

FACET

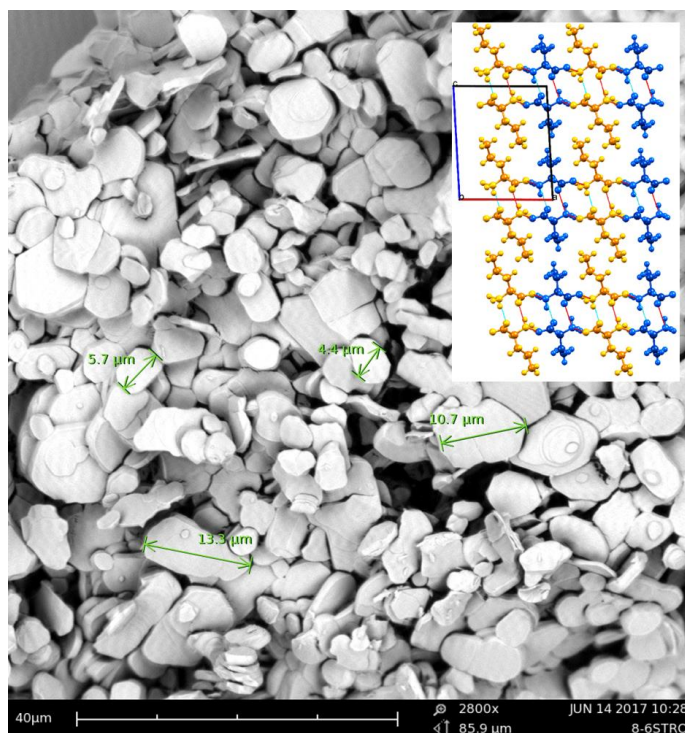
September 2018
 issue 2

FACET

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

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FACET

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WWW

Cover figure

SEM image of quasi-racemic co-crystals of D-2-aminobutyric acid and L-norvaline obtained by liquid assisted grinding; the inset shows the crystal structure consisting of hydrogen bonded bilayers with alternatingly D-Abu (blue) and L-Nva (yellow) molecules. Image by Emma Kalkman; M. Smets et al. Cryst. Eng. Comm. 19 (2017) 5604-5610.

The figure is provided by Radboud University in Nijmegen.

From the editor

This year's second issue of the FACET is full of interesting information, including a long list of recently published articles.

The DACG spring meeting was held in Amsterdam on April 6th. Full coverage is included!

Also, do not forget, the fall meeting is on Wednesday October 3rd in Wageningen! Sign in by September 26th, 2018!

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

[Marketta Uusi-Penttilä](#)

Upcoming events

- [DACG Fall Meeting](#), **Wednesday** 3 October 2018; Wageningen
- DACG Spring meeting; location and date to be decided
- [7th Recrystallization and Grain Grain Growth Conference](#), Ghent (Belgium), 4-9 Aug 2019.
- [ESCG2 SECOND EUROPEAN SCHOOL ON CRYSTAL GROWTH](#), Varna (Bulgaria), 13-16 Sep 2018
- [the Sixth European Conference on Crystal Growth \(ECCG6\)](#), Varna (Bulgaria), 16-20 Sep 2018
- [International Workshop on Modeling in Crystal Growth](#), Big Island, (HI, USA), 21-24 Oct 2018
- [ICCGE-19—OMVPE-19](#), Keystone (Colorado, USA) July 28–August 2, 2019
- [21st International Symposium on Industrial Crystallization - ISIC21](#), Potsdam (Germany), 8-11 Sep 2020

Welcome to correspondents

The NVKG aims to promote the study of all aspects of crystal growth, crystallization and the promotion of scientific and technical contacts between persons working in this area. We do this by organizing biannual meetings and publishing news around crystal growth and crystallization in the Facet.

As board of the DACG, we consider it important to stay into close contact with the crystal growers in science and industry to hear the latest news from our community.

Therefore we are happy to announce our network of correspondents, representing the groups working in crystal growth and/or crystallization in the Netherlands. Our correspondents are our primary contacts; currently we have a list of ten people, representing nine universities and one scientific institute. With their help we can fill the Facet with information about new publications and PhD theses and present interesting speakers at our meetings.

