

FACET

DACG NEWSLETTER

March 2018

issue 1

FACET

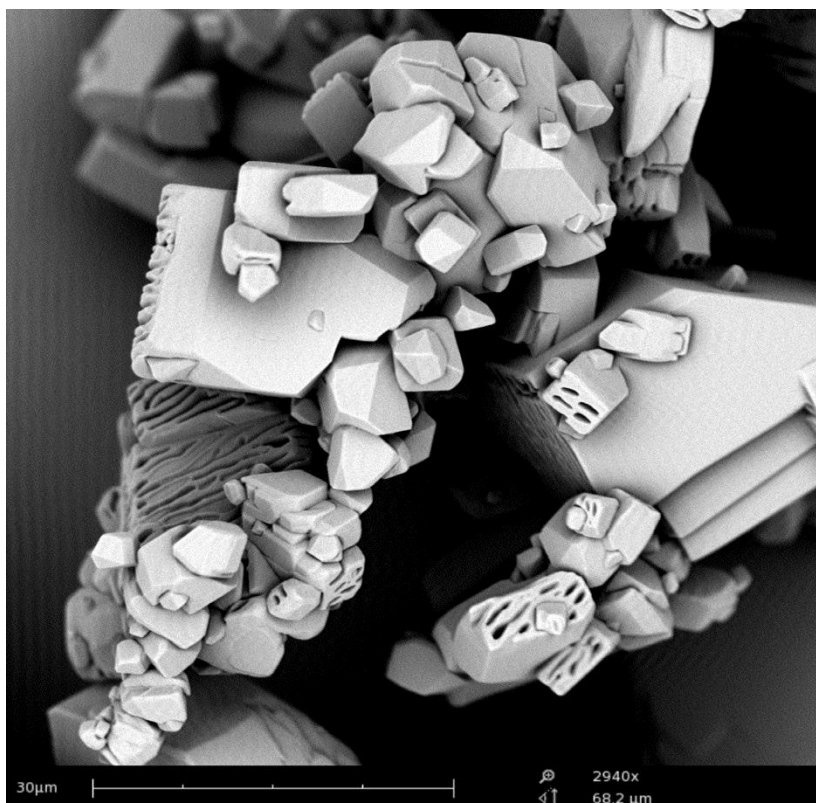
Newsletter of the Dutch
Association for Crystal Growth
(DACG), section of the KNCV and
the NNV.

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Cover figure

API (active pharmaceutical ingredient) crystals having issues with too high solvent content. SEM analysis reveals the hollow structure of crystals. The solvent is trapped in the cavities and cannot escape freely during drying.

The figure is provided by William de Wildt from Aspen Oss B.V. in Oss.

From the editor

This year's first issue of the FACET concentrates on upcoming events and a long list of recently published articles.

The DACG spring meeting will be held in Amsterdam on April 6th. We are looking forward to seeing you there!

Also, do not forget to send in your candidates for the KNCV Piet Bennema Prize for Crystal Growth before April 30th.

As always, it is easy to contribute to the FACET: recently published articles and theses, photos for cover figure, relevant announcements, ... Contributions may be delivered by mail, [e-mail](#), or telephone. Your ideas are welcome, please notify the editor: [Marketta Uusi-Penttilä](#)

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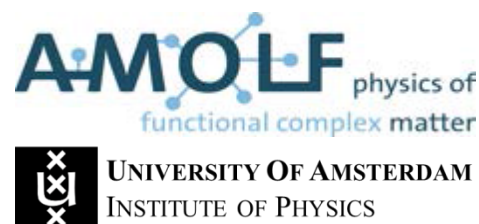
Upcoming events

- DACG Spring Symposium, 6 April 2018, Amsterdam
 - Farewell symposium Willem van Enckevort, 1 June 2018, Radboud University
 - DACG Fall Meeting, October 2018; location and date to be decided
-

Announcement

Program DACG Spring Symposium

Organizers: Dr. Wim Noorduyn and Dr. N. Shahidzadeh
 Amsterdam, 6th April 2018



The Spring Symposium has Prof. Kevin Roberts from University of Leeds as a guest lecturer. Prof. Roberts is an expert on several areas of crystallization including crystallization fundamentals, experimental crystallization science, chemical process r&d, process analytical technology (PAT), synchrotron radiation techniques and crystallization engineering.

This time the symposium includes poster sessions.

For registration see **registration form on next page**.

