aufschluss über den Aktivitätszustand der Proteine liefern. Dazu wurde die Erreichbarkeit des katalytischen Zentrums und die Liganden-Bindung innerhalb des Zentrums betrachtet, Zur Ermittlung der Erreichbarkeit des Zentrums wurde das Tool CAVER benutzt um Tunnel von der Oberfläche des Proteins zum aktiven Zentrum zu berechnen. Das Liganden-Docking wurde mit Autodock realisiert. Die Ergebnisse zeigen, dass die aktive Lipase in ihrer Startkonfiguration eine direkte Erreichbarkeit des katalytischen Zentrums ermöglicht, während die Erreichbarkeit bei der passiven Lipase nicht gegeben ist. Nach Adsorption weist die aktive Lipase ein komplexes Tunnelnetzwerk auf. Bei der passiven Lipase ist dieses Netzwerk deutlich weniger komplex. Um den Einfluss der Grenzfläche von dem des Lösungsmittels zu isolieren, wurden parallel aktive und passive Lipasen in Lösung ohne Anwesenheit der Grenzfläche simuliert. Die Ergebnisse zeigen, dass auch in diesem Fall Tunnelbildung möglich ist, jedoch ist deren Komplexität deutlich geringer und statistischer weniger relevant sind, was auf eine Herabsetzung der energetischen Barriere durch die Anwesenheit der Grenzfläche schließen lässt. Auch ist keine Bewegung der Lid Residuen in Richtung des aktiven Zentrums zu verzeichnen.



**Abbildung 2:** Vergleich der Position der Lid Residuen von aktiver Lipase (a), (b) und passiver Lipase (d),(e) nach 1000ns (b und e) Simulation und die Startkonfiguration (a und d) an SIO2/Wasser Grenzfläche, Individuelle Lid Distanz für aktive Lipase (c) und inaktive Lipase (f)

Die Dockingsimulationen deuten auf eine Selektivität der adsorbierten aktiven Struktur hin, welche die C10 Seitenkette eines modellierten Triglycerides bevorzugt im aktiven Zentrum bindet. Im Gegensatz dazu bindet die nicht adsorbierte Struktur bevorzugt die C8 Seitenkette des Triglycerides, wohingegen keine Interaktionen zur C10 Kette gefunden werden können. Weiterhin lässt sich die Enantioselektivität der adsorbierten Struktur nachweisen.

Mit dem gewonnenen Wissen über Adsorptions- und Aktivierungsvorgänge können im nächsten Schritt Schergradienten beaufschlagt werden um eine scherinduzierte Deaktivierung der Proteine zu analysieren.

## Vorträge

1. "Immobilization and Interfacial Activation of Lipase at Liquid and Solid Interfaces", International Workshop on Molecular Modeling and Simulation (ProcessNet), auf 2023 verschoben



# 6.14 *hbi00042:* Drag reduction by air retaining surfaces

HLRN Project ID:	hbi00042
Run time:	III/2019 — II/2021
Project Leader:	Prof. Dr. Albert Baars
Project Scientists:	Christoph Wilms
Affiliation:	City University of Applied Sciences Bremen

#### Overview

Frictional drag reduction on surfaces has been topic of research for a long time in fluid mechanics. Superhydrophobic surfaces seem to be a promising approach. When submerged under water, these are able to retain an air layer by a structured, superhydrophobic surface. The air exhibits a lower viscosity compared to water and thus reduces the wall shear stress in comparison to an ordinary smooth wall without air layer. Results from experiments and numerical simulations deliver drag reductions in the two-digit percent range depending on Reynolds number, structure size and geometry as well as the deformation of the air-water interface. The drag reduction rises with increasing structure size  $L^*$  but the interface stability (air-water) decreases, which is important for air retention. A suitable structure size for practical applications seems to be in the order of  $L^+ \approx 10$  in wall units (Seo et al. 2018). Due to the high computational effort, simulations with such a structure size are rare in literature. In this project, we investigate fully developed turbulent channel flow at  $Re_{\tau} = 180$  with structured surfaces (pillars) and structure sizes in the range of  $10 \leq L^+ \leq 40$  to evaluate the drag reduction using direct numerical simulation.

#### Methods

The with air filled surface structure is modeled by a plane with no-slip and slip boundary conditions. The no-slip area represents the tips of the pillars in contact with water and the slip boundary condition is assumed at the air-water interface. For all structure sizes  $L^+$  a ratio of 75 % slip to total area ( $A_s/A$ ) is applied.

The computational domain with cyclic boundary conditions in stream- and spanwise direction has a height of  $2h^*$ , a length of about  $2\pi h^*$ , and a width of about  $\pi h^*$ . It contains a newtonian fluid with a constant kinematic viscosity  $\nu^*$  and density  $\rho^*$ . The flow is maintained by a constant volume related force in streamwise direction. Hereafter, all quantities are presented in wall units

$$y^{+} = \frac{y^{+}u_{\tau}^{*}}{v^{*}}$$
;  $u^{+} = \frac{u_{i}^{*}}{u_{\tau}^{*}}$ ;  $\langle u \rangle^{+} = \frac{\langle u \rangle^{*}}{u_{\tau}^{*}}$ ;  $\langle u'v' \rangle^{+} = \frac{\langle u'v' \rangle^{*}}{u_{\tau}^{*2}}$ 

with the friction velocity  $u_{\tau}^* = \sqrt{\tau_w^*/\rho^*}$ ,  $\tau_w^*$  as temporal and spatial averaged wall shear stress,  $y^+$  as wall normal distance,  $u^+$  as velocity, and u'v' as component of the Reynolds-stress tensor. Angle brackets symbolise temporal mean values and primes the root mean square of fluctuations. The simulations are conducted at a constant friction Reynolds number  $Re_{\tau}$  of 180 which is defined as

$$Re_{\tau}=rac{u_{\tau}^*h^*}{v^*}$$
 .

In case of rising drag reduction DR, the friction coefficient  $c_f$  decreases in comparison to the reference case (homogeneous no-slip condition, index 0)  $c_{f0}$ . At constant  $Re_{\tau}$  this leads to a rise in bulk velocity  $u_b^*$  in comparison to  $u_{b0}^*$ .



$$DR = \frac{c_{f0} - c_f}{c_{f0}} = 1 - \left(\frac{u_{b0}^*}{u_b^*}\right)^2 \qquad c_f = \frac{\tau_w^*}{\frac{1}{2}\rho^* u_b^{*2}} = 2\left(\frac{u_t^*}{u_b^*}\right)^2.$$

The continuity and momentum equation are solved with the spectral element code Nek5000 using a 3<sup>rd</sup> order temporal and 5<sup>th</sup> (pressure) / 7<sup>th</sup> order (velocity) spatial discretisation scheme. Comparisons of own results (reference case) with literature data from Iwamoto et al. 2002 show a good agreement.

#### Results

The drag reduction DR rises underproportional with structure size  $L^+$ , depicted in Figure 1. This agrees with literature data form Seo et al. (2018). They find higher values of drag reduction at equal structure geometry and size due to the higher surface ratio slip to total surface  $A_s/A$ . An effect of the friction Reynolds number (180, 300) and the code (OpenFOAM, Nek5000) can not be detected in this plot. For this a higher resolution of data points would be necessary.



**Figure 4:** Drag reduction *DR* plotted versus structure size in wall units *L*<sup>+</sup> of own data (OpenFOAM (Weller et al. 1998):  $Re_{\tau} = 300$  from previous calculations, Nek5000:  $Re_{\tau} = 180$ ,  $A_S/A = 3/4$ ) in comparison with literature data from Seo et al. 2018 ( $Re_{\tau} = 197.5$ ,  $A_S/A = 8/9$ ) for pillars.

Further insight to the physics of drag reduction deliver the velocity profiles in Figure 2. All velocity profiles deviate from the reference (homogeneous no-slip boundary condition at the wall). Due to the slip boundary condition, the velocity profiles above the slip area (dashed line) feature a slope of around zero near the wall. The slope at the wall of the velocity profile above the no-slip area (dotted line) differs from that of the reference profile by a factor  $A/(A - A_S)$ . The mean profiles (solid line) and those above the slip area (dashed line) show an increase in velocity with  $L^+$  in the near wall region, which results from a rise in slip velocity  $u_s^+$  at the wall and leads to an upward shift of the velocity profile, an increase in bulk velocity and drag reduction.

In the logarithmic domain a counter acting effect gets apparent: the upward shift appears diminished, which can be quantified by  $\Delta u^+$ , see also Seo and Mani 2016. With rising  $L^+$ , the downward shift  $\Delta u^+$  grows and the logarithmic domain spreads toward the wall. In the nearer wall region, the deviation between the velocity profiles above the slip (dashed line) and no-slip surfaces (dotted line) increases with  $L^+$ . The wall normal distance where the profiles join is smaller than  $L^+$ . This is an agreement with findings of Martell et al. 2010.

The upward  $(\langle u_s \rangle^+)$  and downward shifts  $(\Delta u^+)$  of the velocity are plotted versus structure size  $L^+$  in Figure 3. Within the investigated domain of  $L^+$ ,  $\langle u_s \rangle^+$  increases underproportionally and  $\Delta u^+$  nearly linearly with  $L^+$ . From the progression of  $\Delta u^+$  one could assume that for  $L^+ < 10$  the downward shift may be neglectable in comparison to  $\langle u_s \rangle^+$ . This has to be proven by simulations with structures of  $L^+ < 10$ . Due to  $\langle u_s \rangle^+ > \Delta u^+$  a drag reduction occurs in the investigated parameter range of  $L^+$ .



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**Figure 5:** Velocity  $\langle u \rangle^+$  plotted versus wall normal distance  $y^+$  in wall units for pillars of different surface structures  $L^+$  in comparison to a reference (homogeneous no-slip boundary condition) at  $Re_{\tau} = 180$ . For  $L^+ > 0$ , mean velocity profiles (solid line), profiles over slip area (dashed line), and over no-slip area (dotted line) are shown.

**Figure 6:** Slip velocity  $u_s^+$  and downward shift velocity  $\Delta u^+$  versus structure size  $L^+$  in wall units.

The downward shift of the logarithmic domain can be explained by the progression of the Reynolds stress component  $-\langle u'v' \rangle^+$  plotted versus  $y^+$  (Figure 3). This component is a measure for the momentum transport to the wall due to turbulent velocity fluctuations. A partial slip boundary condition at the wall leads to a slip velocity at the wall in streamwise direction and in case of turbulent flows to a rise in velocity fluctuations. In comparison to the reference case  $-\langle u'v' \rangle^+$  shows an increase in values with  $L^+$  in the range of  $2 \le y^+ \le 20$ . The higher momentum transport in this domain leads to a smaller slope of the velocity profile and to a downward shift of the logarithmic domain.



**Figure 7:** Component  $-\langle u'v' \rangle^+$  of Reynolds stress tensor versus wall normal distance  $y^+$  for different structure sizes  $L^+$  at  $Re_\tau = 180$  in wall units.

Snapshots of the velocity field on the wall are given in Figure 4. The tips of the pillars can be recognized easily by the squares of zero velocity. In between, the effect of streaks gets apparent. With increasing structure size, the velocity rises on the slip areas. This agrees qualitatively with the development of  $u_s^+$  in



**Figure 8:** Velocity field on the channel wall  $u^+$  for  $L^+ = 10$  (top left), 20 (top right), and 40 (bottom left) at  $Re_{\tau} = 180$ .

## Outlook

The next steps in the project are the investigations of further structure geometries. Focused are holes elongated in flow direction as it seems to be a good compromise concerning drag reduction and air retaining capabilities. Furthermore, data at higher Reynolds numbers would allow conclusions of scaling.

#### Literature

Iwamoto K, Suzuki Y and Kasagi N (2002): "Reynolds number effect on wall turbulence: toward effective feedback control," Int. J. Heat Fluid Flow, **23**, 678

Martell MB, Rothstein JP and Perot JP (2010): "An analysis of superhydrophobic turbulent drag reduction mechanisms using direct numerical simulation." Physics of Fluids **22**, 6

NEK5000 Version 17.0. 17/12/2017. Argonne National Laboratory, Illinois. Available: https://nek5000.mcs.anl.gov.

Seo J and Mani A (2016): "On the scaling of the slip velocity in turbulent flows over superhydrophobic surfaces", Phy. of Fluids, **28**, 025110

Seo J, García-Mayoral R and Mani A (2018): "Turbulent flows over superhydrophobic surfaces: flow induced capillary waves, and robustness of air-water interfaces, J. Fluid Mech., **835**, 45-85

Weller HG, Tabor G, Jasak H and Fureby C (1998): "A tensorial approach to computational continuum mechanics using object-oriented techniques", Computers in Physics, **12**, 6



# 6.15 *hbi00045:* Multifunktionale äußere Steuerfläche

HLRN-Projektkennung:	hbi00045
Laufzeit:	III/2021 – I/2022
Projektleiter:	Prof. Dr. Christof Büskens
Projektbearbeiter.	M.Sc. Matthias Otten
Institut / Einrichtung:	Zentrum für Technomathematik, Universität Bremen

## Überblick

Um die Potentiale neuer Technologien für einen noch sichereren, umweltfreundlicheren und wirtschaftlicheren Luftverkehr zu identifizieren, deren Einführung zu beschleunigen und um technologische Risiken zu reduzieren, sind die Entwurfs-, Entwicklungs-, Test-, Herstellungsund Produktionsprozesse zukünftig weitaus stärker zu virtualisieren. Die beispielhafte Anwendung der multifunktionalen Steuerfläche eines Flugzeugs ist als Bremer "Know-How" hervorragend geeignet, um existierende industrielle Konzepte mit den Fähigkeiten der Großforschung zu Aerodynamik, Lasten und Struktur sowie Systemen mit Ideen zum virtuellen Testen und zur Berücksichtigung von Fertigungs- und Montageaspekten zu verbinden und in einem Simulationsprozess zu demonstrieren. Dies geschieht im Startprojekt des Virtual Product House (VPH), eines Integrationsplateaus des Deutschen Zentrums für Luft- und Raumfahrt (DLR), zusammen mit industriellen Partnern, weiteren Forschungseinrichtungen und Zulassungsbehörden (z.B. der EASA). Die Hochauftriebsaerodynamik ist ein wichtiger Aspekt des VPH und es ist essentiell, die auftretenden physikalischen Phänomene basierend auf hochaufgelösten Rechengittern durch die Anwendung der drei-dimensionalen Reynoldsgemittelten Navier-Stokes (RANS) Gleichungen zu erfassen. Nur dadurch kann eine genaue Vorhersage der Leistungsfähigkeit des Flugzeugs im Start- und Landefall gewährleistet oder auch ein Flugversuch digital abgebildet werden. Für die Bestimmung der aerodynamischen Flugeigenschaften und Lasten wird der vom DLR entwickelte TAU-Code verwendet und vom Zentrum für Technomathematik auf dem HLRN eingerichtet. Ferner wird zur Bereitstellung der Lastenberechnung im Gesamtprozess eine Schnittstelle zur Hochauftriebsaerodynamik aufgebaut. Die berechneten Kennwerte sind für den Gesamtentwurf besonders relevant, denn je genauer die Vorhersage der am realen Flugzeug auftretenden Lasten ist, desto kleiner sind die Unsicherheiten der davon abgeleiteten Auslegungsprozesse. Die Minimierung dieser Unsicherheiten ist essentiell für die spätere Bewertung des Gesamtentwurfs und kann über den Erfolg und die weitere Umsetzung eines Flugzeugentwurfs entscheiden.

Beschleunigte Entwicklungszyklen und Minimierung der Unsicherheiten im Entwurf können neuen Technologien, unter Berücksichtigung der hohen Ansprüche an die Sicherheit in der Luftfahrt, schneller zur Integration verhelfen. Dieses Ziel wird aber nur dann erreicht, wenn die im Projekt gewonnen Daten den Anforderungen der Behörden entsprechen und das Vorgehen eng mit der Industrie abgestimmt ist.

## Ergebnisse

In Q1/2021 und Q2/2021 stand die Überprüfung der geometrischen Modellierung einer dreidimensionalen Hochauftriebskonfiguration mit Hilfe eines Open Source CAD-Kernels statt eines kommerziellen CAD-Programms im Fokus. Hierfür wurden drei Hochauftriebskonfigurationen mit unterschiedlichem Detaillierungsgrad in ihrem gesamten operativen Anstellwinkelbereich simuliert und hinsichtlich ihrer aerodynamischen Leistungsfähigkeit analysiert. Für diese Konfigurationen wurden jeweils Parameterstudien zur Lage der primären



Hochauftriebsflächen an der Flügelhinterkante durchgeführt. In Tabelle 1 ist ersichtlich welche fünf Settings dabei untersucht wurden. Dabei wurde der Gap (minimaler Abstand zwischen Klappe und Spoiler) und Overlap (Überlappung von Klappenvorderkante und Spoilerhinterkante) variiert. Zum Einsatz kamen jeweils Rechennetze mit ca. 100 Millionen Punkten, wie in Abbildung 1 dargestellt. Zur Auflösung der Grenzschichtströmung wurden ausgehend vom unstrukturierten Oberflächennetz 60 Prismenschichten aufgebaut, wodurch die wandnahe Strömung bis zu einem Wandabstand von 367mm detailliert erfasst wird. Die initiale Prismenschicht weist dabei eine Höhe von nur 0.001mm auf.

Zur Berechnung der Strömungszustände und einhergehenden Lasten wurde die kompressible drei-dimensionale RANS-Gleichung mit einem Finite-Volumen Ansatz [1] für die bis zu 100 Millionen Gitterpunkte gelöst. Zur Steigerung der Effizienz wurden ein lokales Zeitschrittverfahren und Mehrgitterverfahren verwendet.

	OVERLAP				
		-1%	0%	1%	3%
GAP	0.3%		Setting 1		Setting 4
U.	1%			Setting 3	
	2%	Setting 2			Setting 5

**Tabelle 1:** Spezifikation der fünf statischen Hochauftriebskonfigurationen.



Abbildung 1: Rechennetz generiert mit Centaur mit einem Schnitt durch die Prismenschicht.



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Abbildung 2: Landekonfiguration mit 40° Klappenausschlag und 12° Spoilerausschlag.

In Abbildung 2 ist beispielhaft der Auftriebsbeiwert C<sub>L</sub> und der Widerstandsbeiwert C<sub>D</sub> für die Landekonfiguration über den Anstellwinkelbereich von 6° bis 24° aufgetragen. Die Untersuchung von Setting 2 wurde bei einem Anstellwinkel von 14° auf Grund starker Strömungsablösungen, einhergehenden instationären Fluktuationen und daraus folgender schlechter Konvergenz nicht weiter fortgesetzt. Anhand der Darstellung ist für den Auftriebsbeiwert C<sub>L</sub> der Versatz der Kennlinien aufgrund der Klappenpositionen gut zu erkennen. Es ist eine klare Korrelation zwischen Auftriebsbeiwert C<sub>L</sub> sein Maximum. Eine weitere Vergrößerung des Anstellwinkels führt zu einem abrupten Strömungsabriss. Dieser ist an dem Einbruch des Auftriebsbeiwert C<sub>L</sub> bei gleichzeitig deutlich erhöhtem Widerstandsbeiwert C<sub>D</sub> zu erkennen.



Abbildung 3: Auftriebsbeiwert für fünf verschiedene Settings bei 10° Abstellwinkel.



In Abbildung 3 ist der Auftriebsbeiwert C<sub>L</sub> der Landekonfiguration bei 10° Anstellwinkel dargestellt. Die Settings entlang der Diagonalen 1, 3 und 5 stellten sich dabei als vorteilhaft heraus. Setting 3 hatte den höchsten Auftriebsbeiwert über den gesamten Anstellwinkelbereich und es konnten keine lokalen Strömungsablösungen vor dem Erreichen des maximalen Auftriebsbeiwerts festgestellt werden. Ergänzend zur Analyse der aerodynamischen Leistungsfähigkeit der Landekonfiguration, wurden die Hochauftriebshilfen aller fünf Settings mit einem kleineren Klappenwinkel von 10° ausgerüstet, um damit die aerodynamischen Eigenschaften im Startsegment bei Anstellwinkel von bis zu 10° zu untersuchen.