You can find the list of correspondents on our internet site: www.dacg.nl/links.html.

Any comments on this list are welcome. Do you miss a group, please let us know.

Please join us in welcoming our correspondents and wish them success in their roles.

Hans te Nijenhuis, chairman

Membership

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

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

Participating in one of the biannual symposia for the first time automatically includes a membership for one year.

New editor of Facet

In the last annual meeting in Beerse, we have introduced a new member to the Board: [Marketta Uusi-Penttilä](mailto:Marketta.Uusi-Penttila@aspenco.com), scientist at Aspen Oss B.V. Marketta works already for more than 10 years in various functions at Aspen and its predecessors, mainly focusing at process development in pharmaceutical manufacturing. Marketta has a master's degree in Chemical Engineering from the Helsinki University of Technology and a PhD in Chemical Engineering from the Michigan State University. Marketta brings a wealth of knowledge in crystal growth and experience in science and industry to the board. She will pick up the task as editor of the Facet.

Marketta is the successor of Arie van Houselt, University Twente, who was a board member for many years. The DACG would like to thank Arie van Houselt for his contribution to the DACG, editing the Facet throughout the years and keeping the dacg.nl website up-to-date. [Hugo Meekes](mailto:Hugo.Meekes@dacg.nl) is our new webmaster.

DACG Fall Symposium & Annual meeting

WUR, Wageningen, 3 October 2018

Biom mineralization

| | |
|---------------|---|
| 09:30 – 10:00 | Registration and coffee |
| 10:00 – 10:15 | Welcome and introduction Hans te Nijenhuis / Cees Buisman |
| 10:15 – 11:00 | Keynote: Biocrystallization for resource recovery and environmental protection Jan Weijma (WUR-ETE) |
| 11:00 – 11:30 | Controlling properties of sulfur particles formed in biological gas desulfurization Annemerel Mol (WUR / WETSUS) |
| 11:30 – 12:00 | Crystallization by particle attachment is a colloidal assembly process Giulia Mirabello (TU Eindhoven) |
| 12:00 – 12:45 | Lunch |
| 12:45 – 14:00 | Annual meeting (<i>parallel: labtour for participants not attending the DACG annual meeting</i>) |
| 14:00 – 14:15 | KNCV Piet Bennema Award for Crystal Growth Announcement prize winner by jury (Tom Leyssens c.s.) |
| 14:15 – 14:45 | Pathway complexity in CaCO₃ crystallization Nico Sommerdijk (TU Eindhoven) on behalf of the prize winner of the KNCV Piet Bennema Award for Crystal Growth |
| 14:45 – 15:15 | Anaerobic calcium phosphate biogranulation Ricardo Cunha (WUR / WETSUS) |
| 15:15 – 15:30 | Coffee break |
| 15:30 – 16:00 | Exploiting bisphosphonate-bioactive glass interactions for development of bone regenerative biomaterials Mani Diba (TU Eindhoven) |
| 16:00 – 17:30 | Labtour, followed by drinks / nibbles |

Venue: Wageningen University & Research, Gaia Gebouw 101, Droevendaalsesteeg 3, 6708 PB Wageningen (www.wur.nl/nl/locatie/Gaia-gebouwnummer-101.htm)

For registration see next page or visit [DACG website](#).

DACG Fall Symposium and annual meeting

WUR, Wageningen, 3 October 2018

Biom mineralization

REGISTRATION FORM

For registration, please complete this form and send the scanned form as an attachment to a.e.d.m.vanderheijden@tudelft.nl, ultimately **by 26 September 2018**.

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

25 EURO for students and DACG members

40 EURO for non-members (you will be offered to be enrolled as a DACG member in 2019)

Payment of symposium fee **preferably by bank transfer**:

Nederlandse Vereniging van Kristal Groei
NL 60 INGB 0004305158

Another possibility is cash payment at the symposium.

Name (first name and surname):

E-mail:

Affiliation:

Postal address:

Postal code:

City:

Member DACG / (PhD-)student / None of the two (*delete what is not applicable*)

Dietary requirements for lunch:

By registering for this symposium, the participant agrees that pictures, taken during the symposium, can be published in the DACG newsletter FACET and/or on the DACG website (www.dacg.nl).