Tentative Program

9.30-9.50	Arrival/Registration/Coffee
9.50-10.00	Opening
10.00-11.45	Presentations 1-3
	1. Kevin Roberts (University of Leeds) <i>"The structural pathway of para amino benzoic acid from solvated molecule through solute clustering to the growth of faceted crystals"</i>
	2. Ton Engwerda (Radboud University Nijmegen) <i>"Deracemization of a racemic compound by using tailor-made additives"</i>
	3. Mohsin Qazi (University of Amsterdam) <i>"Influence of wetting on salt creeping"</i>
11.45-12.30	Poster pitch
12.30-13.30	Lunch, posters
13.30-15.00	Presentation 4 -6
	4. Nico Sommerdijk (Eindhoven University of Technology) <i>"Understanding particle based crystallization in magnetite formation"</i>
	5. Arjun Wadhawan (University of Amsterdam) <i>"Understanding Methane Hydrate Nucleation using Advanced Molecular Simulation"</i>
	6. Krassimir Velikov (Unilever Vlaardingen R&D) <i>"Colloid nanoconfinement as a tool to suppress crystallization"</i>
15.00-15.30	Coffee/posters
15.30-16.15	Presentation 7
	7. Daniël Vanmaekelbergh (Utrecht University) <i>"Formation of atomically coherent honeycomb structures by interfacial assembly of colloidal nanocrystals"</i>
16.15-16.20	Closing remarks
16.15-17.00	Labtour UvA/Closing drinks

DACG Spring Symposium at UvA/AMOLF

Amsterdam, 6th April 2018

Organizers:
Dr. Wim Noorduin and Dr. N. Shahidzadeh



UNIVERSITY OF AMSTERDAM
INSTITUTE OF PHYSICS



REGISTRATION FORM

For registration, please complete this form and send the scanned form as an attachment to dacg-spring2018@amolf.nl, preferably **before 30 March 2018**.

The symposium fee (including coffee, lunch and drinks) is:

- 20 EURO for students and DACG members
- 30 EURO for non-members (you will be offered to be enrolled as a DACG member in 2018)

--Payment: at the meeting in cash

=====

--Name: (first name and surname)

--Email:

--Affiliation:

--Postal address:

--Postal code:

--City:

--Member DACG / student / None of the two

--Dietary requirements for lunch:

--Poster (including 2 minute poster pitch): yes/no

Title:

=====



Announcement KNCV Piet Bennema Prize for Crystal Growth

Every three years the Dutch Association for Crystal Growth DACG distinguishes a young researcher with the KNCV Piet Bennema Award for Crystal Growth for his high-level scientific research in the field of crystal growth. The prize is intended for the author of the best dissertation or other scientific publications (or a series thereof) that have been processed in an industrial context and are of similar importance to a dissertation. The prize consists of a certificate and a sum of money of € 1000.

Piet Bennema

Piet Bennema (1932-2016) is one of the founders of the study of crystal growth in the Netherlands. As a professor of chemistry of the solid state from 1976 until his retirement in 1998, he was affiliated with the Radboud University Nijmegen. In this period he elaborated on the theoretical concepts of crystal growth, leading to an improved understanding of the role of the bond strength in the prediction of the morphology of crystals and the role of supersaturation, two-dimensional nucleation, kinetic roughening and spiral growth during crystal growth processes. For his important contributions to the field of crystal growth, he was awarded the Frank Award in 1995 by the International Organization for Crystal Growth.

Candidates

For the award of the prize both young Dutch and non-Dutch are eligible who have largely carried out their research in the scientific field of crystal growth at a Dutch university or a Dutch company.

The candidate must have shown great competence as a researcher as well as scientific originality and productivity. Moreover, it must have a good understanding of the problems of the field.

For candidates who want to be considered on the basis of their dissertation, the dissertation must have been successfully defended at a Dutch university in the three years prior to the closing of the submission deadline. For academic publications, it also applies that these must have been published for the most part in the preceding three-year period.

Nomination

Supervisors can nominate candidates by means of a letter of recommendation with the thesis or other scientific publications, as well as a motivation. The nomination must be submitted in triplicate to the secretary of the DACG. The submission period for the KNCV Piet Bennema Prize for Crystal Growth is from **1 January 2018 to 30 April 2018**.

Award presentation

The KNCV Piet Bennema Award for Crystal Growth is awarded by the KNCV Board on the recommendation of the DACG Board. To this end, the board of the DACG appoints an assessment committee of three experts, who will test the candidates against their competence in the research of crystal growth, scientific quality, productivity and originality and insight into the field.

The presentation of the prize and the associated certificate will take place during the autumn meeting of the DACG in October 2018.