Zielsetzung in den Quartalen Q3 und Q4 2021 war es, die Flexibilität des VPH-Prozesses durch eine neue Hochauftriebskonfiguration zu demonstrieren. Für diese neue Hochauftriebskonfiguration mit einer Adaptive Dropped Hinge Flap (ADHF) mussten in einem iterativen Prozess die Lasten für jeweils drei Manöver berechnet und Unsicherheiten bestimmt werden. Dazu wurden die Berechnungen auf dem HLRN vollautomatisiert in den multidisziplinären Analyseprozess des VPH eingebunden.

Nur Dank der Bereitstellung von Rechenkapazität durch den HLRN konnten die aerodynamischen Simulationen zertifizierungsrelevanter Lastfälle auf repräsentativen Rechengittern durchgeführt werden.

# Ausblick

Der digitale Gesamtflugzeugentwurf konnte im Rahmen des VPH-Startprojekts gezeigt werden. In Abstimmung mit der EASA werden die gewonnenen Daten und Methoden nun vom DLR/VPH unter anderem hinsichtlich der Potentiale für die simulationsbasierte Zulassung bewertet.

## Quellen

[1] Schwamborn, D., Gerhold, T., Heinrich, R.: *The DLR TAU-Code: Recent Applications in Research and Industry*, ECCOMAS CFD (2006).



# 6.16 *hbi00049:* **Optimization and Extension of Numerical Model for Quenching Process with Experimental Investigation**

HLRN Project ID:	Hbi00049
Run time:	IV/2020 – III/2021
Project Leader:	Prof. DrIng. habil Udo Fritsching, Prof. DrIng. habil Lutz Mädler
Project Scientists:	M.Sc. Nithin Mohan Narayan
Affiliation:	Department of Process Engineering, University of Bremen

# Overview

Water jets and sprays are often used for the heat treatment of metals to improve its properties through intensive cooling (quenching), where a hot material is cooled by water jet or spray. In this context it is highly desirable to understand the detailed physics of quenching process and to determine the local cooling rates by which any material damage can be avoided. If the process is not controlled well, situation arise that the material after quenching will possess distortions or cracks as seen in Figure 9.



Figure 9: 2 mm deformed stainless-steel plate after jet quenching

In the framework of this project quenching based on full jet nozzles, flat and full cone sprays are investigated as depicted in Figure 10. On the first stage full jet nozzle is investigated. Along with this the influence of multiple nozzle configuration, where the configurations such as Inline and Staggered are analysed. The hydrodynamic and thermal effects at the interacting point of two wetting fronts are of high interest.



Figure 10: Left- full jet, middle- flat jet, right- full cone spray

The 2D multiphase model developed by [1], [2] for simulating quenching in commercial program ANSYS Fluent 14.0 has been further developed and extended for 3D quenching process in ANSYS Fluent 19.2. In the existing model source and sink terms for conservation equations of mass, momentum and energy are modified with user defined functions (UDF).





Figure 11: Different boiling regimes during full jet quenching (adopted from [3])

The first project phase focused on developing the following 3D-numerical models and their validation with experimental results.

- 1) Single full jet quenching
- 2) Quenching with nozzle fields: Inline and staggered configuration

# Results

## Single full jet quenching

The modelling is successfully accomplished and the Figure 12 shows the temperature contour from the simulation results where the axial and radial heat transfer can be clearly noticed along with the Leidenfrost effect. The results which are hard to be obtained from an experiment such as the temperature of impinging side, HTC (Heat transfer coefficient) etc. can be obtained directly from the simulation as in Figure 13. The model is successfully validated with experimental results and detailed results can be found in [4]. A parameter variation analysis is carried out further with this validated model.



Figure 12: Simulation results from single full jet quenching of 5 mm Al-alloy





Figure 13: Top and bottom temperature over time for 5 mm Al-alloy

## Full jet nozzle fields

The inline and staggered nozzle fields comprising of full jet nozzles are investigated numerically as presented in Figure 14. The study revealed that the staggered configuration is faster and the temperature gradient within the cold zone is minimum.



Figure 14: (a)- Temperature contour of inline and staggered configuration (b) Average plate temperature

## Outlook

As planned the 3D-numerical models for single full jet quenching and nozzle fields are developed successfully and validated with experimental results. This model can be further optimized for implementing the quenching of moving plates, flat jets as well as spray cooling.

## Publications

 N. M. Narayan, U. Fritsching, S. B. Gopalkrishna, B. Mehdi, H. Woche, and E. Specht, "Investigation of Heat Transfer in Arrays of Water Jets, Modelling/ Simulation and Experimental Approach," presented at the European Conference on Heat Treatment (ECHT) and 2nd International Conference on Quenching and Distortion Engineering (QDE), Online Conference, Germany, 27-28.05.2021, 2021.



#### Presentations

- "Investigation of Heat Transfer in Arrays of Water Jets, Modelling/ Simulation and Experimental Approach," presented at the European Conference on Heat Treatment (ECHT) and 2nd International Conference on Quenching and Distortion Engineering (QDE), Online Conference, Germany, 27-28.05.2021, 2021.
- **2.** "Multiphase Numerical Modeling and Analysis of Quenching", Jahrestreffen ProcessNet Fachgruppen MPH/CFD, Online Konferenz, Germany, 09.03.2021

#### References

- [1] P. Stark, "Prozesssimulation der Bauteil-Abschreckung in flüssigen Medien: Zur Analyse des mehrphasigen Strömungs- und Wärmetransports in Siedeprozessen," PhD Dissertation, Production Technology, University of Bremen, Germany, 2013.
- [2] S. Waldeck, "Untersuchung der intensiven Kühlung von heißen oberflächen mit Wasserstrahlen," PhD Dissertation, Productionstechnik, Universität Bremen, Germany, 2020.
- [3] S. Waldeck, H. Woche, E. Specht, and U. Fritsching, "Evaluation of heat transfer in quenching processes with impinging liquid jets," *International Journal of Thermal Sciences*, vol. 134, pp. 160-167, 2018, doi: 10.1016/j.ijthermalsci.2018.08.001.
- [4] N. M. Narayan, U. Fritsching, S. B. Gopalkrishna, B. Mehdi, H. Woche, and E. Specht, "Investigation of Heat Transfer in Arrays of Water Jets, Modelling/ Simulation and Experimental Approach," presented at the European Conference on Heat Treatment (ECHT) and 2nd International Conference on Quenching and Distortion Engineering (QDE), Online Conference, Germany, 27-28.05.2021, 2021.



# 6.17 *hbi00051:* Characterization of powder flow from discrete coaxial nozzles via Eulerian-Lagrangian approach

HLRN Project ID:	hbi00051
Run time:	III/2021 – II/2022
Project Leader:	Prof. Dr. Rodion Groll
Project Scientists:	Dr. Armin Haghshenas
Affiliation:	Center of Applied Space Technology and Microgravity (ZARM) Universität Bremen

## Overview

Powder-based laser metal deposition (LMD) is an additive manufacturing process, which progressively attracts more attention in the field of production technology owing to its broad application for coating, rapid prototyping, and rapid manufacturing. Despite several advantages of LMD over traditional manufacturing methods, LMD is still away from being a mainstream production technology. The main reason is that the LMD process suffers from a lack of robustness and reproducibility because of a large number of control parameters that influence the quality of the deposited components [1]. The main objective of this research is therefore to advance current knowledge of fundamental aspects of powder flows in the LMD process in order to improve the catchment efficiency as well as the final part precision.

The powder flow, which primarily determines the track geometry in the LMD process, depends on several parameters including the gas and powder flow rates, the size distribution of powder, and the geometry of nozzles. Effects of these parameters on powder flow characteristics have been widely studied [2]. Nonetheless, a comprehensive understanding of underlying mechanisms as well as a precise quantification of the observed dependence of powder flow on controlling parameters remains difficult. In this work, we use a configuration of reduced complexity that is a powder jet issuing from a vertical round nozzle and investigate the powderflow characteristics in LMD process by means of laboratory experiments and numerical simulations.



Figure 1: SEM images of the sieved powder fractions.

## Results

During 2021, we conducted the experiments and numerical simulations using stainless steel particles with three size fractions, namely 45-53  $\mu$ m, 71-80  $\mu$ m, and 90-100  $\mu$ m. Morphology of these particle size fractions is assessed by SEM pictures, as shown in Figure 1. This figure indicates that particles are fairly spherical and each experiment can be considered as a monodisperse case. In numerical simulations, we employed point-particle large-eddy



simulations and adopted a stochastic approach in the soft-sphere model to consider the pronounced effects of the wall roughness on particle-wall collisions.



**Figure 2:** Dependence of the gas and particle statistics on the wall roughness. Instantaneous snapshots of the gas velocity on the vertical plane together with the particle position and the particle velocity for (a) the unladen case, (b) smooth wall, (c) rough wall (roughness angle=3 deg), and (d) rough wall (roughness angle=7 deg).

Figure 2 illustrates the instantaneous snapshots of the gas velocity on the vertical plane together with the position and the velocity of particles for the case with the particle size 50  $\mu$ m, particle mass flow rate 4 g/min, and the gas volumetric flow rate 5 L/min and different wall roughness angles. The most striking features are that with increasing the wall roughness, the spreading rate of the particles grows and the mean particle velocity reduces. This dependence is attributed to higher frequency of inelastic particle-wall collision in cases with higher roughness angle, causing that the particles in these cases lose more kinetic energy within the nozzle and leave it with a larger angle with respect to the nozzle axis. Results evidently indicated that modeling of wall roughness is essential to obtain good agreement between the simulation and experimental results. Figure 3, in which the average particle velocity obtained from the numerical simulation and experiment is compared, shows that the roughness angle for our considered nozzle is approximately 7 degree.



**Figure 3:** Comparison of experimental and numerical simulation results of the average particle velocity for the cases with different wall roughness angle.

We additionally investigated effects of the particle mass flow rate (mass loading) and the particle size (Stokes number) on powder flow characteristics and found that an increase in these two parameters leads to a reduction of the particle velocity and to an enhancement of the particle scattering rate throughout the jet region. All this dependence is rationalized by the fact that the Stokes number and the mass loading determine the correlation between two phases, and the frequency of the particle-particle collisions, respectively.



## Outlook

We have recently submitted a paper containing these results to the Journal of Materials Processing Technology. The next step will be to extend this analysis to discrete coaxial nozzles, where effects of nozzle alignment on powder-flow characteristics can be studied. To this aim, we have to conduct several experiments and numerical simulations.

## Literature

- 1. Huang, D.J., Li, H., 2021. A machine learning guided investigation of qual-ity repeatability in metal laser powder bed fusion additive manufacturing. Materials Design 203, 109606.
- 2. Balu, P., Leggett, P., Kovacevic, R., 2012. Parametric study on a coaxial multi-material powder flow in laser-based powder deposition process. Journal of Materials Processing Technology 212, 1598–1610.


### 6.18 *hbk00032:* Improving physics and efficiency of AWI-CM multiresolution climate model

HLRN Project ID:	hbk00032
Run time:	I/2021–II/2021
Project Leader:	Prof. Dr. Thomas Jung <sup>1</sup>
Project Scientists:	Dmitry Sidorenko <sup>2</sup> , Dirk Barbi, Sergey Danilov, Helge Gößling, Ozgur Gurses, Sven Harig, Jan Hegewald, Nikolay Koldunov, Thomas Rackow, Natalja Rakowsky, Patrick Scholz, Dmitry Sein, Tido Semmler, Qiang Wang, Claudia Wekerle
Affiliation:	<sup>1</sup> also at University of Bremen <sup>2</sup> Alfred - Wegener-Institute for Polar and Marine Research, Bremerhaven

### Summary

The Arctic Ocean can influence the large-scale ocean circulation and climate through the accumulation and release of freshwater. In this project we used high-resolution FESOM simulations to understand the dynamics of the Arctic Ocean freshwater circulation and export. The regionally increased resolution in the Arctic Ocean helped to better resolve the Arctic Ocean circulation and gateway transports. We found that the freshwater pathways in the Arctic Ocean are significantly influenced by the atmospheric circulation regimes. However, the export of Arctic freshwater to the North Atlantic is not only influenced by atmospheric forcing in the Arctic. I found that the drop of the dynamic sea level in the North Atlantic subpolar gyre in the 2010s considerably increased the Arctic freshwater export west of Greenland. After these successful applications, the verified model setups will be used in other climate studies in the future HLRN projects.

### Circulation pathways of Arctic river runoff

River runoff supplies the Arctic Ocean with a large amount of freshwater and land-derived material, so it is important for both the physical and biogeochemical marine environment. We used wind perturbation simulations with FESOM to elucidate the response of the circulation pathways and exports of Arctic river runoff to different atmospheric circulation regimes. Specifically, wind perturbations representing the negative and positive phases of the Arctic Oscillation and Beaufort High modes were imposed over the Arctic Ocean separately in different sensitivity experiments. By comparing these experiments with a control simulation, we revealed the impact of different wind perturbations. The atmospheric circulation regimes influence the Arctic surface geostrophic currents through changing the halosteric height, which is associated with the changes in spatial distribution of surface freshwater. The circulation pathways of river runoff, and Pacific and Atlantic derived surface waters are mainly determined by the surface geostrophic currents (Figure 1). The positive (negative) Arctic Oscillation reduces (increases) freshwater storage and sea surface height in the Makarov and Eurasian basins, thus strengthening (weakening) the cyclonic circulation and weakening (strengthening) the anticyclonic circulation; Accordingly, the Eurasian runoff leaves the Siberian shelf at more eastern (western) locations, and has an enhanced export through the Fram Strait (Canadian





**Figure 1:** Left: Sea surface height (SSH) and upper 150 m mean velocity. Middle column: The inventory of Eurasian runoff (in m). Right: The inventory of Mackenzie River runoff. (A–C): the case with negative Arctic Oscillation (AO) forcing. (D–F): the case with positive AO forcing. (G–I): the case with positive Beaufort High (BH) forcing. (J–L): the case with negative BH forcing. The control run results are shown in the top row of the figure for reference. The red boxes in the middle column indicate the Beaufort Gyre region. (taken from *Wang et al. 2021*).

Arctic Archipelago). The positive (negative) Beaufort High increases (reduces) freshwater Storage and sea surface height in the Amerasian Basin, thus strengthening (weakening) the anticyclonic circulation; Accordingly, the Eurasian runoff export through the Fram Strait and the Mackenzie River runoff export through the Canadian Arctic Archipelago are reduced (increased). The positive Arctic Oscillation increases freshwater available to the Beaufort Gyre, which can be efficiently accumulated there in the presence of a positive Beaufort High forcing.



Our results also showed that Eurasian runoff can only have a relatively small contribution to freshwater accumulation in the Beaufort Gyre region.

### Freshwater export west of Greenland enhanced by subpolar gyre sea level drop

The North Atlantic subpolar gyre influences the climate in many different ways. Using FESOM simulations we identified that it is also responsible for a recent extreme event of Arctic Ocean freshwater export west of Greenland through Davis Strait. A shift in climate regimes occurred in the mid-2000s, with a significant negative trend in the dynamic sea level in the subpolar gyre since then. We found that the dynamic-sea-level drop induced a strong increase in freshwater export west of Greenland, in particular in 2015 - 2017 when the sea level was close to the minimum (Figure 2). We found that sea ice melting and atmospheric variability in the Arctic had only a small contribution to this event. As the exported water from the Arctic Ocean has low salinity and constituents of chemical tracers very different from those in the North Atlantic, such events might have impacts on the North Atlantic ecosystem and the climate as well. Our study suggests that such events might be predictable if the subpolar gyre sea level has certain predictability.



**Figure 2:** Anomalies of (a) volume transport and (b) freshwater transport through Davis Strait in FESOM historical simulation and OMIP2 simulations. The individual OMIP2 model results are shown with thin gray lines, and their multi-model-mean (MMM) is shown with thick blue lines. Positive values indicate larger exports. (c) Anomalies of sea surface height in the North Atlantic subpolar gyre (SPG) in the FESOM historical simulation and satellite observation. (taken from *Wang et al. 2022*).

### References

Wang, Q., Danilov, S., Sidorenko, D., Wang, X. (2021). Circulation Pathways and Exports of Arctic River Runoff Influenced by Atmospheric Circulation Regimes, Frontiers in Marine Science, 8, 707593.

Wang, Q., Shu, Q., Danilov, S. and Sidorenko, D. (2022). The pronounced dynamic-sea-level drop in the North Atlantic subpolar gyre in the mid-late 2010s caused an extreme event of enhanced Arctic Ocean export west of Greenland, Environmental Research Letters, https://doi.org/10.1088/1748-9326/ac5562



# 6.19 *hbk00034:* Ice sheet - ice shelf - ocean interaction in the marginal seas of the Southern Ocean and

## *hbk00038:* Interaction between marine terminating glaciers and the ocean circulation in Northeast Greenland

HLRN Project ID:	hbk00034 / hbk00038
Run time:	III/2013-IV/2021 / III/2014 – III/2021
Project Leader:	Prof. Torsten Kanzow <sup>1,2</sup>
Project Scientists:	Verena Haid <sup>2</sup> , Lukrecia Stulic <sup>2</sup> , Ralph Timmermann <sup>2</sup> , Qiang Wang <sup>2</sup> , Claudia Wekerle <sup>2</sup>
Affiliation:	<ul> <li><sup>1</sup> University of Bremen</li> <li><sup>2</sup> Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research</li> </ul>

### Overview

In these projects, we used global sea ice – ice shelf – ocean models to study the interaction between the deep ocean, the ice shelves fringing the Antarctic continent and part of the Greenland coast, and the ice sheets of Antarctica and Greenland. With its unstructured grid, the Finite Element Sea ice Ocean Model (FESOM) allows for an adequate resolution of the key regions, namely the grounding lines, the ice shelf fronts, and the continental shelf break. Special emphasis is placed on a correct representation of water mass exchange between the deep ocean and the continental shelf regions, and the pathways of water in the cavity beneath Filchner-Ronne Ice Shelf (FRIS) in Antarctica and the 79-North Glacier in northwest Greenland. Coupling with dynamic ice sheet/shelf models is one of the key activities in these projects and allows for a complete and consistent representation of ocean – ice sheet interaction in decadal- to centennial-scale simulations. With the high computational burden imposed by the use of a finite-element ocean model (to which there is no alternative if local processes are to be represented in a global system), these studies depend on resources provided through the HLRN.

### Results

One of the key activities in project hbk00034 was coupling the global Finite-Element Sea iceice shelf-ocean model (FESOM-ice shelf) to the Parallel Ice Sheet Model (PISM) to simulate the dynamics of the Antarctic Ice Sheet in a warming climate and determine feedback mechanisms between the ocean and the cryosphere. We ran simulations with the coupled model for several centuries with atmospheric forcing from a coupled climate model (HadCM3) and determined whether and how a regime shift in the regional ocean circulation and in the cavity beneath the ice shelf can further destabilize deep grounding lines and give rise to selfsustained grounding line retreat. We also investigated how changes in the geometry of iceshelf cavities affect the ocean circulation, and how the relevant mechamisms in fully coupled simulations differ from simulations with fixed ice shelf geometry.





**Figure 1:** Ice shelf basal melt rate offset [m/yr] in the coupled FESOM-PISM simulation with HadCM3-A1B forcing (2165 minus 2000.)



**Figure 2:** FRIS basal mass loss in coupled/standalone experiments with HadCM3-A1B forcing (red/yellow) and in the control simulation with a perpetual 20<sup>th</sup> century forcing (blue/black).