Annual Report Dutch Association for Crystal Growth (DACG)

October 2017 – October 2018

Secretariat

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Members

The total number of members is ca. 60 (this includes 7 “lifetime” members and 10 “calender year” members that have been offered membership in 2018 through the registration fee for the Spring Meeting at AMOLF/UvA, 6 April 2018). In addition to this number, there are a few tens of members from whom payment of contribution is still pending/expected.

Board

The DACG Board is summarized in the table below. The Board had five meetings: one face-to-face meeting (hosted by University of Twente) and four telcons.

| Role | 2017 – 2018 | Appointment dead-line | E-mail |
|-----------|-------------------------|-----------------------|--|
| President | Hans te Nijenhuis | Step down Oct 2018 | hans.te.nijenhuis@panalytical.com |
| Secretary | Antoine van der Heijden | Step down Oct 2019 | a.e.d.m.vanderheijden@tudelft.nl |
| Treasurer | Pieter Vonk | Step down Oct 2018 | pieter.vonk@dsm.com |
| Webmaster | Hugo Meekes | Step down Oct 2020 | h.meekes@science.ru.nl |
| FACET | Marketta Uusi-Penttilä | Step down Oct 2020 | muusipenttila@nl.aspenpharma.com |

In the register of the Chamber of Commerce (KvK) the address of the Delft University of Technology is now officially filed as the address of the DACG.

FACET Newsletter

The DACG Newsletter, FACET, was issued in March and September 2018. The objective of the newsletter is to stimulate the communication between scientists and users in the area of crystallization in the Netherlands. The newsletter publishes summaries of relevant PhD theses, upcoming events related to crystallization (conferences, symposia), highlights in crystal growth research and other activities relevant to crystal growers. Several academic scientists have been requested to collect news from their network/colleagues as input to the newsletter, but also members may submit input. Furthermore, initiatives, decisions and plans of the DACG will be published in the FACET Newsletter. FACET is issued electronically or can be downloaded from the DACG website. Dr Marketta Uusi-Penttilä (muusipenttila@nl.aspenpharma.com) is the new editor of the FACET, after Dr Arie van Houselt stepped down as a board member in 2017.

Website

The DACG website (www.dacg.nl, hosted by the Radboud University Nijmegen) provides information regarding the structure and activities of the association. All issues of the FACET Newsletter since 2000 are available electronically; links to Dutch research groups in the area of crystallization are available as well as those of foreign DACG ‘sister’ associations. We welcome any suggestions for improvements; please contact Dr Hugo Meekes (H.Meekes@science.ru.nl).

GDPR – General Data Protection Regulation

In view of the new privacy legislation, that came into force as of 25 May 2018, the DACG board prepared a privacy statement (posted on the DACG website). Also DACG members and non-members e.g. attending DACG symposia will be explicitly asked for their permission to use specific personal data to be used and stored for the sole purpose of being able to ‘run’ the DACG. Personal data will not be shared with third parties without permission.

Meetings / excursions organized by DACG

On April 6, 2018 the DACG organized its Spring Meeting, hosted by AMOLF/UvA in Amsterdam and organized by Dr Wim Noorduyn (AMOLF) and Dr Noushine Shahidzadeh (UvA). The DACG Fall Meeting “Biom mineralization” was held on October 3, 2018 and was hosted by Wageningen University & Research, Wageningen; this symposium was organized by Dr Renata van der Weijden (WUR/WETSUS/University College Roosevelt).

Activities relevant to DACG community

A shortlist of past activities relevant to the DACG community:

- KNCV-event “Avond van de Chemie”, 24 October 2017, De Flint, Amersfoort; Hans te Nijenhuis attended this KNCV-event.
- BACG conference 2018, 20-22 June 2018, Limerick, UK, www.bacg2018.com; attended by Hugo Meekes.
- KNCV Meet & Greet: 4 July 2018, Teylers Museum, Haarlem. No attendants this year from the DACG board.
- Farewell Symposium Dr Willem van Enckevort, Radboud University Nijmegen: after a career of ca. 40 years in crystallization, Willem van Enckevort retired in June 2018. On the occasion of his retirement a Farewell Symposium was organized by Prof Elias Vlieg and Dr Hugo Meekes on 1 June 2018 in Nijmegen, with several invited speakers (Dr Marcel Verheijen, Dr Bernard Kaptein, Dr John Schermer and Prof Katsuo Tsukamoto).