On behalf of the board of the DACG

Prof. dr. A.E.D.M. van der Heijden
Secretary DACG

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Regulations for the KNCV Piet Bennema Prize for Crystal Growth

1. The Board of the KNCV awards a prize once every three years, consisting of a certificate and a sum of € 1000 to a young researcher for high-level scientific research in the field of crystal growth.
2. The prize is intended for the author of the best dissertation or other scientific publications (or a series thereof) that have been processed in an industrial context and are of similar importance to a thesis. The dissertation must be successfully defended at a Dutch university during the three-year period preceding the selection procedure. The scientific publications should also have appeared in the previous three-year period.
3. The prize will be awarded by the KNCV Board on the basis of a recommendation issued by the Board of the Netherlands Association for Crystal Growth. If the board of the association does not nominate a candidate, no prize will be awarded.
4. The KNCV Board may adopt or reject the recommendation referred to under 3. above. In the latter case the prize is not awarded.
5. Researchers who have carried out their research largely at a Dutch university or at a Dutch company are eligible for the award of the certificate.
6. The requirements for the award are that the candidate must have shown great competence as a researcher as well as scientific originality and productivity. In addition, he / she must have a good understanding of the problems of the field.
7. The Board of the Dutch Association for Crystal Growth ensures that all activities in the context of points 1 to 6 of these regulations are carried out.
8. The Board of the Dutch Association for Crystal Growth will be supported in its work by three experts, from whom it can be expected that they have a good overview of the work of researchers in the field of crystal growth. The experts provide their advice in writing, with documentation, such as publications. Members of the assessment committee cannot nominate candidates themselves.
9. The presentation of the KNCV Piet Bennema Prize for Crystal Growth takes place during the annual meeting of the Dutch Association for Crystal Growth. Justification of the award will be published after the award ceremony in the Chemisch2Weekblad

Membership

Becoming a member of the DACG is easy: send an e-mail message to [Antoine van der Heijden](#).

The annual membership fee in 2018 is € 15 for professionals, € 10 for retired people and € 5 for (PhD) students.

DACG membership runs from 1 January to 31 December of each year. Participating in one of the biannual symposia for the first time automatically includes a membership for that year.

Farewell symposium Willem van Enkevort

1 June 2018, Radboud University



Location: lecture room LIN6
Linnaeusgebouw Collegezalen.

Registering details will appear on the website (www.dacg.nl)

Program

- 13:30 Elias Vlieg & Hugo Meekes (Radboud University)
Welcome / introduction
- 13:45 Marcel Verheijen (Philips Innovation Labs, Technical University Eindhoven)
Semiconductor nanowire growth; microscopy and kinetics
- 14:15 Bernard Kaptein (Innosyn BV, Geleen)
Title to be announced
- 14:45 John Schermer (Radboud University)
Crystal structures for optimal solar energy harvesting
- 15:15 *Coffee/tea break*
- 15:45 Katsuo Tsukamoto (Tohoku University, Osaka University, Japan)
Microscopy of crystal surfaces
- 16:15 Willem van Enkevort
Four decades of watching crystals
- 17:00 *Reception*

Organizing committee: Hugo Meekes
Elias Vlieg
Elizabeth Salem

Sponsored by the Dutch Association for Crystal Growth

Recent publications

- Amirmehdi Saedi and Marcel J. Rost, [Thermodynamics of deposition flux-dependent intrinsic film stress](#), *Nature Communications*, **7** (2016), 10733.

Affiliations:

- Huygens-Kamerlingh Onnes Laboratory, Leiden University, Niels Bohrweg 2, Leiden 2333 CA, The Netherlands

Vapour deposition on polycrystalline films can lead to extremely high levels of compressive stress, exceeding even the yield strength of the films. A significant part of this stress has a reversible nature: it disappears when the deposition is stopped and re-emerges on resumption. Although the debate on the underlying mechanism still continues, insertion of atoms into grain boundaries seems to be the most likely one. However, the required driving force has not been identified. To address the problem we analyse, here, the entire film system using thermodynamic arguments. We find that the observed, tremendous stress levels can be explained by the flux-induced entropic effects in the extremely dilute adatom gas on the surface. Our analysis justifies any adatom incorporation model, as it delivers the underlying thermodynamic driving force. Counterintuitively, we also show that the stress levels decrease, if the barrier(s) for adatoms to reach the grain boundaries are decreased.

- Leon Jacobse, Yi-Fan Huang, Marc T. M. Koper, and Marcel J. Rost, [Correlation of surface site formation to nanoisland growth in the electrochemical roughening of Pt\(111\)](#), *Nature Materials*, **17** (2018), 277-282.