In the coupled FESOM-PISM simulation with HadCM3-A1B climate projection forcing, we find a melt rate increase of typically 20....30 m/yr near the grounding lines of deep-drafted ice streams between the year 2000 and the state projected for 2165 (Fig. 1). The fact that only small to moderate differences between the coupled and standalone simulations occur indicates that for time span investigated here, feedback from a changing ice shelf geometry does not cause a qualitatively different behaviour. The response in basal melt rates in the coupled experiment is slightly larger than for the uncoupled model (Fig. 2); the feedback from a thinning ice sheet slightly enhances rather than damps the response to global warming.





**Figure 3:** Ice sheet/shelf thickness anomaly simulated by PISM in the FESOM-PISM coupled model. Colors indicate thickness change and grounding line migration from 2000 to 2165 in the HadCM3-A1B projection experiment.

The decreasing ice-shelf thickness in the coupled projections for the 21<sup>st</sup>/22<sup>nd</sup> century reduces the buttressing of the ice flow, causing a speedup of ice stream velocities by 500 m/yr and more. Due to the steep slope of the bedrock underlying the grounded ice in this region, we find that ice thickness loss (450 m and more from 2000 to 2165, Fig. 3) is largely confined to floating areas, and grounding line migration is rather moderate. However, due to the large catchment basin of the Filchner-Ronne Ice Shelf, this region alone contributes 2.5 cm to global sea-level rise in this high-emission (but not overly pessimistic) scenario.

Maybe even more dramatic than for the Antarctic, the Greenland ice sheet has been subject to strong mass loss in the last decades. Anomalously high transport of Atlantic Water through the Nordic Seas is thought to increase melting of marine terminating glaciers around Greenland - including the 79 North Glacier (79NG) and the neighboring Zachariae Isstroem - both of which drain the Northeast Greenland Ice Stream. Observations show that warm water of Atlantic origin reaches the 79NG via a system of deep troughs. Heat supply to the cavity is therefore subject to both local and far-field variability.

We carried out a high-resolution ice shelf—ocean simulation focused on the ocean dynamics on the Northeast Greenland shelf, which serves to adress the distribution of basal melt rates and understand which processes are responsible for the heat transport into the cavity of the 79NG and its variability.





Figure 4: Simulated melt rate in m/yr averaged over seven years of integration.



**Figure 5:** Time series of simulated and observed meltwater flux (km3/yr) for the 79° North glacier (79NG) and the neighboring Zachariae Isstrom.

Analysis of our simulations reveals a good agreement between model and observations in terms of temperature on the continental shelf and inflow of warm water to the sub-ice cavity. The pattern of basal melt rates (Fig. 4) fits well with the available observations. Total meltwater flux is well within the range of uncertainties for observation-based estimates (Fig. 5). Increasing temperatures in the Atlantic Water lead to an increasing basal melt rate after about 6 years of simulation, but total meltwater flux is still in the range of observations. Further research is required to evaluate whether the trend towards increasing melt rates represents or overestimates the existing trends in this region.

### Outlook

Following suggestions by the scientific review board, both projects terminated at the end of 2021. Experience gained with and infrastructure developed for the coupled model FESOM-PISM now feeds into a collaboration project with the Potsdam Institute for Climate Impact Research (PIK; HLRN project bbk00016). We will particularly focus on the possible existence of tipping points in the coupled system – not only in the Weddell Sea but also in other sectors with a deep-grounded Antarctic Ice Sheet. For the studies on the Greenland ice sheet, we plan to propose a new project focusing on the implementation of a locally high-resolution coupled ice sheet–ocean model (FESOM-ISSM) later this year. We would like to thank HLRN and BremHLR for the consistent support of our research.



# 6.20 *hbk00059:* Joint state-parameter estimation for the Last Glacial Maximum with CESM1.2

HLRN Project ID:	hbk00059
Run time:	II/2017 – III/2022
Project Leader:	Prof. Dr. Michael Schulz
Project Scientists:	Dr. Tamás Kovács, Dr. André Paul
Affiliation:	Fachbereich Geowissenschaften, MARUMZentrum für Marine Umweltwissenschaften, Universität Bremen

### Overview

This compute project is set within the framework of PALMOD, a BMBF-funded project that seeks to understand climate system dynamics and variability during the last glacial cycle. Specific topics are: i) to identify and quantify the relative contributions of the fundamental processes which determined the Earth's climate trajectory and variability during the last glacial cycle, ii) to simulate with comprehensive Earth System Models (ESMs) the climate from the peak of the last interglacial (the Eemian warm period) up to the present, including the changes in the spectrum of variability, and iii) to assess possible future climate trajectories beyond this century during the next millennia with sophisticated ESMs tested in such a way.

Relevant to this computing project proposal, an expected major outcome of PALMOD is to obtain a comprehensive data synthesis of paleoclimatic conditions during the last glacial cycle, associated with explicit estimates of uncertainty. This involves combining in the best possible ways the outcome of long-term climate model simulations with the latest generation of multi paleo proxy data (planktic foraminifera, diatoms, dinoflagellates, radiolaria, geochemical proxies such as Mg/Ca in planktic foraminifera shells, etc.). In the current phase, our main focus is on the direct forward modeling of stable water isotopes, combined with a comprehensive analysis of reconstructed and simulated isotope distribution. For this, we are using a global and comprehensive Earth system model: the Community Earth System Model version 1.2, in its isotope-enabled configuration (Brady et al. 2019). This version can provide stronger constraints regarding model-data comparison than simulations of only the basic physical variables without the explicit simulation of isotopes.

### Results

The main outcome of this compute project in the previous year was the tuning of model parameters and integrating control simulations with water isotopes under pre-industrial (PI) and last glacial maximum (LGM) climate forcings towards equilibrium, the analysis of results and their comparison with observations. Moreover, we have extended the model code that now enables simulations with additional prescribed meltwater forcing including the isotopic composition of meltwater, and carried out the first test runs.

A metric of high interest in paleoclimate is the sea surface temperature (SST) anomaly between the LGM and PI. A map of simulated values from our control simulations is shown on Fig. 1, compared to reconstructed data points based on observations from the MARGO database (MARGO Project Members, 2009). The simulated global mean anomaly is -3.58°C, somewhat larger than what is suggested by a recent reconstruction of Paul et al. (2021) based on the MARGO data. Comparing the spatial distribution of anomalies, the simulated changes



are closer to reconstructed values at high latitudes, and capture the large anomalies in the North Atlantic remarkably well; however, they show too much cooling at lower latitudes.



**Figure 1:** Anomaly of sea surface temperature between the LGM and PI with simulated values (shading) and reconstructions based on the MARGO database (circles).

The main features of  $\delta^{18}$ O in precipitation are associated with spatial features of precipitation and evaporation. Generally, there are higher delta values in the subtropics where evaporation dominates and lower values in polar regions. According to Fig. 2, the simulated anomalies between the LGM and PI are characterized by a stronger contrast between low and high latitudes, representing more evaporation in the subtropics and a stronger polar terminus for precipitation. The local influence of the ice sheets is also clearly visible with strongly depleted values similar to the polar regions. A comparison to observations is difficult due to the sparse reconstructions from speleothems and ice cores, but the modeled anomalies are closer to observations at high latitudes, especially in Greenland, and show smaller changes at lower latitudes. This can also be seen on Fig. 2 that also presents a scatter plot of the reconstructed values and the closest respective points from our simulation, showing that although the model simulates somewhat too small anomalies compared to what is suggested by (sub-)tropical ice cores and speleothems. However, the model is able to capture the main large-scale patterns, evidenced by the plotted regression slope of 0.80, and the root mean square error of 3.44 between reconstructed and simulated values.

We have also simulated the effect of a local anomalous meltwater discharge on near-surface conditions in the North Atlantic Ocean and on the Atlantic Meridional Overturning Circulation (AMOC). In the experiment presented here, we applied a continuous freshwater forcing of 0.1 Sv on the ocean surface in the North Atlantic (80°W-20°E, 50-70°N) with an prescribed isotopic composition of  $\delta^{18}$ O = -31‰. The simulation was branched from our steady-state LGM simulation at simulation year 1300 and integrated for 150 years.

The response to the additional meltwater on the AMOC is presented on Fig. 3. The maximum strength of the upper North Atlantic Deep Water cell of the AMOC in our control LGM experiment is about 24 Sv; at the onset of the meltwater forcing, this quickly drops to below 20 Sv within 10 years, and stabilizes around 18 Sv. The upper cell becomes significantly weaker at all depths and shoals about 700 meters too, as seen on the AMOC vertical profile at 30°N (right hand side of Fig. 3). The bottom cell strength is much less affected.





**Figure 2:** Anomaly of water isotopes in precipitation between the LGM and PI. Left: map of LGM-PI precipitation  $\delta^{18}$ O with simulated values (shading) and reconstructions based on ice cores (squares) and speleothem data (triangles). Right: scatter plot of reconstructed and simulated LGM-PI precipitation  $\delta^{18}$ O values. The red line shows the linear regression to the data points.



**Figure 3:** Effect of anomalous North Atlantic meltwater discharge on ocean circulation. Green line shows the control run under LGM conditions, blue shows the perturbed run branched from the control at simulation year 1300. Left: time series of the maximum strength of upper North Atlantic Deep Water cell of the AMOC, thick line shows the 5-year running mean of annual averages. Right: Vertical profiles of zonal mean AMOC strength at 30°N, mean of simulation years 1400-1449 (100 years after the start of meltwater forcing). Values represent the barotopic streamfunction in Sverdrups (1 Sv =  $10^6 \text{ ms}^{-1}$ ).

The sudden drop in AMOC strength is caused by changing sea surface conditions and density stratification. The additional meltwater creates a low-density layer near the surface that inhibits convection, significantly weakening the formation of North Atlantic Deep Water. With its weakening, the northward transport of warm and saline surface water is reduced, contributing to further cooling in the North Atlantic and the extension of sea ice cover. These effects feed back on each other until a new equilibrium is reached. Fig. 4. shows the 50-year mean North Atlantic surface conditions 100 years after the start of the meltwater forcing. Comparing the LGM control simulation and the perturbed run (left and right hand side of Fig. 4) the significant extension of sea ice cover is evident in both summer and winter, as well as the almost complete absence of convection as seen through the greatly reduced winter mixed layer depth.





**Figure 4:** Effect of anomalous North Atlantic meltwater discharge on sea ice cover and overturning circulation for simulation years 1400-1449 (100 years after the start of meltwater forcing). Left: control run under LGM conditions. Right: perturbed simulation with additional North Atlantic meltwater discharge branched from tshe control at simulation year 1300. The shaded colors show winter (Jan-Feb-Mar) oceanic mixed layer depth in meters, the solid and dashed lines the winter and summer (Jul-Aug-Sep) sea ice edge (30% coverage).

The changes are strongest in the North Atlantic region, but also have global effects. According to the left plot on Fig. 5, there is a wide-spread cooling of the North Hemisphere both over sea and land. The cooling of surface temperature is mostly around 2-3°C, but in the North Pacific it extends 5°C, and in the North Atlantic it is over 15°C. At the same time, the Southern Hemisphere experiences a slight warming, due to the reduced northward oceanic heat transport in the Atlantic Ocean.

The simulated water isotope response is shown on the right plot of Fig. 5. The  $\delta^{18}$ O in precipitation shows a strong depleted anomaly over the North Atlantic, the Nordic Seas, and Greenland, confirming that water isotope changes are not only impacted by temperature and circulation changes, but also by direct meltwater isotope effects.



**Figure 5:** Effect of anomalous North Atlantic meltwater discharge on surface air temperature (left) and  $\delta^{18}$ O in precipitation (right) for simulation years 1400-1449 (100 years after the start of meltwater forcing).

### Outlook

Our planned experiments for the next year comprise transient simulations of different periods of the last glacial cycle. For the first time, transient simulations of the Marine Isotope Stage 3 characterized by abrupt climate changes (Heinrich events), and the last deglaciation will be performed with a fully coupled model with a full carbon cycle, as well as carbon and oxygen isotopes.



The model results will be compared to the deglacial proxy-data synthesis prepared by the previous project phase. Furthermore, the integration of a proxy-system model and model-data comparison metrics in data assimilation algorithms for CESM will be evaluated, building on Kurahashi-Nakamura et al. (2017) and García-Pintado et al. (2018).

### References

- Brady, E., Stevenson, S., Bailey, D., Liu, Z., Noone, D., Nusbaumer, J., Otto-Bliesner, B. L., Tabor, C., Tomas, R., Wong, T., Zhang, J., Zhu, J, *The connected isotopic water cycle in the Community Earth System Model version 1*. Journal of Advances in Modeling Earth Systems, *11*, 2547–2566 (2019).
- J. García-Pintado, A. Paul, *Evaluation of iterative Kalman smoother schemes for multi-decadal* past climate analysis with comprehensive Earth system models, Geoscientific Model Development, 11, 5051-5084 (2018).
- Kurahashi-Nakamura, T., A. Paul, M. Losch, *Dynamical reconstruction of the global ocean* state during the Last Glacial Maximum, Paleoceanography, 32, 326–350 (2017).
- Paul, A., Mulitza, S., Stein, R., Werner, M, A global climatology of the ocean surface during the Last Glacial Maximum mapped on a regular grid (GLOMAP), Climate of the Past, 17, 805-824 (2021).

### Presentations

Kovács, T., Xiaoxu, S., Cauquoin, A., Paul, A., Werner, M, *Evaluation of water isotope simulations of the LGM*, PalMod General Assembly 2021, 27 May 2021.



# 6.21 *hbk00062:* Retrieval of stratospheric ozone profiles from OMPS observations in limb geometry and long term trends

HLRN Project ID:	hbk00062
Run time:	IV/2017 – IV/2021
Project Leader:	Dr. Alexei Rozanov
Project Scientists:	Dr. Carlo Arosio, Dr. Alexei Rozanov
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### Overview

Stratospheric ozone recovery is expected during the  $21^{st}$  century according to model studies as a consequence of the decreasing emission of chlorine-containing ozone depleting substances (ODSs) and the increasing concentration of  $CO_2$  in the troposphere. The ban of several ODSs after the Montreal Protocol has proven to be beneficial for the ozone layer.

To monitor the status of the ozone layer and the onset of its recovery, satellite measurements are an important tool, as they provide observations with high temporal and spatial resolution. In particular, measurements in limb geometry, as performed by SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric Chartography) and OMPS-LP (Ozone Mapping and Profiler Suite – Limb Profiler), enable the study of ozone profiles with a vertical resolution of about 3 km. However, single satellite missions are generally too short to assess long-term ozone changes and the merging of several time series is required. Several studies using satellite merged data sets detected positive trends in the upper stratosphere, particularly at mid-latitudes: a hint of the ozone recovery.

In this framework, the main activities within this project are related to the retrieval of ozone profiles from OMPS-LP satellite observations, starting from the beginning of 2012 till present. The merging with the SCIAMACHY time series enabled the study of altitude-, latitude- and longitude-resolved ozone changes over the last 15 years. Improvements in the retrieval of ozone profiles are ongoing and the validation with independent data sets showed a general good quality of the produced data set. The comparison of the obtained trends with simulations from a chemistry transport model (CTM) and the study of particular stratospheric events are examples of the usage of the created dataset and will be presented in the report.

### Results

The improvement of the retrieved ozone profiles is a goal of this project and the quality of the profiles has been validated against independent measurements. To this aim, ozonesonde measurements are particularly valuable up to 30 km, whereas observations from the MLS (Microwave Limb Sounder) satellite instrument offer a valuable reference from 15 up to 60 km. Recently, the agreement with ozonesondes in the lower stratosphere was improved, with average discrepancy within 10%. The tropical lower stratosphere is a particularly challenging atmospheric region for satellite observations, as the sensitivity of limb measurements drops and the ozone concentration below ~18 km strongly decreases. Aerosol and cirrus clouds, although accounted for in the ozone retrieval, may still affect the results.

An area where we recently obtained a relevant improvement is the polar regions, where during local summer polar mesospheric clouds (PMC) are found. These clouds are made by ice crystals and are located generally at about 80-85 km altitude but perturb the ozone retrieval



down to 40 km. A retrieval algorithm was implemented to derive particle number density and mean radius of the PMC. This information was then used in the ozone retrieval to take into account the presence of additional scatterers in the instrument field of view. The left panel of Fig.1 shows the relative difference between ozone profiles from OMPS-LP and MLS (not affected by PMC) for the [60°N, 90°N] latitude band in two cases: standard retrieval without taking into account the presence of PMC (blue) and including the PMC retrieved information (red). All observations in the presence of PMC over the period 2012-2020 were averaged. The results show a significant improvement in the ozone profiles above 40 km, with the overestimation shown by OMPS in the first case being strongly reduced and getting closer to MLS observations.

An issue that has to be tackled in the next months, is the OMPS-LP drift with respect to MLS that was identified in the last years, particularly above 35 km. In the right panel of Fig,1 the drift between OMPS and MLS time series is shown as a function of altitude and latitude, in terms of % per decade, over 2012-2020. Investigations from the NASA team are ongoing to better understand the cause of this drift. A collaboration is planned during the next months and a possible adjustment in NASA L1 data is expected before the end of the year.



**Figure 1:** Left panel: relative differences between OMPS-LP retrieved ozone profiles in the presence of PMC w.r.t. MLS ozone profiles, average over [60°N, 90°N], 2012-2020. Panel (b), OMPS drift w.r.t. MLS in % per decade over the period 2012-2020.

### Application 1: Long term ozone trends

By merging SCIAMACHY and OMPS time series, we obtained an ozone data set starting in 2003, vertically resolved every 3.3 km, and spatially binned every 5° latitude and 20° longitude. This enables the study of longitudinally resolved structures and changes in the ozone distribution. To compute trends, a standard multi-linear regression approach was used, accounting for proxies like El Nino, QBO and solar activity. Recently a collaboration with the University of Leeds, made possible a comparison of the satellite trends with simulations of the TOMCAT CTM. The interest was to check whether the model reproduces the zonal asymmetries in trends and better understand their causes and driving mechanisms. To this aim, we also computed seasonal trends, changes in the temperature field, and looked into meridional winds from ERA5 with a focus on the winter season.

A good agreement between the CTM and the satellite trends was generally found. Large asymmetries are seen in winter and spring months. In Fig.2 the focus is brought to winter season, when a comparison of TOMCAT with SCIA+OMPS is more difficult as limb observations do not cover the polar night. This highlights the importance of the usage of a CTM for the study. The satellite observations show larger positive values w.r.t. TOMCAT, possibly due to the positive drift affecting OMPS-LP time series after 2016. When considering the whole TOMCAT time series we discover a more complex structure with two positive and



two negative cores over Greenland and Siberia. Trends in meridional winds show also a 4core structure, similarly to the ozone plot, which point out a sort of rotation of the wave-1 pattern. These findings point out a dynamical origin of the observed asymmetries.



**Figure 2:** Long-term changes over 2003-2020 for winter months (DJF) at 40 km: in the left panel ozone trends from the merged SCIA+OMPS data set, in the middle ozone trends from TOMCAT, on the right meridional wind trends from ERA5. Shaded areas indicate non-significant values.

### Application 2: Polar ozone and extreme event in winter 2019/2020

During winter/spring 2019/20 in the Arctic very low stratospheric temperatures were recorded, associated with an extensive formation of polar stratospheric clouds and a strong depletion of ozone, particularly during March. Total ozone was up to 200 DU lower than the year before, reaching values comparable with the ones in the Antarctic ozone hole. This event was similar to the low ozone recorded in 2010/11. An investigation of this event in comparison with 2010/11 was performed using satellite limb observations from SCIAMACHY and OMPS-LP, together with simulations from the TOMCAT CTM. We observed throughout March a rapid decline of ozone ~18 km altitude. The very stable polar vortex and the extensive formation of polar stratospheric clouds throughout the winter activated chlorine compounds from their reservoir species, leading to a significant chemical ozone depletion in early spring.