KNCV Piet Bennema Crystal Growth Award 2018

End of 2017, the KNCV Board approved the reintroduction of the Crystal Growth Award. To honour prof Piet Bennema, who passed in June 2016, it was decided to rename the award to: KNCV Piet Bennema Crystal Growth Award. In January 2018 a call for nominations was issued and finally three nominations were received. A jury was installed, consisting of Prof Tom Leyssens, Dr ir Herman Kramer and Dr ir Paul Verwer, that judged the nominations according to the award requirements. The jury selected Dr Paul Smeets as the winner of the 2018 award. Their recommendation was formally approved by the KNCV Board. The award (€ 1000) and certificate have been presented to Prof Nico Sommerdijk during the DACG Annual Meeting on 3 October 2018 in Wageningen, since Dr Paul Smeets could not be present (academic position in the USA). The justification of the award has been published in the C2W (monthly magazine issued by the KNCV). The other two nominated scientists, Dr Wester de Poel and Dr ir Simon Hageman, received a certificate with an honorable mention.

Strengthening the relationship with NNV

As a follow-up on strengthening the DACG’s relationship with the KNCV, this year we also reconnected to the NNV (DACG is also an official section of the NNV). The DACG board will be invited to the “adviesraadvergadering” of the NNV on 10 December 2018.

Upcoming activities

- 9 October 2018: KNCV-event “Avond van de Chemie”, Diligentia, Den Haag; more information see: www.kncv.nl/bijeenkomsten/360/avond-van-de-chemie-2018/about#.W4AYR3lIKQy
- 10 December 2018: NNV adviesraadvergadering, Vredenburg Utrecht (section boards will be invited)
- April 2019: DACG Spring Meeting; date/location to be decided
- June/July 2019: symposium on the occasion of the 50th anniversary of BACG
- October 2019: DACG Fall Meeting; date/location to be decided

Toelichting op Algemene Verordening Gegevensbescherming

Beste leden en oud-leden

Per 25 mei jl. is de nieuwe Europese privacy wet in werking getreden: de Algemene Verordening Gegevensbescherming (AVG). Vanaf die datum geldt dezelfde wetgeving in de hele EU.

Ook de NVKG valt onder deze wet. De wet verbindt regels aan het verwerken van persoonsgegevens door organisaties. Het doel van de wet is om mensen controle te geven over hun eigen persoonsgegevens en oneigenlijk gebruik tegen te gaan.

Bij de NVKG worden persoonsgegevens verwerkt zoals namen, werkadressen, e-mailadressen en telefoonnummers om alles rondom onze vereniging alsmede de door de vereniging georganiseerde activiteiten te kunnen regelen. Dit is nodig om de ledenadministratie bij te kunnen houden, voor het innen van de jaarlijkse contributie van de leden, als netwerk voor het zoeken naar geschikte sprekers tijdens door de NVKG georganiseerde symposia, enz. Gebaseerd op de definities van de nieuwe wetgeving zijn deze persoonlijke gegevens als “niet gevoelig” te beschouwen. Er worden geen gegevens bijgehouden van bijvoorbeeld politieke, medische of familiale aard. We gebruiken ook foto's, bijvoorbeeld op onze website www.dacg.nl of in het informatieblad FACET van de NVKG om niet alleen de leden, maar ook andere in kristalgroeionderzoek geïnteresseerde collega's/studenten op de hoogte te houden van het reilen en zeilen van onze vereniging.

Het is de taak van het NVKG-bestuur om alle gegevensverwerkingen binnen de kaders van de wet uit te voeren en daarover transparant te zijn naar alle betrokkenen. Bovendien hebben de betrokkenen bepaalde rechten, zoals inzage in de gegevens of het recht om een eerder gegeven toestemming weer in te trekken. De secretaris is verantwoordelijk voor de opslag en ontsluiting van de gegevens.