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Platinum plays a central role in a variety of electrochemical devices and its practical use depends on the prevention of electrode degradation. However, understanding the underlying atomic processes under conditions of repeated oxidation and reduction inducing irreversible surface structure changes has proved challenging. Here, we examine the correlation between the evolution of the electrochemical signal of Pt(111) and its surface roughening by simultaneously performing cyclic voltammetry and in situ electrochemical scanning tunnelling microscopy (EC-STM). We identify a 'nucleation and early growth' regime of nanoisland formation, and a 'late growth' regime after island coalescence, which continues up to at least 170 cycles. The correlation analysis shows that each step site that is created in the 'late growth' regime contributes equally strongly to both the electrochemical and the roughness evolution. In contrast, in the 'nucleation and early growth' regime, created step sites contribute to the roughness, but not to the electrochemical signal.

- Paul J. M. Smeets, Aaron R. Finney, Wouter J. E. M. Habraken, Fabio Nudelman, Heiner Friedrich, Jozua Laven, James J. De Yoreo, P. Mark Rodger, and Nico A. J. M. Sommerdijk, [Classical view on nonclassical nucleation](#), *Proceedings of the National Academy of Sciences of the United States of America*, (2017)

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- EaStCHEM, School of Chemistry, University of Edinburgh, Edinburgh EH9 3FJ, United Kingdom;
- Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99352;
- Department of Materials Science and Engineering, University of Washington, Seattle, WA 98195

Understanding and controlling nucleation is important for many crystallization applications. Calcium carbonate (CaCO_3) is often used as a model system to investigate nucleation mechanisms. Despite its great importance in geology, biology, and many industrial applications, CaCO_3 nucleation is still a topic of intense discussion, with new pathways for its growth from ions in solution proposed in recent years. These new pathways include the so-called nonclassical nucleation mechanism via the assembly of thermodynamically stable prenucleation clusters, as well as the formation of a dense liquid precursor phase via liquid-liquid phase separation. Here, we present results from a combined experimental and computational investigation on the precipitation of CaCO_3 in dilute aqueous solutions. We propose that a dense liquid phase (containing 4–7 H_2O per CaCO_3 unit) forms in supersaturated solutions through the association of ions and ion pairs without significant participation of larger ion clusters. This liquid acts as the precursor for the formation of solid CaCO_3 in the form of vaterite, which grows via a net transfer of ions from solution according to $z \text{Ca}^{2+} + z \text{CO}_3^{2-} \rightarrow z \text{CaCO}_3$. The results show that all steps in this process can be explained according to classical concepts of crystal nucleation and growth, and that long-standing physical concepts of nucleation can describe multistep, multiphase growth mechanisms.

- Paul J. M. Smeets, Kang Rae Cho, Nico A. J. M. Sommerdijk, James J. De Yoreo, [A Mesocrystal-Like Morphology Formed by Classical Polymer-Mediated Crystal Growth](#), *Advanced Functional Materials*, **27** (2017), Issue 40, 1701658.

Affiliations:

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Growth by oriented assembly of nanoparticles is a widely reported phenomenon for many crystal systems. While often deduced through morphological analyses, direct evidence for this assembly behavior is limited and, in the calcium carbonate (CaCO_3) system, has recently been disputed. However, in the absence of a particle-based pathway, the mechanism responsible for the creation of the striking morphologies that appear to consist of subparticles is unclear. Therefore, in situ atomic force microscopy is used to investigate the growth of calcite crystals in solutions containing a polymer additive known for its ability to generate crystal morphologies associated with mesocrystal formation. It is shown that classical growth processes that begin with impurity pinning of atomic steps, leading to stabilization of new step directions, creation of pseudo-facets, and extreme surface roughening, can produce a microscale morphology previously attributed to nonclassical processes of crystal growth by particle assembly.

- Gopi Krishnan, Sytze de Graaf, Gert H. ten Brink, Marcel A. Verheijen, Bart J. Kooi and George Palasantzas, [Shape and structural motifs control of MgTi bimetallic nanoparticles using hydrogen and methane as trace impurities](#), *Nanoscale*, **10** (2018), 1297-1307.

Affiliations:

- Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
- Center for Nanosciences and Molecular medicine, Amrita University, Kochi, India
- Department of Applied Physics, Eindhoven University of Technology, 5600 MB, Eindhoven, The Netherlands