Panel (a) and (b) of Fig.3 show the accumulated ozone loss as a function of potential temperature (~altitude) during February and March from SCIAMACHY (2010/11) and OMPS-LP (2019/20) respectively. The ozone loss is calculated as the difference between the daily mean observed ozone profiles and the passive ozone from the TOMCAT simulation, which corresponds to the simulated ozone field without changes due to heterogeneous chemistry. By the end of March 2020 a maximum ozone loss of 80 % (2.1 ppmv) near 450K was observed. In 2011 the accumulated loss reached a maximum of 2.2 ppmv which is comparable with the 2020 value. These ozone losses are the highest values found in the time series over the last decades.



**Figure 3:** Time-altitude cross-sections of the estimated ozone loss in % during the late Arctic winter/spring from SCIAMACHY in 2011 and from OMPS-LP in 2020.

### Outlook

After the collaboration with NASA and the expected production of a new version of Level 1 data during the current year, a re-processing of the entire OMPS-LP ozone profile time series will be required.

### **Publications**

- Arosio, C., et al. "Merging of ozone profiles from SCIAMACHY, OMPS and SAGE II observations to study stratospheric ozone changes", Atmospheric Measurement Techniques, 12.4, (2019): 2423-2444.
- Weber, Mark, et al. "The unusual stratospheric Arctic winter 2019/20: Chemical ozone loss from satellite observations and TOMCAT chemical transport model." *Journal of Geophysical Research: Atmospheres* 126.6 (2021): e2020JD034386.

### Presentations in 2021

- Limb Workshop 2021, oral presentation: "Error budget assessment for OMPS-LP ozone retrievals", Arosio C., Rozanov A., Kramarova N., Roth C., Burrows J.P., 11th Limb workshop, May 10-13 2021.
- QOS 2021, poster contribution:"Error budget assessment for OMPS limb ozone retrievals", Arosio C., Rozanov A., Weber M., Gorshelev V., Kramarova N., Roth C., Burrows J.P., QOS, October 3-9 2021.
- ATMOS 2021, oral presentation: "Longitudinally-resolved Long-term Ozone Changes in the Stratosphere from Satellite Limb Observations and CTM Simulations", Arosio C., Chipperfield M.P., Rozanov A., Burrows J.P., ATMOS 2021, November 22-26 2021.



## 6.22 *hbk00064:* Coupled ensemble data assimilation for Earth system models

HLRNProject ID:	hbk00064
Run time:	I/2019 – III/2021
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### Overview

Earth system models simulate different compartments like the ocean, atmosphere, or land surface. Data assimilation (DA) for Earth system modeling is challenging due to the complexity of different compartments within the model. In this project, we explore the role of data assimilation into an Earth system model which contains different compartments like the ocean and the atmosphere. Numerical experiments are carried out using the AWI climate model AWI-CM (Sidorenko et al., 2015) and the parallel data assimilation framework PDAF (http://pdaf.awi.de, Nerger et al., 2005, Nerger and Hiller, 2013). Within AWI-CM, the ocean model FESOM and the atmospheric model ECHAM are coupled through the coupler software OASIS3-MCT, and they are augmented with DA functionality provided by PDAF (Nerger et al., 2020).

In the first step the system allows assimilating global satellite sea surface temperature (SST) and temperature and salinity profiles into the ocean state such that the atmospheric state is only influenced through the model dynamics, which is the so-called 'weakly coupled DA'. During the lst year, the system was extended for 'strongly coupled DA'. In this variant, the ocean observations can directly influence the state of the atmosphere by utilizing ensembleestimated cross-covariances between the ocean and the atmosphere. The satellite SST observations used in this study are the Copernicus Level-3 product, which are available daily covering almost the complete globe (80 °N - 80 °S) with a resolution of 0.1 degrees. Data gaps exist due to clouds. The temperature and salinity profiles are from the EN4 data set from the UK MetOffice. They can reach down to 5000m and the average number of profiles is about 1000 per day. The sea surface height, velocity, temperature and salinity are updated daily using an ensemble Kalman filter (EnKF) for period of the year 2016. The ensemble size is set to 46. For FESOM, the resolution is varying between 160 km in the open ocean and about 30 km in the equatorial region and parts of the Arctic Ocean. For ECHAM a resolution of T63 with 47 layers is used. The initial ensemble was generated from an EOF decomposition of a 1-year model run for the same year 2016. For the one-year assimilation run, 12,144 processor cores were used with fully parallelized codes for 5.5 hours on HLRN.

### Results

Four simulation scenarios are carried out, including 1) Free\_run: Free-run simulations without DA, 2) WCDA: WCDA run updating only ocean variables, 3) SCDA: SCDA run updating both ocean and atmosphere variables, without vertical localization for atmosphere and 4) SCAD\_vert: SCDA run updating both ocean and atmosphere variables with vertical localization for atmosphere. We analyze whether strongly coupled DA can outperform weakly coupled DA



on the prediction of ocean as well as the atmosphere states in a coupled ocean-atmosphere model by assimilating only the SST observations. The performance evaluation measure is the root mean square error (RMSE) of ocean and atmosphere variables to quantify the difference between model simulations (the 24h-forecasts that serve as the model background in the DA) and observations/reanalysis data.

Both WCDA and SCDA improve the forecast of the SST compared to the free-run. The reduction for RMSE of SST is 64%, 61% and 64% for WCDA, SCDA and SCDA\_vert, respectively. As SCDA directly updates the atmosphere variables, the following discussion will concentrate on the performance of different DA runs on the atmosphere component. Figure 1 shows the average bias of temperature at 2m above surface for the free run and assimilation runs.



**Figure 1:** (a-d) Average bias (model simulation - ERA-interim) of temperature at 2m above surface for the free run and assimilation runs; (e, f) average difference of the absolute bias of 2m temperature between two SCDA runs and WCDA run. Values are averaged over months March to December.



Compared to the free run, DA slightly warms up the atmosphere almost everywhere in the ocean (Figure 1(a-d)). Over the ocean, DA leads to a small rather uniform warm bias everywhere except for a negative bias in the Arctic. Over the continents there are warm and cold biases. WCDA reduces the warm bias around the west coast of South Africa and northern Pacific. However, this reduction is smaller in case of SCDA, see Figure 1(e). Over Europe, Asia, North and South America the amplitude of the bias is mainly reduced in SCDA compared to WCDA, while it is increased over the tropical South America and parts of Antarctica. Further, the amount of bias is slightly increased over Australia. Generally, while differences between SCDA and WCDA are only moderate (Figure 1e), differences between SCDA are caused by the changes in the free atmosphere, which dynamically feed back to the planetary boundary layer.



**Figure 2**: (a-d) Average bias (model simulation - ERA-interim) of wind speed at 10m above surface for the free run and assimilation runs; (e, f) average difference of 10m wind speed between the two SCDA runs and WCDA run. Values are averaged over months March to December.

Regarding the wind speed at 10m height, compared to the free run, both the positive and negative biases along the Equator in the Pacific Ocean and the Atlantic Ocean are strongly reduced by WCDA (Figure 2(b)) and SCDA (Figure 2(c, d)). The bias reduction by SCDA is weaker than by WCDA, shown in Figure 2(e). WCDA also reduces the bias in the Southern



and Northern Pacific, which is not the case for SCDA. The positive bias is strengthened by WCDA in the Southern Indian Ocean, and this is even stronger by SCDA. Both WCDA and SCDA introduce positive bias in the Southern Ocean, south of Africa, where the free run shows negative bias. Again, when vertical localization is used in SCDA\_vert, the DA effect is more similar to that of WCDA.



**Figure 3:** (a) Zonal mean RMSE of temperature as a function of pressure for Free\_run; (b) RMSE difference of temperature between WCDA and Free\_run; (c, d) RMSE difference of temperature between SCDA and WCDA; (e) zonal mean RMSE of wind speed for Free\_run; (f) RMSE difference of wind speed between WCDA and Free\_run, (g, h) RMSE difference of wind speed between SCDA and WCDA.

Figure 3 shows the zonal mean RMSE of the atmosphere temperature and wind speed at different pressure levels. In the lower half of the troposphere, the zonal mean RMSE of temperature (RMSE(T)) is reduced almost everywhere by DA. This is especially the case in the tropics and lower latitudes between 30 °N and 30 °S (Figure 3(b)). Between 900hPa and 500hPa the RMSE(T) is slightly increased by WCDA in the Arctic (Figure 3(b)), while the two SCDA runs reduce it (Figure 3(c, d)). However, DA increases the RMSE(T) close to the equator between 10 °N and 10 °S in the height range between 650hPa and 450hPa, independent of



whether WCDA or SCDA is applied. Compared to WCDA, SCDA yields up to 0.5 K larger RMSE(T) between 25 °N and 25 °S but smaller RMSE(T) in the high-latitude regions. The difference between SCDA\_vert and WCDA is again minor, except for the notable error reduction in the Arctic troposphere.

The assimilation also influences the winds at different levels in the atmosphere. Between 800hPa and the ground level, the zonal mean RMSE of horizontal wind speed (RMSE (*ws*)) in the equatorial region is reduced by WCDA and SCDA\_vert (Figure 3(f, h)). SCDA gives almost the same RMSE (*ws*) as the free run in this region (Figure 3(g)). Slightly increased RMSE (*ws*) is observed north of the equator between 800hPa and 600hPa, the region between 20 °N and 20 °S above 500hPa and the northern high latitude regions above 800hPa in WCDA. For the rest of the regions WCDA reduces the RMSE (*ws*). In general, SCDA shows larger RMSE (*ws*) between 25 °N and 25 °S than the free run and WCDA from ground to the free atmosphere up to 300hPa, but outside of the tropical region the velocity is improved compared to the free run (Figure 3(g)). SCDA\_vert gives similar results as WCDA (Figure 3(h)).

### **Publications**

Tang, Q., Mu, L., Goessling, H., Semmler, T., Nerger, L. (2021) Strongly Coupled Data Assimilation of Ocean Observations into an Ocean-Atmosphere Model, Geophysical Research Letters, 48, e2021GL094941. https://doi.org/10.1029/2021GL094941

### References

Berrisford, P., et al. (2011). The ERA-Interim archive, version 2.0.

- Nerger, L., and W. Hiller (2013), Software for ensemble-based data assimilation systems Implementation strategies and scalability, Computers & Geosciences, 55, 110-118.
- Nerger, L., W. Hiller, and J. Schröter (2005), *PDAF-the parallel data assimilation framework: experiences with Kalman filtering*, in Use Of High Performance Computing In Meteorology, edited, pp. 63-83, World Scientific.
- Nerger, L., Tang, Q., Mu, L. (2020). Efficient ensemble data assimilation for coupled models with the Parallel Data Assimilation Framework: Example of AWI-CM. Geoscientific Model Development, 13, 4305–4321, doi:10.5194/gmd-13-4305-2020
- Sidorenko, D., et al. (2015), *Towards multi-resolution global climate modeling with ECHAM6– FESOM. Part I: model formulation and mean climate*, Climate Dynamics, 44(3), 757-780.



# 6.23 *hbk00071:* Development of an Earth system model coupled with a sediment diagenesis model toward long-term paleoclimate simulations

HLRN Project ID:	hbk00071
Run time:	I/2021 – IV/2021
Project Leader:	Prof. Dr. Michael Schulz
Project Scientists:	Dr. Takasumi Kurahashi-Nakamura
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### Overview

The CO<sub>2</sub> concentration in the atmosphere (hereafter, CO<sub>2</sub> level) has been increasing so that it has reached a level that is unprecedented for at least the last 800,000 years. To reliably project the CO<sub>2</sub> level in the future, it is essential to understand the mechanisms for CO<sub>2</sub>-level changes and to have comprehensive Earth System Models (ESMs) including the latest knowledge and skills. The last glacial cycle in the last 100 kyrs is considered to be one of the most qualified research targets offering many test cases with large variations in the CO<sub>2</sub> level.

Thus far, comprehensive models are unable to quantitatively reproduce the  $CO_2$ -level history in the 100 kyrs. This project will tackle that issue by focusing on the marine carbon cycle that would have played a key role in the variations of the  $CO_2$  level.

In the previous phases of this project, we completed an interactive coupling of the Community Earth System Model version 1.2 (CESM1.2) and Model of Early Diagenesis in the Upper Sediment of Adjustable complexity (MEDUSA) and found that the MEDUSA-coupled CESM outperformed the uncoupled CESM in reproducing the observation-based global distribution of sediment properties through modern-based simulations (Kurahashi-Nakamura et al., 2020). The coupling will also contribute to the improvement of model representation of seawater chemistry. Moreover, the sediment model will act as a "bridge" between the ocean model and paleoceanographic data providing an important fingerprint for the paleo-carbon cycle.

We have subsequently carried out key time-slice simulations that will be followed by future simulations in a transient framework.

### Results

### LGM carbon-cycle simulations with calibrated total inventories of dissolved inorganic carbon (DIC) and total alkalinity

We conducted three fully-coupled LGM simulations that had different global ocean circulation fields. In addition to glacial boundary conditions based on the PMIP4 protocol, we adjusted the total inventories of DIC and total alkalinity in the ocean to satisfy important observation-based constraints in terms of the size of carbon reservoirs. The simulations successfully reproduced

the glacial CO<sub>2</sub> level. This fact has proven the model's great potential to simulate the climatic evolution since the LGM including the carbon cycle dynamics. We also explicitly simulate the mass accumulation rate (MAR) of CaCO<sub>3</sub> at the ocean floor with MEDUSA. The model–data comparison regarding CaCO<sub>3</sub> MAR supported the LGM state with a shallower and weaker AMOC better (Fig.1). Transient simulations in the coming phase will provide an opportunity to



**Figure: 1**: Mass accumulation rate (MAR) of CaCO<sub>3</sub> in the upper sediment simulated with MEDUSA. The ratio of MAR in the LGM runs to that in the reference pre-industrial run are shown in a logarithmic scale. Each panel corresponds to a LGM simulation with CESM that has a different AMOC state compared to the modern counterpart: (a) stronger and deeper, (b) stronger and shallower, and (c) weaker and shallower, respectively. The observation-based data by Cartapanis et al. (2018) are shown as overlaid dots.

examine the mechanisms for the glacial climate based on the trajectory leading to the modern age.

### Preliminary fully-coupled carbon-cycle simulations for MIS3

We applied a similar methodology to intermediate glacial climate states as represented by MIS3. We carried out a simulation for 38ka by *giving* boundary conditions corresponding to the time slice, and also conducted several sensitivity experiments where we replaced some components of the boundary conditions with the LGM counterpart (Fig.2). The standard 38ka experiment predicted 210 ppm for the CO<sub>2</sub> level. This predicted CO<sub>2</sub> level was in remarkable agreement with the observation-based reconstruction (210 ppm), implying that the total ocean inventories of DIC and total alkalinity for 38ka would be similar to those in the LGM. The sensitivity runs showed that the change of marine biological production induced by the different dust input, and the change of solubility induced by different sea surface temperature would have played important roles in differentiating the carbon cycle at 38ka from that in the LGM.



### Predicted $pCO_2$ (ppm)

**Figure: 2**: Predicted CO<sub>2</sub> level in the 38ka experiment (shown in red), the LGM experiment (blue), and in other sensitivity runs (black). To decompose the total effect of different boundary conditions, we altered each of three components of the boundary conditions (greenhouse gas, dust, and ice sheets) separately and systematically.



### Development of an interactively-coupled CESM–PISM model

The time-slice LGM simulations suggested that the evolution of the total inventories of DIC and alkalinity accompanied by the sea-level change would play a key role in the transition from the glacial climate state to the modern state. Considering that the sea-level rise is a direct consequence of the ice-sheet evolution induced by climate changes, it would be fundamental to analyse and dis- cuss the co-evolution of the coupled carbon cycle-ice sheet system. Adopting the Parallel Ice Sheet Model (PISM) as an ice-sheet model, we developed and tested an interactive coupling of CESM and PISM. Following the initial spin up of stand-alone PISM, both the models were coupled asynchronously and sequentially in an offline manner. The behaviors of the modelled climate, ocean circulation,  $CO_2$  level, and Greenland ice sheet were stable and reasonable in the coupled phase (Fig.3).



**Figure: 3**: History of the mass of Greenland ice sheet simulated with PISM. The normalized values are shown for the initial spin up with a stand-alone PISM (left) and for the coupled CESM-PISM run (right).

### Outlook

In the coming phase of the project, we will extend the current time-slice scheme to a timeevolving framework. We will move on to transient simulations, where we will attempt to reconstruct the transition of the climate system from the glacial regime to the interglacial regime (Termination I). Preparatory work to configure the model for those simulations has been already in progress. We propose a set of time- evolving carbon-cycle experiments for MIS3 as well. Those work will provide other test cases to investigate the responses and roles of the carbon cycle in paleo climate variations.

### Publications

Kurahashi-Nakamura, T., Paul, A., Merkel, U., and Schulz, M.: Glacial state of the global carbon cycle: time-slice simulations for the last glacial maximum with an Earth-system model, Clim. Past Discuss. [preprint], https://doi.org/10.5194/cp-2022-8, in review, 2022.

### References

Kurahashi-Nakamura, T., Paul, A., Munhoven, G., Merkel, U., and Schulz, M.: Coupling of a sediment diagenesis model (MEDUSA) and an Earth system model (CESM1.2): a contribution toward enhanced marine biogeochemical modelling and long-term climate simulations, Geoscientific Model Development, 13, 825–840, https://doi.org/10.5194/gmd-13-825-2020, 2020.

Cartapanis, O., Galbraith, E. D., Bianchi, D., and Jaccard, S. L.: Carbon burial in deep-sea sediment and implications for oceanic inventories of carbon and alkalinity over the last glacial cycle, Climate of the Past, 14, 1819–1850, https://doi.org/10.5194/cp-14-1819-2018, 2018.



# 6.24 *hbk00075:* Assessing the effect of environmental and biological conditions on Antarctic krill large-scale connectivity facilitated by ocean currents

HLRN Project ID:	hbk00075
Run time:	IV/2019 – IV/2022
Project Leader:	Prof. Dr. Björn Rost <sup>1</sup>
Project Scientists:	Dr. Judith Hauck <sup>2</sup> , Dr. Bettina Fach, Dr. Ralph Timmermann
Affiliation:	Alfred-Wegener-Institut, Helmholtz Zentrum für Polar- und Meeresforschung <sup>1</sup> principal investigator, also at the University of Bremen, <sup>2</sup> project administrator

### Overview

Antarctic krill, *Euphausia superba*, has long been recognized as a key component of the Antarctic marine food web (Marr, 1962) playing a fundamental role in the transfer of energy between the lower and the upper trophic levels. It inhabits the Southern Ocean predominantly south of the Polar Front, with recent estimates of the total stock biomass ranging between 169 and 379 million metric tons (Siegel, 2005; Atkinson et al., 2009). Antarctic krill, like other species, has been shown to be impacted by the observed regional warming. Specifically, their distribution in the south-west Atlantic sector, their main population center, has been shown to shift southward, retreating towards the Antarctic continental shelves (Atkinson et al., 2019).

Many marine populations, including Antarctic krill or other zooplankton and fish stocks, are structured by their physical environment. As a result, the spatial relationships between physical and biological processes are potentially key to understanding their distribution and abundance. Dispersal occurs mostly during early life through advection by ocean currents, when young individuals are not yet capable of active movement. Older life stages exhibit behavior and active movement and can therefore often move on different spatial scales. Larval dispersal by ocean currents and the resulting connectivity between different oceanic regions have been identified as crucial factors for structuring marine populations (Cowen et al., 2006) as well as for designing networks of Marine Protected Areas (MPAs) (Lester et al., 2009), or even understanding the spread of marine pests (Glasby and Lobb, 2008).