Het NVKG-bestuur is aan de slag gegaan om te kunnen voldoen aan de nieuwe wet. We hebben daarbij o.a. informatie gehad vanuit de KNCV. Dit zijn de punten waar het bestuur aandacht aan dient te geven:

- Hoewel de opslag van de meeste gegevens noodzakelijk is voor de vereniging, dienen leden van de vereniging toestemming te geven voor de opslag van alle gegevens. Binnenkort zal de leden gevraagd worden een toestemmingsverklaring te ondertekenen.
- Nieuwe leden vragen we om toestemming op het inschrijfformulier.
- Bij vertrekkende leden zal toestemming gevraagd worden de gegevens nog langer te bewaren. Mocht het vertrekkende lid daar geen behoefte aan hebben en daar (dus) geen toestemming voor geven, dan zullen de gegevens verwijderd en vernietigd worden.
- Oud-leden zullen dezelfde vraag krijgen als vertrekkende leden. Na uitblijven van een reactie na een herhaald verzoek om een reactie zullen hun gegevens ook verwijderd en vernietigd worden.

Als U vragen en/of opmerkingen hebt: stel ze aan de secretaris d.m.v. een mail:
a.e.d.m.vanderheijden@tudelft.nl.

De Privacyverklaring van NVKG is te vinden op [onze website](#).

DACG Spring Meeting, April 6, 2018, AMOLF / UvA

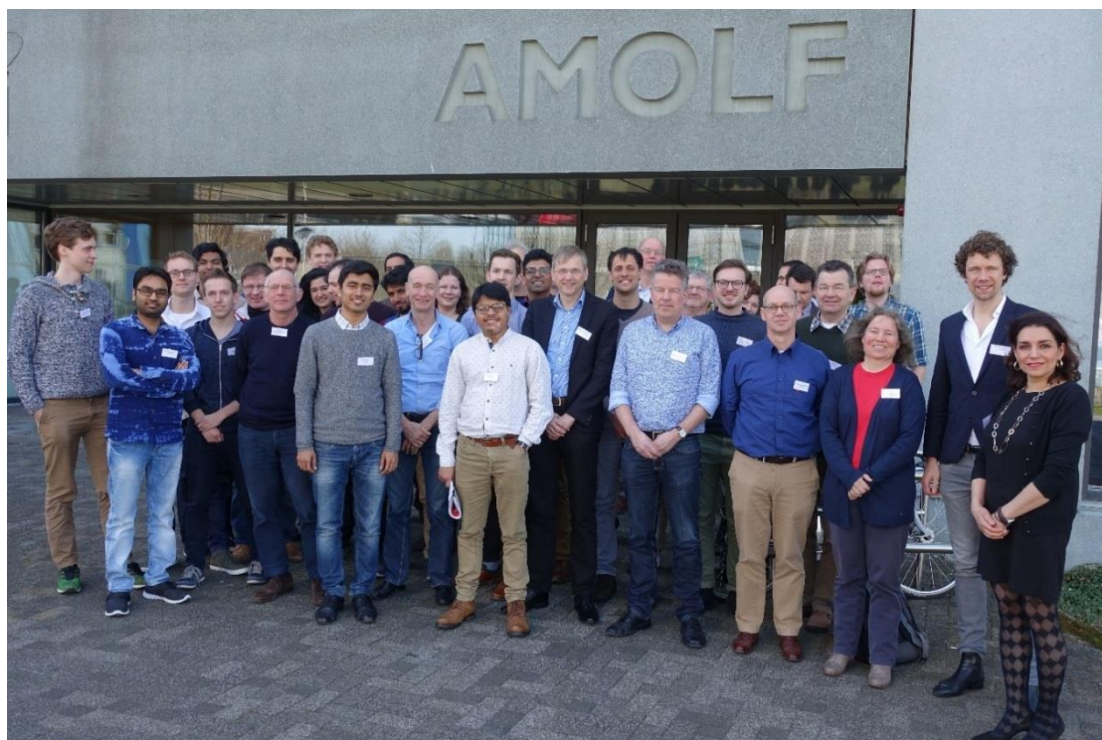
By: Antoine van der Heijden

On April 6, the DACG Spring Symposium was held at AMOLF/UvA. An interesting program with a diverse number of topics related to crystal growth was put together which was attractive to a broad audience of ca. 40 participants. The opening lecture was given by **Kevin Roberts** (University of Leeds, UK), who advocated the approach to perform a very detailed study on a single compound (in this case para-amino benzoic acid), rather than less thorough studies on a range of different compounds. **Ton Engwerda** (PhD student, Radboud University, Nijmegen) showed how tailor-made additives may promote racemization. **Mohsin Qazi** (PhD student, UvA) showed the influence of wetting on salt creeping.