In this work we report the influence of methane/hydrogen on the nucleation and formation of MgTi bimetallic nanoparticles (NPs) prepared by gas phase synthesis. We show that a diverse variety of structural motifs can be obtained from MgTi alloy, $\text{TiC}_x/\text{Mg}/\text{MgO}$, TiC_x/MgO and TiH_x/MgO core/shell NPs via synthesis using CH_4/H_2 as a trace gas, and with good control of the final NP morphology and size distribution. Moreover, depending on the concentration of Ti and type of employed trace gas, the as prepared MgTi NPs can be tuned from truncated hexagonal pyramid to triangular and hexagonal platelet shapes. The shape of MgTi NPs is identified using detailed analysis from selected area electron diffraction (SAED) patterns and tomography (3D reconstruction based on a tilt series of Bright-Field transmission electron microscopy (TEM) micrographs). We observe the truncated hexagonal pyramid as a shape of MgTi alloy NPs in contrast to Mg NPs that show a hexagonal prismatic shape. Moreover, based on our experimental observations and generic geometrical model analysis, we also prove that the formation of the various structural motifs is based on a sequential growth mechanism instead of phase separation. One of the prime reasons for such mechanism is based on the inadequacy of Mg to nucleate without template in the synthesis condition. In addition, the shape of the $\text{TiC}_x/\text{TiH}_x$ core, and the concentration of Mg have strong influence on the shape evolution of TiC_x/MgO and TiH_x/MgO NPs compared to $\text{TiC}_x/\text{Mg}/\text{MgO}$ NPs, where the thermodynamics and growth rates of the Mg crystal planes dominate the final shape. Finally, it is demonstrated that the core shape of TiC_x and TiH_x is affected by the Mg/Ti target ratio (affecting the composition in the plasma), and the type of the trace gas employed. In the case of CH_4 the TiC_x core forms a triangular platelet, while in the case of H_2 the TiH_x core transforms into a hexagonal platelet. We elucidate the reason for the $\text{TiC}_x/\text{TiH}_x$ core shape based on the presence of (i) defects, and (ii) hydrogen and carbon adsorption on $\{111\}$ planes that alter the growth rates and surface facet stabilization.

- V. Vonk, D. Pontoni, M. Cremers, A. Kerkenaar, A.A.C. Bode, W. Szweryn, G. Nowak, A.E.F. de Jong, H. Dosch, E. Vlieg, [Observation of ultrathin precursor film formation during Ge-Si liquid-phase epitaxy from an undersaturated solution](#), *Langmuir*, **33** (2017), 814-819.

Affiliations:

- Institute for Molecules and Materials, Radboud University Nijmegen, Nijmegen 6525AJ, The Netherlands
- Deutsches Elektronen-Synchrotron (DESY), Hamburg 22607, Germany
- European Synchrotron Radiation Facility, Grenoble 38000, France

Our in situ X-ray study shows that a silicon substrate in contact with an undersaturated In(Ge) solution is wetted by an approximately 1 nm thin germanium film, which does not grow any thicker. The results can be understood by the use of thickness-dependent correlated interfacial energies. This near-equilibrium heterogeneous interface structure marks the initial stage of crystal growth before the formation of bulk material, which can only form under conditions of supersaturation. This finding uncovers a fundamental aspect of the thermodynamics at solid-liquid interfaces relevant for understanding the transition from equilibrium to supersaturation and is of importance for nanoscale solution growth methods.

- E. Grothe, H. Meekes, R. de Gelder, [Searching for stereoisomerism in crystallographic databases: algorithm, an analysis and chiral curiosities](#), *Acta Cryst.*, **B73** (2017), 453-464.

Affiliations:

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The automated identification of chiral centres in molecular residues is a non-trivial task. Current tools that allow the user to analyze crystallographic data entries do not identify chiral centres in some of the more complex ring structures, or lack the possibility to determine and compare the chirality of multiple structures. This article presents an approach to identify asymmetric C atoms, which is based on the atomic walk count algorithm presented by Rücker & Rücker [(1993), *J. Chem. Inf. Comput. Sci.* **33**, 683–695]. The algorithm, which we implemented in a computer program named *ChiChi*, is able to compare isomeric residues based on the chiral centres that were identified. This allows for discrimination between enantiomers, diastereomers and constitutional isomers that are present in crystallographic databases. *ChiChi* was used to process 254 354 organic entries from the Cambridge Structural Database (CSD). A thorough analysis of stereoisomerism in the CSD is presented accompanied by a collection of chiral curiosities that illustrate the strength and versatility of this approach.

- E.R. Townsend, W.J.P. van Enkevort, J.A.M. Meijer, E. Vlieg, [Additive enhanced creeping of sodium chloride crystals](#), *Cryst. Growth Des.*, **17** (2017), 3107-3115.

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This article investigates the mechanism behind the creeping of sodium chloride induced by additives. Here, an experimental approach is complemented with theoretical considerations to describe how creeping patterns of brine evolve and how the introduction of additives into the solution affects the morphology of the resultant crystals. We have found that these additives cause kinetic roughening and

morphological instability mainly due to the reduction of surface free energy. There was also a marked increase in three-dimensional nucleation of the NaCl crystals and thus branching.