Studies in the Lazarev Sea concluded that this region does not support a single selfmaintaining krill population, but represents a complex transition zone of stocks with different origins. Krill recruitment is strongly influenced by the environmental conditions that krill face upstream of the region under investigation as krill is subject to large-scale transport by ocean currents (Hofmann et al., 1998; Fach et al, 2006, Pinones and Fedorov, 2016) and a constantly changing seascape that provides changing food environments during this transport.

In this project we use a global version of the Finite Element Sea Ice-Ocean Model (FESOM) coupled with the Regulated Ecosystem Model 2 (REcoM2) to investigate the possible connectivity of Antarctic krill (*Euphausia superba*) throughout the Southern Ocean via ocean currents with special focus on the Lazarev Sea. Lagrangian particle simulations with an individual based model (IBM) of krill utilize the FESOM-REcoM2 model output in form of environmental conditions (temperature, salinity and currents) as well as biological conditions (phytoplankton and zooplankton distribution and abundance) The aim is to find populations

supplying input to the Lazarev Sea krill population, and investigate how environmental and biological factors impact population dynamics of Antarctic krill during transport.

### Results

The year 2021 marked the second project phase and we have accomplished to tune FESOM-REcoM2 for a simulation with the BOLD grid and achieved a final 10-year simulation (2001-2010) with outputs of both physics and biochemistry saved daily. This adds to the already existing 10-year simulations with the CORE grid, which has a lower resolution than the BOLD grid (Figure 1). As expected, the high resolution (BOLD mesh) is showing much more detail in current structure of the ACC and the drifter paths that is evident between the CORE and the BOLD simulation (Figure 1). This is of importance in the context of this study, as eddies are important features for krill retention and accumulation of food such as phytoplankton and copepods.



**Figure 1:** Surface circulation field in December 2005 with A) the simulation using the CORE mesh and B) the simulation using the BOLD. Notable changes in current variability and eddy activity apparent in the higher resolution simulation B.

With these two FESOM-REcoM2 simulations the proposed Lagrangian drifter simulations to investigate the connectivity of Antarctic krill focusing on the Lazarev Sea were conducted. This includes running the separate krill IBM with the results from both simulations. In the previous period it had already been accomplished to parameterize sea ice algae biomass, an important input parameter to the Antarctic krill IBM, from FESOM shortwave radiation and sea-ice thickness and distribution output. Therefore, all modeling components necessary to test the hypothesis of the project have been set up and tested and gave first exciting results detailed below:

Lagrangian drifter simulations show three main transport patterns in the Lazarev Sea with retention in the Lazarev Sea (~67S to 63S), transport into the Weddell Sea via ASC, and northward transport and entrainment into currents of the ACC with export out of the study area (Figure 2). The three patterns make for very different environmental conditions and, more importantly, available food for krill. The effect of these different conditions was tested with a krill IBM (Fach et al. 2008) and results show that retention in the Lazarev Sea provides the best environment for growth of larvae and juveniles (Figure 3A). Also, recruitment is best when krill larvae are retained in the Lazarev Sea, while transport into the ACC increases recruitment of juvenile krill. Recruitment is defined as follows: larvae are able to reach juvenile stages and juveniles reach adult stage during transport. These results are very encouraging and prove that the concept is working and gives a first insight into the connectivity and population dynamics of krill.





**Figure 15:** Left panel: Lagrangian drifter paths of particles representing Antarctic krill in the surface layer of the FESOM-REcoM2 simulation using Core grid starting December 2005. Right panel: summary of all Core grid simulation drifter paths over 10 years and three release months (December, January, February).



**Figure 16:** Left panel: Time series of Antarctic krill growth rates of (A) larval krill and B) juvenile krill when feeding on food available along drifter paths using a biochemical krill IBM (Fach et al., 2008). Right lower panel: Recruitment of Antarctic krill into the Lazarev Sea population considering the three different main transport pathways of Figure 2.

The results further indicate that the high resolution (BOLD mesh) is showing much more detail in current structure of the ACC and the drifter paths that is evident between the CORE and the BOLD simulation (Figure 1) as was expected. This is of importance in the context of this study, as eddies are important features for krill retention and accumulation of food such as phytoplankton and copepods.

### Outlook

Currently, the tuning of the FESOM-REcoM2 model on the locally high-resolution LAZAREV grid is underway. This includes test runs concerning time stepping and viscosity. Building on the two existing and the ongoing simulations, we plan an additional 10-year reference simulation for the time frame 2000-2010 with the high-resolution mesh. This will allow us to investigate the effect of a higher grid resolution on the connectivity and help understand the population dynamics of the Lazarev Sea krill population.



### References

- Atkinson A., Siegel V., Pakhomov E.A., Jessopp M.J., (2009) A re-appraisal of the total biomass and annual production of Antarctic krill. Deep-Sea Research Part I: Oceanographic Research Papers 56: 727–740.
- Atkinson A., Hill, S.L., Siegel V., Pakhomov E.A., Siegel, V., Reiss, C.S., Loeb V., Steinberg, D.K., Schmidt, K., Tarling, G.A., Gerrish, L., Sailley, S.F. (2019) Nature Climate Change. https://doi.org/10.1038/s41558-018-0370-z
- Cowen, R.K., Paris, C.B., Srinivasan, A. 2006. "Scaling of connectivity in marine populations," Science 311:522-527. doi: 10.1126/science.1122039
- Fach, B. A., Hofmann, E. E., & Murphy, E. J. (2006). Transport of Antarctic krill (Euphausia superba) across the Scotia Sea. Part II: Krill growth and survival. Deep-Sea Research Part I: Oceanographic Research Papers, 53(6).
- Fach, B.A., Meyer, B., Wolf-Gladrow, D., Bathmann, U. (2008). A biochemically based model of the growth and development of Antarctic krill (Euphausia superba). *Marine Ecology Progress Series*, 360: 147-161.
- Hofmann, E.E., Klinck, J.M., Locarnini, R.A., Fach, B., Murphy, E., 1998. Krill transport in the Scotia Sea and environs. Antarctic Science 10 (4), 406–415.
- Lester, S., Halpern, B., Grorud-Colvert, K., Lubchenco, J., Ruttenberg, B., Gaines, S., Airam<sup>e</sup>, S. and Warner, R.R. 2009. Biological effects within no take marine reserves: a global synthesis, Mar. Ecol. Prog. Ser., 384: 33–46.
- Marr, J.W.S., 1962. The natural history and geography of the Antarctic krill *Euphausia superba* Dana. Discovery Reports 32, pp. 37-465.
- Pinones, A., and A. V. Fedorov (2016), Projected changes of Antarctic krill habitat by the end of the 21st century, Geophys. Res. Lett., 43, 8580–8589.

### Publications

Additional model experiments and the analysis of completed experiments are on-going, therefore there is no publications or presentation of the results yet.

#### Presentations

Fach, B.A., Cagdas, B., Sadighrad, E., Gurses, O., Hauck, J., Timmermann, R., Wekerle, C. (Talk) Modeling the connectivity of Antarctic krill in the Lazarev Sea. ICED krill modeling workshop, Hobart, Australia, May 17-20, 2021.

Cagdas, B., Fach, B.A., Sadighrad, E., Gurses, O., Hauck, J., Timmermann, R., Wekerle, C. (Poster) Modeling the connectivity of Antarctic krill (Euphausia superba) in the Lazarev Sea. AMEMR International Symposium, Plymouth, UK, July12-15, 2021.



# 6.25 *hbk00079:* Tipping points in Antarctic Bottom Water formation and Southern Ocean carbon sequestration

HLRN Project ID:	hbk00079
Run time:	I/2021 – IV/2021
Project Leader:	Prof. Dr. Björn Rost <sup>1</sup>
Project Scientists:	Dr. Cara Nissen <sup>2</sup> , Dr. Judith Hauck, Dr. Mario Hoppema, Dr. Ralph Timmermann
Affiliation:	Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research
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### Overview

The Southern Ocean plays an essential role in oceanic carbon uptake, carbon sequestration, global ocean circulation, and hence global climate, but the ability of this ocean basin to draw down atmospheric  $CO_2$  has varied in the past and is projected to be altered in the future due to on-going climate change (Hauck et al., 2015). In general, ocean circulation largely controls the oceanic uptake of  $CO_2$  and the transfer of carbon to greater depths in the Southern Ocean. On the one hand, the upwelling of deep water masses brings naturally carbon-rich waters to the surface layers, where the carbon can be released to the atmosphere (Fig. 1a). On the other hand, large amounts of carbon are locked away from the atmosphere by the sinking of water masses to the ocean floor at high-latitudes, i.e., the formation of Antarctic Bottom Water. In this context, the Antarctic Bottom Water formation regions have been suggested to dominantly set global atmospheric  $CO_2$  levels (Marinov et al., 2006), as these can sequester carbon on time scales of centuries to millenia. Amongst all Antarctic Bottom Water formation regions, the Weddell Sea has been suggested to be the most important one (Orsi et al., 1999), making any change in Antarctic Bottom Water formation in this area especially critical for global carbon cycling and climate.

The formation of Antarctic Bottom Water is a result of an increase in the density of surface waters (Orsi et al. 1999), due to air-ocean and ice-ocean interactions, i.e., due to a cooling from the overlying atmosphere and due to the increase in salinity as a result of ice formation, respectively (Fig. 1a). Similarly, this suggests that any addition of freshwater to the Southern Ocean, which leads to a decrease in water density, directly impacts the formation rates of Antarctic Bottom Water and subsequently Southern Ocean carbon transfer to depth. In fact, as a consequence of the recent warming, the mass loss of Antarctic ice sheets has accelerated over the last decades (Rignot et al., 2019), discharging additional freshwater into the coastal areas of the Southern Ocean. While especially the melt rates of ice shelves in West Antarctica have accelerated, those in East Antarctica, including the Weddell Sea, have done so to a much lesser extent (Rignot et al., 2019). However, modeling experiments have demonstrated the possibility of accelerating melt rates of ice shelves in the Weddell Sea in the upcoming centuries as well (Timmermann & Hellmer 2013), with a possible complete shutdown of Antarctic Bottom Water formation within a few decades (Lago & England 2019). Yet, the possible response of Antarctic Bottom Water formation rates and Southern Ocean carbon cycling to the expected future changes in freshwater discharge remain surrounded by large uncertainties or largely unquantified altogether, as these have so far been hindered by model



resolution and/or missing model complexity, e.g., by not accounting for changing freshwater discharge from ice shelves and associated feedbacks in their simulations.

In this project, our goal is to quantify changes in Antarctic Bottom Water formation and carbon sequestration over the 21<sup>st</sup> century by performing model experiments with FESOM1.4-REcoM2 (Timmermann et al., 2012; Schourup-Kristensen et al., 2018). The setup used here resolves ice shelf cavities and has a higher grid resolution in the Weddell Sea, allowing for a realistic representation of processes inducing Antarctic Bottom Water formation in this area.



**Figure 1:** a) Sketch illustrating the main features of high-latitude Southern Ocean circulation (black arrows), the air-ocean and ice-ocean interactions involved in water mass transformations (green), and the main features of Southern Ocean carbon cycling (blue). CDW = Circumpolar Deep Water, AAIW = Antarctic Intermediate Water, and AABW = Antarctic Bottom Water and b) Horizontal grid resolution in km of the COARZE mesh in the Weddell Sea as used in this project.

### Results

Over the past year, we have completed several model experiments with FESOM1.4-REcoM2 (Wang et al., 2014; Danilov et al., 2015; Hauck et al., 2013; Schourup-Kristensen et al., 2018). All simulations were run on the COARZE mesh with elevated resolution in the southern Weddell Sea (Fig. 1b), include an ice-shelf component (Timmermann et al., 2012), and are forced with atmospheric output for the period 1950-2100 from the AWI Climate Model (Semmler et al., 2020). Under historical and high-emission scenario forcing (SSP5-8.5; *simA;* O'Neill et al., 2016), our analysis reveals an abrupt attenuation of carbon sequestration with Weddell Sea dense waters at the end of the 21<sup>st</sup> century. Comparing *simA* to the control simulation *simB* (constant atmospheric forcing of the year 1955), we mainly attribute this decline in *simA* to an increased presence of Warm Deep Water on the southern Weddell Sea continental shelf, a 16% reduction in sea-ice formation, and a 79% increase in ice-shelf basal melt, which together lower the density of newly formed dense waters and reduce the carbon transfer to the deep ocean. This work is currently under review for publication in Nature Communications (Nissen et al., 2021).

Further, we have completed two additional model experiments, in which either all atmo- spheric forcing variables except atmospheric  $CO_2$  levels (*simC*) or only atmospheric  $CO_2$  levels (*simD*) are held constant. This allows us to quantify a) the impact of variability and trends in climate on marine carbon cycling and b) the changes in the cycling of natural vs. anthropogenic carbon in the Weddell Sea. The analysis is on-going, but preliminary results indicate that in the Weddell Sea, climate variability acts to enhance oceanic  $CO_2$  uptake by the end of the 21<sup>st</sup> century, which is a consequence of enhanced uptake of anthropogenic  $CO_2$ , which outweighs enhanced outgassing of natural  $CO_2$  (not shown).



### Outlook

While the existing experiments with FESOM1.4-REcoM2 provide a comprehensive overview of possible changes in future Weddell Sea carbon cycling under a high-emission scenario, it remains an open question whether (some of) these changes are avoidable under a lower-emission scenario. To address this question, we plan to perform additional scenario experiments over the course of the next months (SSP3-7.0, SSP2-4.5, and SSP1-2.6; see O'Neill et al., 2016).

### References

- Danilov, S., Wang, Q., Timmermann, R., Iakovlev, N., Sidorenko, D., Kimmritz, M., Jung, T., & Schröter, J. (2015). Finite-Element Sea Ice Model (FESIM), version 2. *Geoscientific Model Development*, 8(6), 1747–1761. https://doi.org/10.5194/gmd-8-1747-2015
- Hauck, J., Völker, C., Wang, T., Hoppema, M., Losch, M., & Wolf-Gladrow, D. A. (2013). Seasonally different carbon flux changes in the Southern Ocean in response to the southern annular mode. *Global Biogeochemical Cycles*, 27(4), 1236–1245. https://doi.org/10.1002/2013GB004600
- Hauck, J., Völker, C., Wolf-Gladrow, D. A., Laufkötter, C., Vogt, M., Aumont, O., Bopp, L., Buitenhuis, E. T., Doney, S. C., Dunne, J., Gruber, N., Hashioka, T., John, J., Quéré, C. Le, Lima, I. D., Nakano, H., Séférian, R., & Totterdell, I. (2015). On the Southern Ocean CO<sub>2</sub> uptake and the role of the biological carbon pump in the 21st century. *Global Biogeochemical Cycles*, *29*(9), 1451–1470. https://doi.org/10.1002/2015GB005140
- Lago, V., & England, M. H. (2019). Projected Slowdown of Antarctic Bottom Water Formation in Response to Amplified Meltwater Contributions. *Journal of Climate*, 32(19), 6319– 6335. https://doi.org/10.1175/JCLI-D-18-0622.1
- Marinov, I., Gnanadesikan, A., Toggweiler, J. R., & Sarmiento, J. L. (2006). The Southern Ocean biogeochemical divide. *Nature*, *441*(7096), 964–967. https://doi.org/10.1038/nature04883
- Nissen, C., Timmermann, R., Hoppema, M., Gürses, Ö., Hauck, J. (2021). Abruptly attenuated carbon sequestration with Weddell Sea dense waters towards the end of the 21<sup>st</sup> century. *Nature Communications*, in review. https://doi.org/10.21203/rs.3.rs-934877/v1
- O'Neill, B. C., Tebaldi, C., van Vuuren, D. P., Eyring, V., Friedlingstein, P., Hurtt, G., Knutti, R., Kriegler, E., Lamarque, J.-F., Lowe, J., Meehl, G. A., Moss, R., Riahi, K., & Sanderson, B. M. (2016). The Scenario Model Intercomparison Project (ScenarioMIP) for CMIP6. *Geoscientific Model Development*, 9(9), 3461–3482. https://doi.org/10.5194/gmd-9-3461-2016
- Orsi, A. H., Johnson, G. C., & Bullister, J. L. (1999). Circulation, mixing, and production of Antarctic Bottom Water. *Progress in Oceanography*, *43*(1), 55–109. https://doi.org/10.1016/S0079-6611(99)00004-X
- Rignot, E., Mouginot, J., Scheuchl, B., van den Broeke, M., van Wessem, M. J., & Morlighem, M. (2019). Four decades of Antarctic Ice Sheet mass balance from 1979–2017. *Proceedings of the National Academy of Sciences*, *116*(4), 1095–1103. https://doi.org/10.1073/pnas.1812883116
- Schourup-Kristensen, V., Wekerle, C., Wolf-gladrow, D. A., & Völker, C. (2018). Progress in Oceanography Arctic Ocean biogeochemistry in the high resolution FESOM 1 . 4-REcoM2 model. *Progress in Oceanography*, *168*(August), 65–81. https://doi.org/10.1016/j.pocean.2018.09.006



- Timmermann, R., Wang, Q., & Hellmer, H. H. (2012). Ice-shelf basal melting in a global finiteelement sea-ice/ice-shelf/ocean model. *Annals of Glaciology*, 53(60), 303–314. https://doi.org/10.3189/2012AoG60A156
- Timmermann, R., & Hellmer, H. H. (2013). Southern Ocean warming and increased ice shelf basal melting in the twenty-first and twenty-second centuries based on coupled ice-ocean finite-element modelling. *Ocean Dynamics*, *63*(9–10), 1011–1026. https://doi.org/10.1007/s10236-013-0642-0
- Rignot, E., Mouginot, J., Scheuchl, B., van den Broeke, M., van Wessem, M. J., & Morlighem, M. (2019). Four decades of Antarctic Ice Sheet mass balance from 1979–2017. *Proceedings of the National Academy of Sciences*, *116*(4), 1095–1103. https://doi.org/10.1073/pnas.1812883116
- Semmler, T., Danilov, S., Gierz, P., Goessling, H. F., Hegewald, J., Hinrichs, C., Koldunov, N., Khosravi, N., Mu, L., Rackow, T., Sein, D. V., Sidorenko, D., Wang, Q., & Jung, T. (2020). Simulations for CMIP6 With the AWI Climate Model AWI-CM-1-1. *Journal of Advances in Modeling Earth Systems*, *12*(9), 1–34. https://doi.org/10.1029/2019MS002009
- Wang, Q., Danilov, S., Sidorenko, D., Timmermann, R., Wekerle, C., Wang, X., Jung, T., & Schröter, J. (2014). The Finite Element Sea Ice-Ocean Model (FESOM) v.1.4: formulation of an ocean general circulation model. *Geoscientific Model Development*, 7(2), 663–693. https://doi.org/10.5194/gmd-7-663-2014

### **Publications**

Nissen, C., R. Timmermann, M. Hoppema, Ö. Gürses, and J. Hauck (2021), Abruptly attenuated carbon sequestration with Weddell Sea dense waters towards the end of the 21<sup>st</sup> century, *Nature Communications*, in review. https://doi.org/10.21203/rs.3.rs-934877/v1

### Presentations

- vEGU21: Gather online (April 2021), *Virtual PICO*: C. Nissen et al.: Attenuated carbon sequestration by Weddell Sea dense waters over the 21<sup>st</sup> century an assessment with FESOM-REcoM, https://meetingorganizer.copernicus.org/EGU21/EGU21-6248.html
- COMFORT Annual Project Meeting (virtual, September 2021), *Oral*: C. Nissen et al.: Attenuated carbon sequestration by Weddell Sea dense waters over the 21<sup>st</sup> century an assessment with FESOM-REcoM

## 6.26 *hbk00080:* The Greenland Ice Sheet in past interglacials and the future

HLRN Project ID:	hbk00080
Run time:	III/2020 – II/2022
Project Leader:	Prof. M. Schulz
Project Scientists:	Dr. M. Prange, B. Crow, Dr. S. Beyer
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### Overview

As part of a broader effort to understand how warming of the climate will impact critical components of the Earth system such as ice sheets, we have undertaken climate modeling of past periods that can provide insights on key processes that are relevant to the current and near-future climate (Crow et al., in press). Of specific interest is the response of the Greenland ice sheet to radiative forcing. As the Earth's orbit and axial tilt slowly vary through cycles of differing lengths, the distribution of incoming solar radiation across the planet and over the seasons changes. Interglacial climate conditions are thus related to astronomical conditions that favor long and warm Northern Hemisphere summers. An unusually long period of time from around 423,000 years ago (423 ka) to around 398 ka of interglacial conditions was the Marine Isotope Stage (MIS) 11. There is evidence of a strongly reduced Greenland ice sheet during this interval, which likely contributed to a 6-13 m higher sea level than today (Dutton et al., 2015).