New in this symposium was a poster pitch where Fatma Ibis (PhD student, TU Delft), Roberto Meijers (MSc student, TU Delft), Mehul Jain (MSc student, TU Delft) and Hans Hendrikse (PhD student, AMOLF) gave a sneak-preview of their research as a teaser to invite people to visit their poster. The posters (4) could be visited and discussed with the authors during the lunch break.

After the lunch break the program continued with a presentation by **Nico Sommerdijk** (TU Eindhoven) on crystallization phenomena in magnetite formation. This was followed by **Arjun Wadhawan** (UvA) with a presentation on molecular simulation of methane hydrate nucleation. **Krassimir Velikov** (Unilever R&D / UvA) presented results on the suppression of crystallization in the field of nutraceuticals. Finally, **Daniël Vermaekelberge** (University of Utrecht) showed achievements on the formation of atomically coherent honeycomb structures by interfacial assembly of colloidal nanocrystals.

The DACG kindly acknowledges **Wim Noorduin** (AMOLF) and **Noushine Shahidzadeh** (UvA) for a very diverse and successful organization of this symposium!



Farewell symposium Willem van Enckevort

By: *Hugo Meekes*

On Friday afternoon, June 1, 2018, a farewell symposium was held on the occasion of the retirement of dr Willem van Enckevort from the Radboud University. The symposium, sponsored by the DACG was held at the University in Nijmegen.



The meeting was attended by former PhD students of the Solid State Chemistry group, colleagues, co-workers and family members, in total there were some 70 participants. The program was opened by former PhD student Marcel Verheijen who gave a presentation with the title "Semiconductor nanowire growth; microscopy and kinetics" on his electron microscopy work at Philips Innovation Labs and the Technical University Eindhoven. Bernard Kaptein (Innosyn BV, Geleen) gave a talk on deracimization of chiral compounds, reflecting back on the successful cooperation between him and the Nijmegen group. John Schermer of the Applied Materials Science group in Nijmegen followed by presenting the work of the AMS group on crystal structures for optimal solar energy harvesting.



After a short break our special guest Katsuo Tsukamoto (Tohoku University, Osaka University, Japan), with whom Willem van Enckevort has had an inspiring collaboration in the early days of the SSC group, gave an impressive talk on Willem's and his own inspiration in crystal growth.



The final man on the stage was Willem van Enckevort, who gave an overview of the many phenomena in crystal growth he and his colleagues and students unraveled during his scientific career. His presentation with title "Four decades of watching crystals" was a typical Willem performance showing his enthusiasm not only about crystal growth, but also for birds and astronomy.



The symposium was concluded with words of thanks by Elias Vlieg, after which a reception was held, which had the nice atmosphere of a reunion.

Fortunately, Willem van Enckevort intends to visit the SSC group one or two days per week to devote his attention to topics in crystal growth that he considers as a hobby. Nevertheless, the past has shown that his good nose, or rather eyes, for sometimes seemingly unimportant experimental observations can lead to important insights in the science of crystal growth.

Recent publications

- Yifei Xu, Koen C. H. Tijssen, Paul H.H. Bomans, Anat Akiva, Heiner Friedrich, Arno P.M. Kentgens and Nico A.J.M. Sommerdijk, [Microscopic structure of the polymer-induced liquid precursor for calcium carbonate](#), *Nature Communications*, **9** (2018), 2528.