- M.M.H. Smets, E. Kalkman, P. Tinnemans, A.M. Krieger, H. Meekes, H.M. Cuppen, [Polymorphism of the quasiracemate d-2-aminobutyric acid:l-norvaline](#), *Cryst. Eng. Comm*, **19** (2017), 5604-5610.

Affiliations:

- Institute for Molecules and Materials, Radboud University Nijmegen, Nijmegen 6525AJ, The Netherlands

Here we report two new crystal structures of the amino acid quasiracemate D-2-aminobutyric acid:L-norvaline, as well as the fully reversible solid-state phase transition which connects the two forms. The room temperature form II is obtained by co-crystallisation through slow evaporation from an equimolar aqueous solution. Form I is obtained through cooling of form II below 150 K. The crystal structures of forms I and II have been determined using single crystal X-ray diffraction at 100 and 150 K, respectively. Both forms consist of 2D hydrogen bonded bilayers with an LD-LD hydrogen bonding pattern. The room temperature form II shows two conformations for the L-norvaline side chain in a disordered 50/50 occupancy distribution. The solid-state phase transition between the two polymorphic forms involves a displacement of the bilayers and conformational changes in all molecules. It has been further characterised using differential scanning calorimetry and thermal polarisation microscopy. These crystal structures and the single-crystal-to-single-crystal phase transition are similar to other quasiracemates and racemates of linear chain aliphatic amino acids.

- W. de Poel, S.L. Vaessen, J. Drnec, A.H.J. Engwerda, E.R. Townsend, S. Pintea, A.E.F. de Jong, M. Jankowski, F. Carla, R. Felici, J.A.A.W. Elemans, W.J.P. van Enckevort, A.E. Rowan, E. Vlieg, [Metal ion-exchange on the muscovite mica surface](#), *Surface Science*, **665** (2017), 56-61.

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The surface potassium ions of muscovite mica were exchanged for several different metal ions from aqueous solution (Ag, Ca, V, Mn, Fe, Ni, Cu, Zn, Co, and Cd). The surfaces were rinsed in water, dried under nitrogen atmosphere, and subsequently analysed using atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and, for half the systems, surface X-ray diffraction (SXRD). XPS and SXRD confirmed the presence of the different metal ions at the muscovite mica surface, with a partial monolayer of the monovalent and divalent ions present on the surface. No counter ions from the used salts were detected. AFM revealed that Ni-, and Fe-terminated muscovite mica surfaces were partially covered by nanoparticles, most likely consisting of metal (hydr)oxide. The exchanged ions remained on the surface after rinsing with ultra pure water three times. SXRD showed that Cd and Ag have a lower affinity for the muscovite mica surface than Cu, Ca, and Mn.

- A.H.J. Engwerda, P. van Schayik, H. Jagtenberg, H. Meekes, F.P.J.T. Rutjes, E. Vlieg, [Solid Phase Deracemization of an atropisomer](#), *Cryst. Growth Des.*, **17** (2017), 5583-5585.

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Atropisomers are chiral rotamers that possess an axis of chirality. By applying temperature cycling or Viedma ripening, one such atropisomer could successfully be deracemized.

The scope of Viedma ripening and temperature cycling with respect to chiral molecules has remained mostly limited to molecules with a single stereogenic center, while racemization proceeds through inversion at that particular stereocenter. In this article we demonstrate for the first time that atropisomers, chiral rotamers that possess an axis of chirality, can be successfully deracemized in the solid phase by either applying temperature cycling or Viedma ripening.

- L.C. Sögütöglu, M. Lutz, H. Meekes, R. de Gelder, E. Vlieg, [Polymorphism and Modulation of Para-Substituted L-Phenylalanine](#), *Cryst. Growth Des.*, **17** (2017), 6231-6238.

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The crystal structure of para-methyl-L-phenylalanine at 230 K resembles that of the para-fluorinated analogue from the literature but is commensurately modulated with seven molecules in the asymmetric unit ($Z' = 7$). At 100 K, the superstructure loses its modulation, leading to a unit cell with $Z' = 1$, with clear disorder in the phenyl ring orientations. The methyl-substituent in para-methyl-L-phenylalanine has, in contrast to fluorine, no polar interactions with protons of neighboring molecules, which might allow for the well-defined modulation of the crystal structure at 230 K.

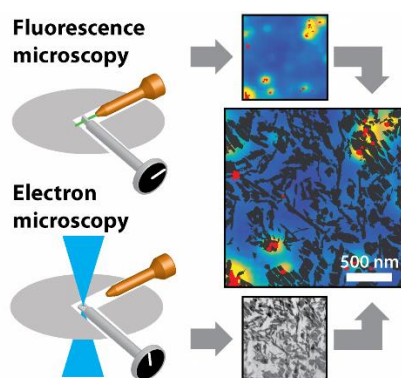
- J. Feenstra, M. van Eerden, A.K. Lemmens, W. de Poel, P.H.J. Kouwer, A.E. Rowan, J. Schermer, [Muscovite mica as a growth template of PC₆₁BM crystallites for organic photovoltaics](#), *CrystEngComm*, **19** (2017), 4424-4436.