Using the Community Earth System Model version 1.2.2 (henceforth CESM), we simulated thousand-year slices for a selection of six representative times within this period (423 ka, 418 ka, 413 ka, 408 ka, 403 ka, and 398 ka; cf. Fig. 1) such that a quasi-transient climate evolution of MIS 11 can be constructed. For each simulation, orbital conditions were kept constant. HLRN resources enable such relatively lengthy simulations to be conducted with this state-of-the-art comprehensive climate model, using a ~2° horizontal resolution for the atmosphere and ~1° resolution for the ocean component. The simulations were based on and compared to a preindustrial baseline simulation, with only the orbital parameters and greenhouse gas concentrations altered to fit contemporary values.

### Results

Figure 1 shows simulated temperatures for the boreal summer season (June-August; i.e. the Greenland melt season) from the final 100 years of each time slice simulation, with the dark blue series indicating global mean temperature anomalies and the light blue indicating temperature anomalies over and around Greenland. The temperature time series is presented in a pseudo-continuous manner to visualize the quasi-transient character of our experimental setup. Both global and Greenland temperatures show an increasing trend during the first phase of MIS 11 in response to changing orbital forcing and rising greenhouse gas concentrations. A thermal maximum is reached at 413 ka. Temperatures remain on a very high level until 408 ka before a relatively fast cooling occurs, which sets the stage for a subsequent glaciation around 398 ka, when Greenland summer temperatures are about 2°C lower than during the preindustrial period. Previous simulations of MIS 11 climate have been conducted with simplified or coarse-resolution models only (Kleinen et al., 2014; Rachmayani et al., 2016;



Robinson et al., 2017; Yin et al., 2021). The use of a state-of-the-art high-resolution climate model, as in our study, now allows a much deeper investigation of systemic interactions and dynamic responses in the atmosphere, which may have modulated Greenland climate and melting of the ice sheet during MIS 11.

Over most parts of the MIS 11 interglacial, CESM simulates a state of reduced atmospheric baroclinicity. Moreover, both minima in orbital precession (corresponding to an alignment of Earth's closest annual approach to the sun and boreal summer) and maxima in obliquity (Earth's axial tilt) are shown to enhance summer monsoon activity across western and central Africa. A change in monsoon means a change in the strength and epicenter of the tropical circulation, which in turn affects the favored location of the atmospheric jet stream. The enhanced monsoon also results in more cloud cover and precipitation across the tropics, causing low-level temperatures in a narrow band to actually be cooler than in preindustrial times.

Due to the combination of precession and obliquity changes (Fig. 1; left), the monsoon strengthening persists through 423-403 ka, shifting the subtropical jet northward and causing it to merge with the midlatitude jet. This dominant single-jet state leads to a reduction in poleward atmospheric heat flux over the North Atlantic and Greenland by transient eddies. The warmer the air temperatures over Greenland, the stronger this eddy-jet effect, thus demonstrating a negative feedback relationship. Figure 2 provides an overview of this effect, with the mean jet latitude (left panel) and mean jet speed (right panel) of each summer season plotted against each summer mean temperature in the Greenland region. While the relationship between jet latitude and Greenland temperature is somewhat weaker, the correlation between maximum jet strength and Greenland temperature is highly robust.



**Figure 1:** (Left) Variation of orbital parameters throughout the MIS 11 interglacial (Laskar et al., 2004). (Right) Evolution of 2-meter air temperatures through the MIS 11 interglacial as simulated by CESM. The two blue time series represent mean temperature anomalies for the globe (dark) and for Greenland (light; area defined by 55-85°N, 280-350°E) compared to preindustrial. Green dots indicate the cumulative radiative forcing anomaly relative to preindustrial, as given by the combined effects of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O. The pseudo-time series depict seasonal-mean boreal summer (June-July-August; JJA) values from the final 100 years of each simulation; the time axis is therefore not to scale and the discontinuities are larger than depicted.



The eddy-jet effect partially counteracts conditions favorable for widespread melting of the Greenland ice sheet. The relationship between Greenland precipitation and the state of the North Atlantic jet is less apparent, but slight summer changes in precipitation appear to be more than offset by increases during the remainder of the year. Such a dynamic state is surprising, as it bears stronger resemblance to the unified-jet state postulated as typical for glacial states than to the modern-day interglacial state.



**Figure 2:** (Left) The relationship between June-August mean 2-meter air temperature over Greenland (55-85°N, 280-350°E) and the latitude of maximum 300 hPa (upper troposphere) winds across the North Atlantic. (Right) Relationship between 2-meter summer Greenland temperature and the maximum velocity of 300 hPa winds across the North Atlantic. In both panels, bold dots correspond to the mean values for each of the six time slices. Smaller dots correspond to the seasonal-mean values for each of the 100 years from each time slice (n=600 total).

### Outlook

Our high-resolution CESM simulations enable us to explore the atmospheric response to different orbital conditions in a detailed way that no study has attempted before. Our findings reveal specific feedbacks that have occurred in past warm climates and may therefore be expected again in the future. The continuation of this project will yield further insight into what consequences atmospheric feedbacks have on the melting of the Greenland ice sheet, aimed at improving our understanding and enabling better preparedness for future climate changes.

### References

- Crow, B. R., M. Prange, and M. Schulz: *Dynamic boreal summer atmospheric circulation response as a negative feedback to Greenland melt during the MIS-11 interglacial*, Clim. Past, in press.
- Dutton, A., Carlson, A. E., Long, A. J., Milne, G. A., Clark, P. U., DeConto, R., Horton, B. P., Rahmstorf, S., and Raymo, M. E.: *Sea-level rise due to polar ice-sheet mass loss during past warm periods*, Science, 349, https://doi.org/10.1126/science.aaa4019, 2015.
- Kleinen, T., Hildebrandt, S., Prange, M., Rachmayani, R., Müller, S., Bezrukova, E., Brovkin, V., and Tarasov, P. E.: *The climate and vegetation of Marine Isotope Stage 11 Model*

*results and proxy-based reconstructions at global and regional scale*, Quatern. Int., 348, 247-265, https://doi.org/10.1016/j.quaint.2013.12.028, 2014.

- Laskar, J., Robutel, P., Joutel, F., Gastineau, M., Correia, A. C. M., and Levrard, B.: A longterm numerical solution for the insolation quantities of the Earth, Astron. Astrophys., 428, 261-285, https://doi.org/10.1051/0004-6361:20041335, 2004.
- Rachmayani, R., Prange, M., and Schulz, M.: Intra-interglacial climate variability: model simulations of Marine Isotope Stages 1, 5, 11, 13, and 15, Clim. Past, 12, 677-695, https://doi.org/10.5194/cp-12-677-2016, 2016.
- Robinson, A., Alvarez-Solas, J., Calov, R., Ganopolski, A., and Montoya, M.: *MIS-11 duration key to disappearance of the Greenland ice sheet*, Nat. Comm., 8, 16008, https://doi.org/10.1038/ncomms16008, 2017.
- Yin, Q. Z., Wu, Z. P., Berger, A., Goosse, H., and Hodell, D.: *Insolation triggered abrupt weakening of Atlantic circulation at the end of interglacials*, Science, 373, 1035-1040, https://doi.org/10.1126/science.abg1737, 2021.

### Publications

1. Crow, B. R., M. Prange, and M. Schulz: *Dynamic boreal summer atmospheric circulation response as a negative feedback to Greenland melt during the MIS-11 interglacial*, Clim. Past, in press.

### Presentations

- Crow, B. R., M. Prange, and M. Schulz: On the role of atmospheric feedbacks in sustaining the anomalous warmth of the MIS 11 interglacial, PICO talk/virtual poster at EGU 2021, session CL4.19 ("Dynamics of the atmospheric circulation in past, present, and future climates"), 29 April 2021.
- 3. Crow, B. R., M. Prange, and M. Schulz: *On the role of atmospheric feedbacks in sustaining the anomalous warmth of the MIS 11 interglacial*, Poster at the ArcTrain Annual Meeting 2021, 21 Oct 2021.


# 6.27 *hbk00083:* Tipping points in the ecosystem of the 'new Arctic' Ocean

HLRN Project ID:	hbk00083
Run time:	I/2021 – IV/2022
Project Leader:	Prof. Dr. B. Rost
Project Scientists:	L. Oziel, J. Hauck, Ö. Gürses
Affiliation:	Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research

## Overview

Net Primary production (NPP) in the Arctic Ocean by phytoplankton forms the basis of a unique ecosystem and is controlled by a complex interplay of light and nutrients. For the last three decades, NPP has been continuously increasing (Arrigo and van Dijken, 2015) stimulated by the loss of sea-ice which allows longer growing seasons (Arrigo et al. 2008) and therefore more light to penetrate into the water column (Nicolaus et al. 2012). The approximately 50% reduction of sea-ice volume in the last three decades (Kwok 2018, Stroeve and Notz, 2018; Serreze and Meiers, 2019) is one of the most striking illustrations of Climate Change globally. In the Arctic Ocean, it is accompanied by an atmospheric warming more than twice as fast as in temperate regions (a phenomenon referred as Arctic amplification; Serreze and Francis, 2006). Climate Change projections estimate a likely summer ice-free Arctic Ocean by the middle of the century (e.g. Sigmond et al. 2018). Therefore, we can expect the Arctic Ocean to generally move from a predominantly light-controlled (ice-covered) to a more nutrient-controlled (open water) system (Babin 2020).

However, it remains largely uncertain how the nutrient biogeochemical cycles will evolve which is of major importance for the Arctic ecosystem. 'State-of-the-art' biogeochemical models still show large uncertainties due to the poor coupling of external inputs such as aeolian deposition, rivers, erosion, benthic fluxes, etc (Séférian et al. 2020). In this project, we are addressing the most urgent modelling limitation for the Arctic Ocean by implementing dynamically coupled river and erosion inputs, from the most 'up-to-date' in situ nutrient and carbon database from Arctic River and coastal erosion (spatially and monthly resolved). We make use of the Regulated Ecosystem Model, version 2.1 (REcoM2.1, Gürses et al. 2022) and propose to assess possible tipping points in the Arctic NPP and their environmental drivers. We run hindcast and forecast biogeochemical simulations with the highest resolution (4.5 km, Fig. 1) in the Arctic Ocean at present time.





**Figure 1:** (a) The horizontal grid size of a mesh with 4.5 km in the Arctic Ocean (referred to as 'farc'). (b) Ratio between the first baroclinic Rossby radius and grid size shown with the log2 scale. With resolution finer than two grid cells per Rossby radius, models may start to resolve mesoscale eddies depending on numerical mixing in the model (b). Figure from Wang et al. 2018.

## Results

We hypothesize that terrigenous inputs could compensate for the decreasing concentration of nutrients in the Arctic Ocean and sustain the current increase in NPP. This ongoing work (the simulations are not finished) will lead to spear-heading results for the community in at least one peer-reviewed article.

## **Expected Publications**

Oziel L., Ö. Gurses, B. Rost, J. Hauck. *Increasing terrigenous inputs alleviate nutrient limitation in the Arctic Ocean*.



## 6.28 *hbp00041:* Multi-Messenger Signals from Compact Objects

HLRN Project ID:	hbp00041
Run time:	I/2018 – II/2023
Project Leader:	Prof. Claus Lämmerzahl
Project Scientists:	Prof. Stephan Rosswog
Affiliation:	Universität Bremen, Centre for Applied Space Technology and Microgravity, Am Fallturm, 28359 Bremen

## Overview

The first detection of a binary black hole merger in 2015 has heralded the long-awaited era of gravitational wave (GW) astronomy. This watershed event confirmed a 100-year-old prediction of Einstein's General Theory of Relativity. Even more importantly, it opened up a completely new channel to observe the Universe. GW astronomy allows to probe how the strongest gravitational fields warp space-time, how ultra-gravity binary stars contribute to the heaviest elements in the cosmos, how such binary systems form and, eventually, how their mergers can be used to probe of the expansion history of the Universe. All these exciting prospects, however, hinge on detecting electromagnetic counterparts of gravitational wave sources. A coincident detection of both gravitational and electromagnetic waves had been a scientific dream for decades.

This dream came true on August 17, 2017: the LIGO/Virgo detectors recorded for the first time the gravitational waves from a binary neutron star merger and subsequently telescopes around the world detected the event all across the electromagnetic spectrum (Abbott et al. 2017). This observation proved that neutron star mergers are indeed strong sources of gravitational waves, that they produce short gamma ray bursts and are a major cosmic factory for the heaviest elements as theoretically predicted (Rosswog et al. 1999, Freiburghaus et al. 1999). Moreover, the subtle tidal imprint on the gravitational wave signal constrained the behaviour of nuclear matter at high densities and the arrival time differences of gravitational waves and photons demonstrated that both propagate at the same speed with a relative precision of 10<sup>-15</sup>. The combined detection also allowed for an entirely new approach to probe the expansion of the Universe. For all these reasons, this first "multi-messenger" detection of a binary neutron star merger was celebrated by *Science* Magazine as ``2017 Breakthrough of the Year".

The main topic of this HLRN project is the theoretical prediction of observable signatures from encounters between compact objects.

## Results

One of our major goals is the physically accurate simulation of neutron star mergers. All of the electromagnetic emission from a neutron star merger is caused by only ~1% of the initial binary mass that is ejected into space. The properties of this small amount of material are of paramount importance for the modelling and the understanding of observed merger events. All of today's Numerical Relativity codes are Eulerian, i.e. they solve the relativistic hydrodynamic equations on computational meshes. While these codes have delivered many important results, they are very severly challenged in following the small amounts of ejecta. For this reason, we have developed the worldwide first (and so far only) Lagrangian Numerical Relativity code [Rosswog & Diener 2021]. This code solves the full set of Einstein field equations to evolve the spacetime on a refined mesh, similarly to more conventional Eulerian



Numerical Relativity codes. The part that is completely different from existing methods is that we evolve matter by freely moving, Lagrangian particles. This approach is "on par" with established Eulerian Numerical Relativity approaches when it comes to evolving dynamical spacetimes, but has major advantages in evolving the small amounts of matter that are ejected into space during the merger of a neutron star.

Our new code is named SPHINCS\_BSSN which stands for *Smoothed Particle Hydrodynamics In Curved Spacetime* and the "BSSN" in the code name stands for the method with which the spacetime is evolved (due to Baumgarte, Shapiro, Shibata, Nakamura). This is the world-wide first and only code that is both Lagrangian and fully general relativistic in its spacetime evolution. SPHINCS\_BSSN has passed a large number of test cases with excellent precision [Rosswog & Diener 2021]. As an example, we show in Figure 2 a relativistic neutron star that has been evolved (both hydrodynamics and spacetime) for many oscillation periods. The star remains very accurately on the initial solution that had been obtained by solving the Tolman-Oppenheimer-Volkoff equations. In the last year we have also made major progress in simulating merging neutron star binaries. An example of one of our first neutron star merger simulations with SPHINCS\_BSSN, performed on HLRN resources, is shown in Figure 2.



**Figure 1:** Simulation of a relativistic neutron star where both the fluid and the spacetime are evolved. The left panel shows the distribution of the SPH particles, the right panel shows that after many oscillation periods the evolved solution (red) is practically in perfect agreement with the initial condition (black).



**Figure 2:** Neutron star merger simulation (2 x1.3 solar masses, MPA1 equation of state) simulated with the Lagrangian Numerical Relativity code SPHINCS\_BSSN (Rosswog, Diener & Torsello, in prep. 2022).



## Outlook

In the year 2021 we have made major progress in developing new the Numerical Relativity code SPHINCS\_BSSN. This code will be one of our major "workhorses" for future studies. We will in particular explore the ejecta from neutron star mergers, their long-term evolution, nucleosynthesis and the variety of electromagnetic signals the produce. Such studies will be crucial for the interpretation of future multi-messenger detections.

## References

Abbott et al., ApJL 848, L12 (2017)

Rosswog et al., A&A 341, 499 (1999)

Freiburghaus, Rosswog, Thielemann, ApJ 525, L121 (1999)

## Publications

- 1. Can jets make the radioactively powered emission from neutron star mergers bluer? Nativi et al., MNRAS 500, 1772 (2021)
- 2. The fate of the merger remnant in GW170817 and its imprint on the jet structure. Murguia-Berthier et al., ApJ 908, 152 (2021)
- *3. Axisymmetric models for neutron star merger remnants with realistic thermal profiles.* Camelio et al., Phys. Rev. D., 103f3014C (2021)
- 4. Axisymmetric radiative transfer models of kilonovae. Korobkin et al., ApJ 910, 116 (2021)
- 5. SPHINCS\_BSSN: a general relativistic smooth particle hydrodynamics code for dynamical spacetimes. Rosswog & Diener, Class. Quant. Grav. 38k5002 (2021)
- 6. Calibration of the advanced spectral leakage scheme for neutron star merger simulations and extension to smoothed-particle hydrodynamics. Gizzi et al., MNRAS 505, 2575 (2021)
- 7. Are interactions with neutron star merger winds shaping the jets? Nativi et al., MNRAS 509, 903 (2021)
- 8. Modeling astrophysical fluids with particles. Rosswog. Eprint arXiv:2201.05896 (2022)
- 9. Inhomogeneous jets from neutron star mergers: one jet to rule them all. Lamb et al., eprint arXiv:2201.09796 (2022)
- 10. Simulating neutron star mergers with the Lagrangian Numerical Relativity code SPHINCS\_BSSN; submitted to Nucl. Phys. A (2021)

## Presentations

- 1. The future of hydrodynamics and n-body simulations. Invited lecture at "UK Research and Innovation STFC Introductory course in astronomy for research students", Armagh Observatory, Northern Ireland, January 14, 2021
- 2. Simulating astrophysical fluids with particles. NORDITA seminar, Stockholm, Sweden, February 03, 2021
- 3. Simulating astrophysical fluids with particles. Astrophysics Seminar Milano-Bicocca, Italy, February 17, 2021
- 4. Multi-messenger astrophysics with merging neutron stars. Lecture at Schools on Nuclear Astrophysics Questions ("SNAQs"), March 10, 2021
- 5. *Neutron star mergers as factories for heavy elements.* AlbaNova Colloquium, Stockholm, April 08, 2021
- 6. *Multi-messenger signatures from neutron star mergers: recent developments.* Joint highenergy Astrophysics Seminar of several Mexican Physics Institutions, Mexico City, May 13, 2021
- 7. *Modelling neutron star mergers.* Review talk at "Probing nuclear physics with neutron star mergers", Trento, Italy, July 12, 2021



- 8. *Thinking outside the box: modelling relativistic fluids with particles.* Invited review talk International Astronomical Union, Symposium 362: Predictive power of computational astrophysics as a discovery tool. November 12, 2021
- 9. Neutron star mergers as cosmic factories of heavy elements. Colloquium Bath, UK, December 08, 2021
- 10. Multi-messenger observations: r-process nucleosynthesis. Keynote speaker at "Gravitational Wave Physics and Astronomy Workshop". Hannover, Germany, December 14, 2021
- 11. Lecture Simulating neutron star mergers as sources of gravitational waves and heavy elements. NORDITA winterschool "Waves in Astrophysics", January 13, 2022



# 6.29 *hbp00058:* Exploring the mechanistic process of vitamin B<sub>12</sub> acquisition by human gut bacteria

HLRN Project ID:	hbp00058
Run time:	III/2021 – II/2022
Project Leader:	Professor Dr. Ulrich Kleinekathöfer
Project Scientists:	Kalyanashis Jana
Affiliation:	Jacobs University Bremen

## Overview

The Gram-negative bacterium B. thetaiotaomicron acquires vitamin B<sub>12</sub>, one of the essential cofactors, through the outer membrane (OM) protein BtuB associated with surface-exposed lipoprotein BtuG in a competing manner with the intrinsic factor (IF), which transports B<sub>12</sub> to the cell in the human body.<sup>1,2</sup> It has recently been reported the lipoprotein BtuG directly binds vitamin B<sub>12</sub> with femtomolar affinity, thereby facilitating vitamin B<sub>12</sub> intake and competing with the IF in association with the membrane protein BtuB. In the previous project year, the newly crystalized BtuBG crystal structure and the cyanocobalamin (CNCbl) bound BtuG protein of B. thetaiotaomicron were considered for a computational study to explore the CNCbl acquisition by BtuG within the BtuBG protein, and transport of CNCbl across from BtuG active site to the active site of BtuB.<sup>3</sup> The MD simulations revealed that the BtuG molecule can pull vitamin CNCbl from a closeby but more or less arbitrary position to its active site by strong electrostatic and noncovalent interactions. Using multiple-walker WTMtD we calculated the binding free energy consisted with an experimental dissociation constant of 10<sup>-14</sup> M. Moreover, the BtuG lid opening process using biased and unbiased MD simulations revealed that the BtuG moves away from BtuB via a hinge loop and can open up to 40° to facilitate the acquisition of CNCbI from the surrounding. Furthermore, unbiased simulations were performed with a starting structure of 40° open structure with CNCbl being outside of the BtuG protein. The BtuG lid started closing very quickly, where the BtuG lid angle was around 20°, and the CNCbl molecule reached the BtuG active site cavity after 1µs. Finally, the CNCbl bound BtuBG was considered to reveal conformational dynamics of BtuBG protein and translocation process of the CNCbl from the active site cavity of BtuG to BtuB. In the close state of CNCbl bound-BtuBG, BtuG binds CNCbl weakly compared to the results for CNCbl-BtuG due to several loop rearrangements, which further enables CNCbl molecules to move toward BtuG cavity.