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Controlling the microscopic organization of active components is crucial for the performance of organic photovoltaic (OPV) cells. In this work, (001) muscovite mica was used as a growth template to study the formation of PC₆₁BM crystallites in the active layer structure of OPV cells. The structures were spin-coated from a PC₆₁BM : P3HT solution and subsequently annealed. The parameter range to produce layers with high surface density of (sub)micrometer sized PC₆₁BM crystallites was significantly larger for mica than for other substrates. The enhanced PC₆₁BM nucleation is attributed to an epitaxial relation between the mica surface and PC₆₁BM, which was found to crystallise in a hexagonal crystal structure. Through a float-off procedure, the active layer was transferred from the mica substrate to a conductive substrate, which formed the basis of the transferred inverted solar cell. A power conversion efficiency of 2.1% was obtained for this transferred device, which with a 22% higher short-circuit current density outperforms its conventional counterpart that was directly produced on the conductive substrate. A set-up for simultaneous laser beam induced current (LBIC) and surface reflection analysis revealed that the increased current density originates from large circular areas with a radius of about 10 μm around the PC₆₁BM crystallites.

- Thesis:
 Frank Hendriks, [Accessibility, Structure and Reactivity of Individual Catalyst Particles Studied by Fluorescence Microscopy](#)
 On 20 December 2017 Frank Hendriks defended his PhD thesis at the Utrecht University.



Summary

This PhD thesis is aimed at using fluorescence microscopy to study accessibility, structure and reactivity of two types of systems. The first part of this thesis is focused on model zeolite crystals. Fundamental insights into the accessibility and internal structure of zeolite powders and crystals is gained. Four fluorescent organic probe molecules were synthesized, varied in size by adding bulky substituents. The ability of these probe molecules to enter zeolite powders with different pore sizes was studied; the results show a clear correlation between the size of the molecule versus the total amount of molecules are taken up. Furthermore, UV-Vis absorption spectroscopy showed that the electronic properties of these molecules are influenced by the highly polar interior of the zeolite.

Next, this series of molecules of different size was used to probe the large zeolite crystals MFI and BEA, giving insight into the accessibility of these important zeolite model systems. Because the probe molecules fluoresce without the need for external activation, their distribution inside a zeolite crystal was studied using confocal fluorescence microscopy and we showed that certain subunits in the crystals are prone to defects. Furthermore, for BEA, the pore orientation proposed in earlier studies was confirmed. Finally, crystals of zeolite ferrierite (FER) were studied using these probes and a range of alternative techniques. Crystals of this zeolite are platelet-shaped with a 2-dimensional pore system with different pore sizes in each direction. Several techniques, based on optical and confocal fluorescence microscopy, are discussed that can be used to provide the pore orientation of this system in a facile way.

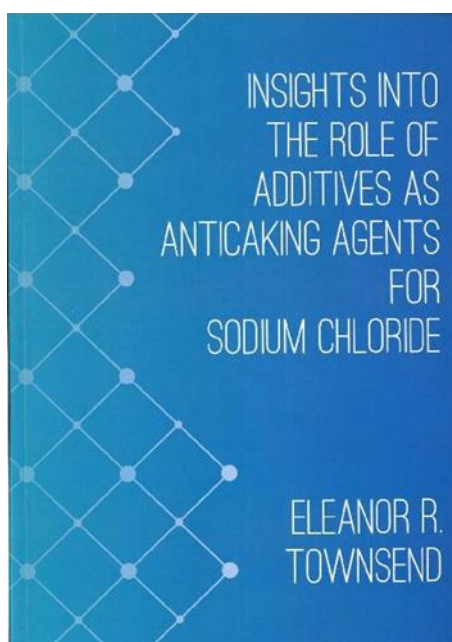
In the second part, real industrial FCC catalysts are studied, which add a layer of complexity because the catalyst particles consist of zeolites embedded within a matrix of multiple types of materials. Using single-molecule fluorescence microscopy, the diffusion of individual feedstock-like organic probe molecules in the pore system of a single FCC particle was studied. Two states were detected for the probe molecules: immobile (i.e. trapped or adsorbed to the pore wall) and mobile, moving through the catalyst pore network. The obtained information is highly localized and can be used to evaluate and map heterogeneities in diffusion properties within hierarchically structured catalysts. At the same time, the results shine light on the macroscopic properties of the catalyst particles such as the diffusion coefficient and the catalyst efficiency under reaction conditions.