Hydroxocobalamin (HOCbI) and cyanocobalamin (CNCbI) are commonly used for supplementation in case of a vitamin B<sub>12</sub> deficiency in the human body.<sup>4</sup> Nowadays, methylcobalamin (MeCbI) and adenosylcobalamin (AdoCbI) have been considered as alternative forms of these supplements since MeCbI and AdoCbI are coenzymes for methionine synthase and methylmalonyl-CoA mutase, respectively. The experimental binding constants of CNCbI or HOCbI (both containing the small axial ligands CN or OH) with the transporters are comparable to that of AdoCbI (containing the relatively large axial group adenosyl). Most of the reports available in the literature show a CNCbI binding and translocation through a protein of the Gram-negative bacteria outer membrane. In this context, the binding affinity of all cyanocobalamin variants (Me, Ado, HO, or CN) toward the surface-exposed BtuG protein as well as the BtuG lid closing and translocation of cyanocobalamin through the BtuBG protein will be examined extensively for the first time. The electrostatic



potential map will be calculated to understand how the different axial groups influence the extent of the electrostatic interactions as well the binding affinity.

Furthermore, the HOCbl, MeCbl, and AdoCbl acquisition by the BtuG protein in BtuBG will be studied using unbiased MD simulation, whereas the translocation free energies will be calculated using WTMtD simulations in a symmetric POPE bilayer membrane. The AdoCbl is larger in size compared to the analogous Cbl molecule and it is guite difficult to accommodate such a large substrate in the BtuBG protein cavity. Subsequently, it is interesting to investigate how the relatively large adenosylcobalamin molecule moves to and through BtuB in comparison to CNCbl. To this end, mutated BtuG having a stronger binding affinity with CNCbl, will be further considered to calculate the unbinding free energy for HOCbl, MeCbl, and AdoCbl. It was observed from the CNCbl-BtuG study that the positive pole of CNCbl was attracted by the negatively charged active site. The mutation study will shed light on effect of the acidic, aromatic, and basic amino acid restudies on the binding affinity as well as the electrostatic interactions between CNCbl and BtuG and further exploration of the binding affinity of HOCbl, AdoCbl, and MeCbl with the mutated-BtuG would be important for a detailed molecular-level understanding. Herein, we have employed unbiased molecular dynamics (MD) simulation, enhanced sampling techniques, applied field simulations and umbrella sampling to demonstrate the above-mentioned objectives.<sup>5</sup>

## Results

## Simulations of mutated BtuG

To explore the role of acidic, aromatic, and basic amino acid restudies on the binding affinity and electrostatic interaction between the active site of BtuG and CN-Cbl, the residues E55A, F58A, N107A, R133A, Y196A, and Q336A in BtuG were mutated and studied in the presence of CN-Cbl. Using multiple walker WTMtD simulations, the binding affinity of CN-Cbl towards each of the mutated BtuG proteins was determined. Moreover, the results showed that the acidic amino residues impact the binding affinity of the CN-Cbl due to the strong electrostatic interactions between the cationic dipole of CN-Cbl and the negatively charged acidic group.

#### BtuG simulations with Me-Cbl and AdoCbl

Furthermore, we explored BtuG in the presence of the Me-Cbl and AdoCbl liganda. The force field parameters for Me-Cbl and AdoCbl were obtained from the literature. Initially, a 1 µs unbiased simulation was performed to examine the stability of Me-Cbl and AdoCbl in the cavity of the BtuG protein. Figure 1 depicts the COM distances between the active site of BtuG and AdoCbl as well as Me-Cbl. In addition the ligand-bound BtuG is shown. The unbiased simulations yield that the Me-Cbl ligand molecule is remarkably stable at the active site of the BtuG protein. However, the COM distance between the AdoCbl and active site BtuG how some marginal fluctuatzion during the unbiased simulation. In a next step, the Me-Cbl and AdoCbl affinity toward BtuG was determined using multiple walker WTMtD simulations. The unbinding of the ligands from the active site using WTMtD simulations revealed that the binding affinity of Me-Cbl and AdoCbl are very similar to those of CN-Cbl.



**Figure 1: (a)** Structure of Me-Cbl boundto BtuG simulated using unbiased MD simulatios. **(b)** The COM distance between the active cavity of BtuG and Me-Cbl. **(c)** and **(d)** Same as (a) and (b) for AdoCbl bound to BtuG.



**Figure 2:** Translocation of the Me-Cbl molecule from the active site cavity of BtuG to ButB. The initial position of Me-Cbl is shown in red sticks (BtuG cavity), whereas the final position is depicted in magenta (BtuB cavity).



## Simulations of Me-Cbl bound to BtuBG

A simulation of Me-Cbl bound to the BtuBG protein was carried out in POPE bilayer to explore the translocation of Me-Cbl through the BtuBG protein. The free energy associated with the translocation process is very similar to that of the translocation process of CN-Cbl through the BtuBG channel. The WTMtD simulation showed that Me-Cbl moves toward the BtuB cavity in a tilted manner and reorients itself in the BtuBG channel during this low-energy translocation process.

Preliminary MD simulations of AdoCbl bound to BtuBG suggest that the translocation process might be difficult due to the large size and its similar binding affinity toward the BtuG protein.

## Outlook

In a next step, the translocation process of the AdoCbl will be carried out using multiple walker WTMtD simulations. The force field parameter of the HOCbl is not available in the literature. Therefore, the missing parameters will be generated, and thebinding affinity with BtuG and the translocation through the BtuBG will be examined. The mutation study revealed the importance of the acidic amino acid residues in the binding of Cn-Cbl. Therefore, a further exploration of the binding affinities of HOCbl, AdoCbl, and MeCbl with the BtuG mutated at E55A and Q336A is necessary for a detailed molecular-level understanding.

## References

- S. J. Hickman, R. E. M. Cooper, L. Bellucci, E. Paci and D. J. Brockwell, Gating of TonBdependent transporters by substrate-specific forced remodelling, *Nat. Commun.*, 2017, 8, 14804.
- 2 A. G. Wexler, W. B. Schofield, P. H. Degnan, E. Folta-Stogniew, N. A. Barry and A. L. Goodman, Human gut Bacteroides capture vitamin B 12 via cell surface-exposed lipoproteins, *Elife*, 2018, **18**, 7.
- 3 K. Jana, J. Abellón-Ruiz, U. Kleinekathöfer, and B. van den Berg, Demonstrating the function of the surface-exposed lipoprotein BtuG in efficient B12 transport in association with the outer-membrane BtuB protein (*in preparation*)
- 4 R. Obeid, S. N. Fedosov and E. Nexo, Cobalamin coenzyme forms are not likely to be superior to cyano- and hydroxyl-cobalamin in prevention or treatment of cobalamin deficiency, *Mol. Nutr. Food Res.*, 2015, **59**, 1364–1372.
- 5 J. D. Prajapati, U. Kleinekathöfer and M. Winterhalter, How to Enter a Bacterium: Bacterial Porins and the Permeation of Antibiotics, *Chem. Rev.*, 2021, **121**, 5158.



# 6.30 *hbp00067:* Excited state molecular dynamics to study the charge transfer dynamics using TDDFT/B in the frequency and time domain

HLRN Project ID:	hbp00067
Run time:	III/2020 — III/2022
Project Leader:	Professor Thomas Frauenheim
Project Scientists:	Yuxiang Liu
Affiliation:	Bremen Center for Computational Materials Science, University of Bremen

## Overview

In the past fewer years, vertical van der Waals (vdW) heterostucture constructed from graphene, and boron nitride and TMDCs, have attracted intensive attentions. Since vdW heterostructures have established a remarkable platform for photoactive applications, including photodetectors, light-emitting diodes, and atomically thin photovoltaics. Graphene/TMDCs heterostructures have been considered as prospective exciting material system in electronic and optoelectronics applications due to their ecient interfacial carrier generation. Graphene is a versatile component to couple with TMDCs due to its high carrier mobility in combination with chemical inertness, high thermal conductance, and extraordinary stability, while TMDCs' wide range of band gap broaden the detection range. Therefore, a deeper understanding of the interfacial carrier generation and transfer is essential, and the key to an improved understanding of fundamental process relevant to 2D heterostructure materials' practical applications.

## Results

With real-time time-dependent density functional theory method, we stimulated the photoinduced charge dynamics in graphene/WS<sub>2</sub> heterostructure. As show in Figure 1(A), amount of photoexcited hole transferred to graphene oscillates by periodically filling and emptying graphene states at a period of 35 fs, and a gradual accumulation of 0.30 hole on the graphene layer is observed within 100 fs. Meanwhile, photoexcited electron shows a relatively slow and steadily increasing trend, with about 0.15 electron transferring to graphene layer. These results are in accordance with results attained via transient reaction measurements and time-resolved photoemission spectroscopy, in which transfer of light-induced holes to graphene is more effcient than that of electrons, with a lifetime of 200 fs and 1 ps for hole and electron, respectively [1, 2]. Aeschlimann attributed this difference to the energetic alignment of the heterostructure, in which p-doped graphene has 6 times higher density of states available for hole transfer as compared to that for electron transfer [3]. However, in this work, pristine graphene is employed and the density of acceptor states for electrons and holes are similar.

As shown in Figure 1D, the energies of acceptor states on graphene locate between  $\varepsilon_h(t)$  and  $\varepsilon_e(t)$ . As the system evolves, both hole and electron get closer to their acceptor states. Consequently, hole and acceptor states on graphene overlap at 15 fs while this only happens at a later time 25 fs for electron. The overlap of energy states enhances the coupling between donor and acceptor states, resulting in an ultrafast charge transfer to graphene. Based on our simulation results, the faster interlayer hole transfer can be attributed to the stronger coupling. Figure 1E shows hole couples stronger to the states on graphene while electron couples



stronger to the states on WS<sub>2</sub>. Precisely, the time averaged value of  $\tau_{h;G}(t)$  is 0.27, which is twice as large as that of  $\tau_{h;W}(t)$  (0.14). This is consistent with the tunneling model founded by Krause etc al. They demonstrated that interlayer charge transfer is determined by the direct tunnelling at points in Brillouin zone where WS<sub>2</sub> and graphene band cross, while the tunneling matrix element for hole is much larger than that for electron [4]. Thus, despite the weak binding of the heterostructure, photoexcited hole interlayer transfer occurs at an ultrafast timescale. On the other hand, intralayer relaxation within WS<sub>2</sub> are more ecient for the photoexcited electron. As shown in Figure 1B-C, the excited hole delocalized more rapidly to graphene due to the strong coupling  $\tau_{h;G}(t)$ , while a large proportion of electron remains localized on the WS<sub>2</sub> layer due to the more efficient intralayer relaxation. Therefore, the ultrafast interlayer charge transfer in graphene/WS2 heterostructure is a result of competition between carrier interlayer and intralayer relaxation which is determined by the orbital coupling between donor and acceptor states.



**Figure 1:** Excitation dynamics of graphene/WS<sub>2</sub> heterostructure. (A) Amount of photoexcited hole and electron transferred from WS<sub>2</sub> to graphene. The electron and hole transfer are shown in blue and red, respectively as a function of time. Time evolution of photoexcited (B) hole and (C) electron localization  $\gamma_{e/h}(t)$  on graphene and WS<sub>2</sub> layers. (D) Time evolution of energy levels  $\varepsilon(t)$ . The color of each band indicates the degree of localization of each state to graphene and WS<sub>2</sub>, where one (red) represents that the state completely localizes to graphene, while zero (blue) represents that the state completely localizes to graphene, while zero (blue) represents that the state completely localizes to WS<sub>2</sub>. (E) Time evolution of the couplings,  $\tau_{e;G}(t)$ ,  $\tau_{e;W}(t)$ ,  $\tau_{h;G}(t)$  and  $\tau_{h;W}(t)$ . The color indicates the strength of the coupling between photoexcited carriers and acceptor states.

As aforementioned, ultrafast interlayer charge transfer in heterostructure is the result of competition between interlayer and intralayer relaxation which is controlled by the corresponding coupling. Thus, understanding how  $\tau_{e/h;L}(t)$  can be controlled by external fields is a key to manipulate charge dynamics at heterointerfaces. We apply vertical external electric fields to the heterostructure, with strengths varying from -0.3 V/A to +0.3 V/A. Comparing the couplings in Figure 2C with that in Figure 1E, the applied electric field indeed has significant effects on the coupling between donor and acceptor states. Obviously, applied with negative



electric field enhances the orbital coupling between hole and graphene states  $\tau_{h:G}(t)$ , and then facilitates interlayer hole transfer. There is 0.35 of hole transferred to graphene layer within 100 fs, which is faster than the case without electric field. Meanwhile interlayer electron transfer is completely impeded. Contrary to this, the positive electric field has the same effect on electron and thus stronger  $\tau_{e:G}(t)$  accelerates electron transfer, with 0.25 excited electron delocalized to graphene after 100 fs, compared to the amount of 0.15 in the case without electric field. These results are consistent with experimental observations in graphene/MoS<sub>2</sub>/graphene heterostructure, where applied with a -6 V top-gate bias accelerates photoexcited hole transfer to top graphene while a +4 V bias modulates the polarity of photocurrent by motivating electron transfer to graphene [5]. Therefore, by applying electric field perpendicular to the heterostructure, it it possible to accelerate or slow down interlayer charge transfer selectively and therefore aids the separation of photo-generated carriers. This offers a versatile method to control the photoinduced carrier generation, separation and transport process in graphene/TMDCs heterostructures.



**Figure 2:** Excitation dynamics of graphene/WS<sub>2</sub> heterostructure with external electric fields varying from -0.3 V/A to +0.3 V/A. (A) Amount of photoexcited electron and hole transferred from WS<sub>2</sub> to graphene. (B) Time evolution of the energy levels (t). Same color map as the Figure 1D is employed to show the charge localization. (C)Time evolution of the couplings,  $\tau_{e;G}(t)$ ,  $\tau_{e;W}(t)$ ,  $\tau_{h;G}(t)$  and  $\tau_{h;W}(t)$ . The color indicates the strength of the coupling between photoexcited carriers and acceptor states.

## **Publications**

Yuxiang Liu, Jin Zhang, Sheng Meng, ChiYung Yam, and Thomas Frauenheim Nano Letters 2021 21 (10), 4403-4409

#### References

[1] Jiaqi He, Nardeep Kumar, Matthew Z Bellus, Hsin-Ying Chiu, Dawei He, Yongsheng Wang, and Hui Zhao. Electron transfer and coupling in graphene/tungsten disulde van der waals heterostructures. Nat. Commun., 5(1):1-5, 2014.



- [2] Jiaqi He, Dawei He, Yongsheng Wang, and Hui Zhao. Probing eect of electric eld on photocarrier transfer in graphene-ws2 van der waals heterostructures. Opt. Express, 25(3):1949-1957, 2017.
- [3] Sven Aeschlimann, Antonio Rossi, Mariana Chavez-Cervantes, Razvan Krause, Benito Arnoldi, Benjamin Stadtmüller, Martin Aeschlimann, Stiven Forti, Filippo Fabbri, Camilla Coletti, et al. Direct evidence for ecient ultrafast charge separation in epitaxial ws2/graphene heterostructures. Sci. Adv., 6(20):eaay0761, 2020.
- [4] R Krause, S Aeschlimann, M Chavez-Cervantes, R Perea-Causin, S Brem, E Malic, S Forti, F Fabbri, C Coletti, and I Gierz. Microscopic understanding of ultrafast charge transfer in van-der-waals heterostructures. arXiv: 2012.09268:Cond. Mat. Mes. Hall., https://arxiv.org/abs/2012.09268 (accessed Dec. 16, 2020), 2020.
- [5] Woo Jong Yu, Yuan Liu, Hailong Zhou, Anxiang Yin, Zheng Li, Yu Huang, and Xiangfeng Duan. Highly ecient gate-tunable photocurrent generation in vertical heterostructures of layered materials. Nat. Nanotechnol., 8(12):952{958, 2013.



# 6.31 *hbp00068:* Enhanced sampling methods for constructing free energy surfaces of antibiotic permeation through porins

HLRN Project ID:	hbp00068
Run time:	IV/2020 – IV/2022
Project Leader:	Professor Dr. Ulrich Kleinekathöfer
Project Scientists:	Abhishek Acharya, Jigneshkumar D. Prajapati
Affiliation:	Jacobs University Bremen

## Overview

Development of novel antibiotics is necessary for tackling the growing menace of antibiotic resistance. In addition to effectively inhibiting a bacterial intracellular target, a prospective antibiotic molecule must also accumulate inside the bacterial cell in sufficient amount for effective antibiotic action. The effective antibiotic concentration is essentially the net result of antibiotic influx and efflux mechanism. General diffusion channels called porins have been implicated in the influx of several antibiotics such as chloramphenicol, fluoroquinones, and the  $\beta$ -lactam class of antibiotics into the Gram-negative bacterial cell. Of critical importance is the molecular mechanism of permeation in case of efficiently permeating molecules that would enable the design of improved antibiotics.



**Figure 1: A**. A cartoon representation of the OmpF channel with constriction loop at the center of the channel (in orange). This loop forms a narrow constriction region at the center that poses a large entropic barrier. **B**. Results obtained with the initial temperature accelerated sliced sampling (TASS) simulations of ciprofloxacin permeation through OmpF. The upper panel shows the one-dimensional free energy estimates obtained from three independent TASS runs in the three OmpF monomers. The error is shaded in light blue. The lower panels show for each TASS run the two-dimensional free energy surface along the *z*-vs-*z<sub>ij</sub>* space is depicted in the upper panel, where *z* describes the translation of the antibiotic along the *z*-axis and *z<sub>ij</sub>* described the orientation of the antibiotic with respect to the *z*-axis. Copyright 2020 American Chemical Society.



Recent studies have identified certain physico-chemical features that promote good accumulation. However, obtaining a detailed molecular picture of permeation that can explain the empirical trends has proved to be difficult due to the limitations of atomistic simulation methods in the study of large and complex biomolecular systems. In this project, our key objective is to employ enhanced sampling methods for the accurate estimation of free energy for the permeation of antibiotics through the OmpF porin. Enhanced sampling methods are technically superior to conventional simulation methods, and thereby allow better sampling and reliable estimates of various system properties. In this direction, we studied ciprofloxacin permeation through OmpF and demonstrated that one such method – the temperature accelerated sliced sampling (TASS) approach – shows a remarkable improvement in sampling and convergence of free energy estimates from independent simulation.

#### Results

The results of the TASS simulations are depicted in Figure 1. The one-dimensional free energy profile demonstrates good convergence and superior sampling in three independent simulations. The independent two-dimensional free energy profiles also indicate a consistent sampling of the free energy surface, particularly at the central barrier region (Figure 1B). We also used the zero-temperature string method to find the minimum free energy paths on the two-dimensional surface. Two possible paths were observed path I and path II (Figure 2). Based on the free energies along the two path we can conclude that path I is energetically more feasible that path II. This is in line with previous experimental reports on zwitterionic antibiotics of similar class.



**Figure 2:** Two-dimensional free energy surface for antibiotic permeation through OmpF and its homologs as calculated from temperature accelerated sliced sampling (TASS) simulations and minimum free energy paths (MFEPs) as calculated using the zero-temperature string as obtained for the ciprofloxacin and OmpF system. Copyright 2020 American Chemical Society.

Although the present results are quite promising, we are also in the process of simulating the translocation of other interesting antibiotics through OmpF and its homologs to demonstrate the applicability and consistency of the method towards the study of other antibiotics and porin homologs. Homologs of OmpF from other bacterial pathogens such as *Enterobacter cloacae* 



and *Klebsiella pneumoniae* show interesting variations that result in differences in pore diameter (Figure 3). Simulations of permeation through the homologous porins would be helpful in studying effect of variations in the pore on the permeation mechanism. In this direction, we have already performed TASS simulations for the permeation of ciprofloxacin through the homologs, and the preliminary data suggests that TASS enables good sampling and acceptable convergence in case of other system as well (unpublished work). Detailed analysis of the permeation paths for these systems is underway.



**Figure 3:** Structural superposition and multiple sequence alignment of the contriction loop of OmpF and its homologs – Omp35, OmpE35 and OmpK35 highlights the variations observed at the constriction. These variations result in a larger pore size in case of OmpK35 (from *Klebsiella pneumoniae*) and Omp35 (*Enterobacter aerogenes*) have been suggested to affect the permeation rates.

## Outlook

The long-term goal is to study how variations in the antibiotic and the channel properties affect the permeation rate. The TASS method enables a detailed investigation on the molecular mechanism of permeation, and studies of diverse antibiotics and OmpF homologs is expected to provide important insights that may aid in the development of novel antibacterials.

#### Publications

Acharya, A.; Prajapati, J. D.; Kleinekathöfer, U. Improved Sampling and Free Energy Estimates for Antibiotic Permeation through Bacterial Porins. J. Chem. Theory Comput. 2021, 17 (7), 4564–4577.



# 6.32 *hbp00070:* Cluster Dynamical Mean-Field Approach to correlated electron superconductivity in real materials

HLRN Project ID:	hbp00070
Run time:	II/2021 – I/2022
Project Leader:	Prof. Dr. Tim Wehling
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## Overview

Many complex phenomena and competing phases appear in materials with strong electron correlations, like Mott-insulating behavior, charge density waves, or magnetic order. In addition, unconventional superconductivity emerges in many strongly correlated materials, a state of matter with zero electrical resistance and perfect diamagnetic properties.

Over time, many materials have been found that show this complex state of matter, like heavy fermion compounds, cuprates, and potentially more recent findings in magic angle twisted bilayer graphene. An ab-initio based or realistic material specific description of superconductivity presents an outstanding problem in condensed matter physics.

In our project we attempt to advance on this and extend the analysis to material realistic descriptions based on ab initio calculations. We initially wanted to integrate Wannier- and projector-based downfolding methods [1] in the framework of cluster dynamical mean-field theory (CDMFT) and Josephson lattice model (JLM) [2]. The facilities of the HLRN enable us to run the numerically demanding large-scale calculations of the CDMFT method. However, during the run time of the project we changed our initial plan due to (i) a bug deep in the underlying code and (ii) a new experimental collaboration with the experimental group of Prof. N. Hussey (Radboud University Nijmegen, University of Bristol) on the subject.

In this report, we first give a short explanation of the code benchmarking that revealed a subtle but very serious bug in our CDMFT, more specificially its basis, the state-of-the-art Toolkit for Research on Interacting Quantum Systems (TRIQS) [3] and its Continuous-Time Hybridization (CTHYB) [4] impurity solver. Secondly, we show preliminary results of our collaboration on transport properties of overdoped cuprate materials and describe the next steps.

Since all project members moved during the run time of the project to the University of Hamburg, a follow up project at the HLRN is applied for there.

## Status report: CDMFT benchmarks

Our CDMFT code (developed by M. Harland [2]) is based on the TRIQS package [3,4]. The TRIQS package is an open source project that aims to provide high level, efficient and simple to use code libraries on which basis the scientific community can build applications and perform numerical large-scale calculations.

During benchmarks of the code, we could trace out an over two years old bug in the construction of the density operator used for the quantum Monte Carlo (QMC) sampling of the impurtity solver. This is a very dangerous bug with a hard-to-find origin that can (potentially) lead to wrong results of the QMC solver for non-density-density multi-orbital models, e.g., as

given in the superconducting state description of the CDMFT cluster. More information is given in the github issue #819 and its fix in pull request #820 [5] of the TRIQS code.

Here, we briefly want to illustrate the effect of the bug by showing a benchmark calculation for the single-orbital square lattice Hubbard model. In Figure 1 we show the different (pseudo-)spin components of the impurity Green function  $G_{imp}$  which is an output to the CTHYB solver. As can be seen, the wrong results do not show any anomalous components  $G_{\uparrow\downarrow}$  for the X- and Y-momenta which would be expected for *d*-wave superconductivity. The wrong results generally do have different shapes which are not expected.



**Figure 1:** Benchmark of CDMFT calculations in the symmetry-broken superconducting phase (Nambu space). Calculations were performed for a single-orbital square lattice Hubbard model with nearest-neighbor hopping t = -1, Hubbard interaction U/|t| = 6, chemical potential  $\mu/|t| = 2.6$  and inverse temperature  $\beta/|t| = 52$ . Reference data from Ref. [2].

## **Results: Transport properties of overdoped cuprates**

The high-temperature-superconductor (high- $T_c$ ) cuprate materials have a complex phase diagram. A longstanding problem is the description of the anomalous normal state T-linear resistivity measured in the strange metal phase [6] or optimally to overdoped region. It is different to the conventional  $T^2$ -behavior of a metal as described by Fermi liquid (FL) theory which sets in at very large dopings beyond the superconducting dome. However, the exact transition between these two phases is not clear and it is often attributed to the existence of a quantum critical point (QCP) inside the superconducting dome [7]. Recent measurements by the group of N. Hussey [6,8] indicate the possibility that the transition between these regions can be explained by two charge sectors, one with coherent quasiparticles and the other with incoherent non-quasiparticle charge carriers. If being true, it raises the question from which carriers (high- $T_c$ ) superconductivity arises and how it fits to the description of the microscopic mechanism forming this state. As such, the collaboration fits very well to the overarching goal of this project.

We aim to answer this problem by studying the applicability of a FL description and by quantifying which carriers contribute to transport. For this, we investigate the optimally to overdoped regions of a generic single-orbital Hubbard model with up to next-nearest neighbor hopping t' = 0.2, since the strange metal T-linear resistivity is an universally observed property of cuprate materials, i.e., independent of the particular material details.

The overdoped region of cuprates is far away from the antiferromagnetic quasi-ordering at half-filling and as such does not contain long-ranged antiferromagnetic fluctuations. In CDMFT, we use a 2x2 cluster which should sufficiently describe the system in this region. On the other hand, the limitations of a FL description can be studied well in perturbative weak-coupling approaches. Because of this, we performed additional calculations using the Fluctuation Exchange (FLEX) approximation which we recently implemented in a very efficient numerical basis because of which we can reach very low temperatures (10<sup>-4</sup> in units of the bandwidth) [9]. Contrary to CDMFT, we also have a good momentum-resolution of quantities in FLEX. By comparing complementary approaches, we gain an unbiased insight on the properties of the model these two We performed several CDMFT and FLEX calculations for different temperatures and dopings on the HLRN cluster.



The temperature dependence of the resistivity ( $\propto T \text{ or } \propto T^2$ ) and its doping dependence can be characterized by analyzing scattering rates or inverse lifetimes  $\gamma = \tau^{-1}$ . We obtain these from the zero-frequency limit of imaginary part of the self-energy Im $\Sigma(i\omega_n \rightarrow 0)$ . In the analysis of coherent and incoherent charge carriers as well as the pseudo gap phenomenon<sup>3</sup>, the nodal (N) and antinodal (AN) directions in momentum space take a special role. In Figure 2 we show the temperature dependence of the N and AN scattering rates for different hole dopings p as obtained from FLEX and CDMFT. At large dopings, N and AN scatterings are the same and follow a T<sup>2</sup> power law. For smaller dopings the N and AN curves start to split and gain T-linear components. In comparison, the AN scattering becomes more linear and a dichotomy between both regions develop. Both methods CDMFT and FLEX show the same qualitative behavior, indicating a shared physical origin. Recent calculations using the Dynamical Cluster Approximation, a related cluster extension of DMFT, found similar results [10]. This behavior can be well explained by the formation of short-ranged spin fluctuations arising from Fermi surface nesting which affect the AN region of the Fermi surface more than the N region.



**Figure 2**: Temperature dependence of the scattering rates (inverse lifetimes) at the nodal (N) and antinodal (AN) points for dopings in the optimally ( $p \sim 0.18$ ) to overdoped region ( $p \gtrsim 0.2$ ). Calculations were performed using the FLEX and CDMFT method.

## Outlook

Currently, we are analyzing FLEX and CDMFT data for different parameters to gauge their influence. In addition, we are calculating transport properties (conductivity, Hall resistance) to understand how the nodal-antinodal dichotomy affects them and to compare with experimental data [8]. Additionally, we plan to perform CDMFT calculations in the symmetry-broken superconducting state in order to determine a phase transition line and draw a comprehensive phase diagram. We believe that the results can be summarized in a publication in the next half year.

In the next year we also want to address the material realistic description of superconductivity in cuprate materials as initially planned. This consists of a two step process: The first part entails the model building by downfolding techniques [1] and generating material realistic input for the CDMFT calculations. The second part entails the numerically highly-demanding CDMFT calculations with which we plan to sample temperature-doping phase diagrams for the downfolded models of different cuprate materials (La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub>, HgBa<sub>2</sub>CuO<sub>4</sub>, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>) [11]. We want to compare these to existing models and analyze the influence of lattice

<sup>&</sup>lt;sup>1</sup> The pseudo gap is a precursor to the superconducting state in which momentum-selected spectral weight of the Fermi surface in the antinodal direction is suppressed.



distortions within the JLM as experimentally realized by the Cavalleiri group in Hamburg [12]. A follow-up project (hhp00056) at the University of Hamburg is currently under review.

## Presentations

N. Witt, T. Wehling, Joined seminar with Nijmegen/Bristol, University of Hamburg (digital), December 13<sup>th</sup>, 2021

## References

- [1] M. Rösner, E. Şaşıoğlu, C. Friedrich, S. Blügel, Phys. Rev. B 92, 085102 (2015)
- [2] M. Harland, S. Brener, A. I. Lichtenstein, M. I. Katsnelson, Phys. Rev. B 100, 024510 (2019); Code available at: https://github.com/MHarland/cdmft
- [3] O. Parcollet, M. Ferrero, T. Ayral, H. Hafermann, I. Krivenko, L. Messio, P. Seth, Comp. Phys. Comm. 196, 308 (2015); Code available at: https://github.com/TRIQS
- [4] P. Seth, I. Krivenko, M. Ferrero, O. Parcollet, Comp. Phys. Comm. 200, 274 (2016)
- [5] GitHub Issue #819: https://github.com/TRIQS/triqs/issues/819 GitHub pull Request #820: https://github.com/TRIQS/triqs/pull/820
- [6] J. Ayres, M. Berben, M. Čulo, Y.-T. Hsu, E. van Heumen, Y. Huang, J. Zaanen, T. Kondo, T. Takeuchi, J. R. Cooper, C. Putzke, S. Friedemann, A. Carrington, N. E. Hussey, Nature **595**, 661 (2021)
- [7] B. Keimer, S. A. Kivelson, M. R. Norman, S. Uchida, J. Zaanen, Nature 518, 179 (2015)
- [8] M. Culo, C. Duffy, J. Ayres, M. Berben, Y.-T. Hsu, R. D. H. Hinlopen, B. Bernáth, N. Hussey, SciPost Phys. 11, 012 (2021)
- [9] N. Witt, E. G. C. P. van Loon, T. Nomoto, R. Arita, T. Wehling, Phys. Rev. B 103, 205148 (2021); Code available at: https://github.com/nikwitt/FLEX\_IR
- [10] W. Wu, X. Wang, A.-S. Tremblay, arXiv: 2109.02635
- [11] M. Hirayama, Y. Yamaji, T. Misawa, M. Imada, Phys. Rev. B 98, 134501 (2018)
- [12] R. Mankowsky, A. Subedi, M. Först, S. O. Mariager, M. Chollet, H. T. Lemke, J. S. Robinson, J. M. Glownia, M. P. Minitti, A. Frano, M. Fechner, N. A. Spaldin, T. Loew, B. Keimer, A. Georges, A. Cavalleri, Nature **516**, 71 (2014)



## 6.33 nak00001: Seamless sea ice prediction with AWI Climate Model

HLRN Project ID:	nak00001
Run time:	III/2021 – II/2022
Project Leader:	Dr. Goessling
Project Scientists:	L. Mu, L. Nerger, S. Losa, M. Athanase
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## Overview

The Young Investigator Group Seamless Sea-Ice Prediction (SSIP) funded by BMBF aims at advancing sea-ice prediction capacity on timescales from hours to years and beyond. A core activity of the group is to develop a seamless sea ice prediction system based on a state-of-the-art climate model. The latter is combined with a sophisticated data assimilation system for the estimation of forecast initial conditions. The system also allows for new approaches to model error diagnosis and parameter optimization.

The recently developed climate model AWI-CM3.0 in the Alfred-Wegener-Institute (AWI), which is based on the finite volume sea ice-ocean model FESOM2.0 for the ocean component and the Integrated Forecasting System (OpenIFS) developed by European Centre for Medium-Range Weather Forecasts for the atmosphere component, has shown faster integrations and relatively reliable simulations in the polar regions than its ancestor AWI-CM1.1 which uses the finite-element sea ice-ocean model FESOM1.0 and the atmosphere model ECHAM from the Max Planck Institute for Meteorology. We have adapted our previous seamless sea ice prediction system based on AWI-CM1.1 to AWI-CM3.0. The project continued the successful development of the SSIP2 system, which required running extensive sets of re-forecasts for the recent two decades for testing, evaluation, and optimization. Our further developments are targeted at the improvement of seasonal sea-ice prediction skill, in particular by complementing the Ensemble-Kalman Filter (EnKF)-based data assimilation in the ocean/sea-ice component with relaxation (nudging) of the large-scale atmospheric dynamics based on atmospheric (re-)analysis data and associated recalibration of the EnKF.

## Results

Thanks to the computational resources granted by HLRN, we have successfully completed the development of version 2.0 of the AWI seamless sea ice prediction system (Mu et al., 2021, 2022). The system was further updated based upon a higher-resolution version of the atmospheric component (OpenIFS) of the AWI-CM3. The new resolution (TCO159L91 vs. TL159L60) features 91 instead of 60 vertical levels as well as a higher horizontal grid-point resolution by a factor 2 (times 2 dimensions) while the horizontal spectral resolution (where the model dynamics are computed) is the same.

We have conducted several experiments with the updated SSIP2.1 system assimilating different types of observations (sea ice concentration, sea ice thickness, sea ice velocity, sea surface height, sea surface temperature, sea surface salinity, temperature and salinity profile observations). Figure 1 depicts results exemplifying the SSIP performance for January 2016 (with the general setting following the study by Mu et. al 2022). As in Mu et. al. (2022), the data assimilation is implemented with the Parallel Data Assimilation Framework (PDAF; Nerger and

Hiller, 2013) and based upon the experiences gained with the first version based on AWI-CM1.0 (Mu et al., 2020, Nerger et al. 2020).

To further develop the SSIP system, we have introduced and use the nudging method to constrain the atmosphere with large-scale dynamics (winds) from reanalysis (ERA5). First sensitivity experiments with nudging in the atmosphere without oceanic data assimilation allowed to identify a setting suitable for experiments with oceanic data assimilation and nudged atmosphere combined. The setting we are now using nudged only divergence and vorticity above 700hPa (that is, leaving the boundary layer free) and nudging only large wave numbers up to T20, so that a certain level of ensemble spread is maintained. Figure 2 shows that this setup, without ocean data assimilation, is able to reproduce spatial patterns of anomalies of sea-ice concentrations, exemplified for October 2017 (in comparison with ERA5 and AWICM3 without nudging).



**Figure 1:** Example of the SSIP performance on a daily basis in January 2016. Upper panels depict spatial distribution of the sea ice thickness as observed (a), predicted (b) and SSIP analysis on 2 January 2016.



**Figure 2:** Example of sea-ice concentration (SIC, %) anomalies in October 2017, in (a) ERA5, (b) AWI-CM-3 nudged simulation and (c) AWI-CM-3 simulation without nudging.



When applied in our forecast system, the nudging impacts significantly the ensemble spread in the atmosphere and in the assimilated ice/ocean ensemble, which requires intense sensitivity study.

## Outlook

The SSIP system with atmospheric nudging will be calibrated to enable good predictive skills and sea ice state analysis over last two decades.

## Publications

L. Mu, L. Nerger, J. Streffing, Q. Tang, B. Niraula, L. Zampieri, H.F. Goessling, Verification of sea ice forecasts in the AWI Seamless Sea Ice Prediction System (version 2). In preparation.

#### Presentations

L. Mu, J. Streffing, L. Nerger, Q. Tang, H. F. Goessling, A second version of the seamless sea ice prediction system based on AWI-CM3. 10th International Workshop on Sea Ice Modelling, Data Assimilation and Verification. Toulouse, France, online 26 to 28 October 2021

#### References

- L. Mu, L. Nerger, Q. Tang, S.N. Losa, D. Sidorenko, Q. Wang, T. Semmler, L. Zampieri, M. Losch, H.F. Goessling, Towards a data assimilation system for seamless sea ice prediction based on the AWI Climate Model. Journal of Advances in Modeling Earth Systems, p.e 2019MS001937, https://doi.org/10.1029/2019MS001937
- L. Nerger, Q. Tang, L. Mu, 2020. Efficient ensemble data assimilation for coupled models with the Parallel Data Assimilation Framework: example of AWI-CM (AWI-CM-PDAF 1.0). Geoscientific Model Development, 13(9), pp.4305-4321.
- L. Nerger and W. Hiller, 2013. Software for ensemble-based data assimilation systems -Implementation strategies and scalability. Computers & Geosciences, 55, pp.110-118.