To study structure activity relationships, a multimodal approach to study thin sections of industrially used fresh and aged FCC particles was developed. A novel sample preparation method allowed a combination of transmission electron microscopy (TEM) to determine structure of the catalyst materials, correlated with single-molecule fluorescence (SMF) microscopy, to map the reactivity. Ultrastructure components of zeolitic and non-zeolitic material could be distinguished and showed differences in reactivity in the thiophene oligomerization reaction. It was found that seemingly identical zeolite crystals can exhibit large differences in reactivity. The approach allowed structure-activity relationships to be visualized, for the first time with nanometer precision.

- Thesis

Ellie Townsend, [Insights into the role of additives as anticaking agents for sodium chloride](#).

On 16 February 2018 Ellie Townsend defended her PhD thesis at the Radboud University in Nijmegen.



Summary

Sodium chloride is a crystalline material which has the tendency to cake when exposed to conditions of high humidity, leading to impaired physical properties. Additives can be employed to prevent this effect from occurring, these are thus named anticaking agents. Anticaking agents are compounds applied in minimal amounts to the bulk sodium chloride product which cause growth blocking at an atomic level. This growth blocking inhibits the formation of bridges between the individual crystallites, thus preventing caking. In this work, we investigate the effects of both known and previously unknown additives on sodium chloride, consequently leading to a deeper understanding of how the additives interact with the surface and leading us towards our ultimate goal of determining what makes the perfect anticaking agent for sodium chloride.

Chapter Two introduces a new technique which we have employed throughout our subsequent investigations as a powerful screening method. This technique is named "creeping" and follows the same mechanism as that of anticaking, i.e. atomic scale growth blocking. In this chapter, we investigated the relationship between the amount of creeping observed for sodium chloride droplets containing various levels of additive and the corresponding anticaking activity of the additive, thus concluding that this

technique was viable as a screening technique, as well as being extremely simple and fast.

Following from Chapter Two, in the third chapter we combined experimental observations with theoretical considerations to discuss fully the mechanism of additive induced creeping in sodium chloride. We found that a number of factors contribute to this phenomenon, the additives causing both an increase in 3D nucleation and a decrease in surface energy. This surface energy decrease leads to increased morphological instability and surface roughening, which when coupled with the increase in 3D nucleation, leads to the characteristic creeping patterns we observe.

Chapter Four investigates the growth effect and anticaking potential of polymers on sodium chloride, drawing comparisons to their respective monomers. We found that polymers have a strong effect on the surface of sodium chloride, promoting macrostep formation and causing nucleation inhibition. Polymers with an amide functional group were shown to have a much greater effect on the growth of the sodium chloride crystals than the respective amide containing monomer, roughly one to two orders of magnitude larger. However, the polymers tested here were all found to produce a "pro-caking" effect on the sodium chloride crystals and thus were not found to be effective anticaking agents.

The fifth chapter explores the effect that specific amide containing additives have on sodium chloride growth, namely the formation of ultrathin needle crystals. This additive induced crystal morphology has been previously unreported for sodium chloride; we have coupled experimental work with theoretical inferences in order to fully explain this unique phenomenon. The needle crystals were fully characterised using a range of techniques such as x-ray diffraction, energy dispersive x-ray spectroscopy and scanning electron microscopy and shown to consist of cubic NaCl which grow in the {100} direction. We suggest that this is due to morphological instability at the earliest stage of nucleation, leading to enhanced additive adsorption on the sides of the needles and subsequent additive incorporation.

Chapter Six investigates the capabilities of the amide functional group in an anticaking agent and why a triple branched variant is necessary to have the desired anticaking effect. Through creeping tests, supersaturation experiments and powder flow analysis we confirmed that in order to have an anticaking effect, a compound containing three amide branches radiating from one nitrogen centre is necessary. We also showed that effective anticaking agents must obey a set of criteria, if they fail in any one of these categories then they are ineffective.

Finally, in Chapter Seven, we discuss the mechanism of the adsorption of lead chloride to the sodium chloride {100} surface. Lead chloride is a previously reported habit modifier and growth blocker for sodium chloride but up until now, the exact mechanism at an atomic scale was unknown. Using surface x-ray diffraction, we found that lead adsorbs to the NaCl surface replacing a sodium ion, which cannot be incorporated into the bulk as there is a charge mismatch of which it is energetically unfavourable to compensate for. This thus slows the growth of NaCl {100}. Lead chloride has therefore clear similarities with the best-known anticaking agent ferrocyanide, but is found to be much less efficient.