Affiliations:

- Department of Chemical Engineering and Chemistry, Laboratory of Materials and Interface Chemistry and Centre for Multiscale Electron Microscopy, Eindhoven University of Technology, PO Box 513, 5600 MB, Eindhoven, The Netherlands (Xu, Bomans, Akiva, Friedrich, Sommerdijk)
- Institute for Complex Molecular Systems, Eindhoven University of Technology, PO Box 513, 5600 MB, Eindhoven, The Netherlands (Xu, Bomans, Akiva, Friedrich, Sommerdijk)
- Solid-state NMR Group, Institute for Molecules and Materials, Radboud University Nijmegen, Heyendaalseweg 135, 6525 AJ, Nijmegen, The Netherlands (Tijssen, Kentgens)

Many biomineral crystals form complex non-equilibrium shapes, often via transient amorphous precursors. Also in vitro crystals can be grown with non-equilibrium morphologies, such as thin films or nanorods. In many cases this involves charged polymeric additives that form a polymer-induced liquid precursor (PILP). Here, we investigate the CaCO₃ based PILP process with a variety of techniques including cryoTEM and NMR. The initial products are 30–50 nm amorphous calcium carbonate (ACC) nanoparticles with ~2 nm nanoparticulate texture. We show the polymers strongly interact with ACC in the early stages, and become excluded during crystallization, with no liquid–liquid phase separation detected during the process. Our results suggest that “PILP” is actually a polymer-driven assembly of ACC clusters, and that its liquid-like behavior at the macroscopic level is due to the small size and surface properties of the assemblies. We propose that a similar biopolymer-stabilized nanogranular phase may be active in biomineralization.

- R. Kacker, M. Radoiu and H.J.M. Kramer, [Novel Design Integrating a Microwave Applicator into a Crystallizer for Rapid Temperature Cycling. A Direct Nucleation Control](#), *Crystal Growth & Design*, **17**(2017), 3766-3774.

Affiliations:

- Intensified Reaction & Separation Systems, Process & Energy Laboratory, Delft University of Technology, Leeghwaterstraat 39, 2628 CB Delft, The Netherlands (Kacker, Kramer)
- Sairem SAS, 12 Porte du Grand Lyon, 01700 Neyron, France (Radoiu)

The control of nucleation in crystallization processes is a challenging task due to the often lacking knowledge on the process kinetics. Inflexible (predetermined) control strategies fail to grow the nucleated crystals to the desired quality because of the variability in the process conditions, disturbances, and the stochastic nature of crystal nucleation. Previously, the concept of microwave assisted direct nucleation control (DNC) was demonstrated in a laboratory setup to control the crystal size distribution in a batch crystallization process by manipulating the number of particles in the system. Rapid temperature cycling was used to manipulate the super(under)saturation and hence the number of crystals. The rapid heating response achieved with the microwave heating improved the DNC control efficiency, resulting in halving of the batch time. As an extension, this work presents a

novel design in which the microwave applicator is integrated in the crystallizer, hence avoiding the external loop though the microwaves oven. DNC implemented in the 4 L unseeded crystallizer, at various count set points, resulted in strong efficiency enhancement of DNC, when compared to the performance with a slow responding system. The demonstrated crystallizer design is a basis for extending the enhanced process control opportunity to other applications.

- R. Kacker, S. Maaß, J. Emmerich and H. Kramer, [Application of inline imaging for monitoring crystallization process in a continuous oscillatory baffled crystallizer](#), *AIChE J*, **64** (2018), 2450–2461.

Affiliations:

- Process & Energy Dept., Delft University of Technology, Delft, The Netherlands (Kacker, Kramer)
- SOPAT GmbH, Boyenstraße 41, Berlin 10115, Germany (Maaß, Emmerich)

In this study, an in situ imaging system has been analysed to characterize the crystal size, the shape and the number of particles during a continuous crystallization process in a Continuous Oscillatory Baffled Crystallizer (COBC). Two image analysis approaches were examined for particle characterization in the suspension containing both small nuclei and larger grown crystals (nonspherical and irregular in shape). The pattern matching approach, in which the particles are approximated to be spherical, did result in an overestimation of the size. Alternatively, a segmentation-based algorithm resulted in reliable crystal size and shape characteristics. The laser diffraction analysis in comparison to the image analysis overestimated the particle sizes due to the agglomeration of particles upon filtration and drying. The trend in the particle counts during the start of crystallization process, including nucleation, determined by the image analysis probe was comparable with the one measured by FBRM, highlighting the potential of in situ imaging for process monitoring.

- R. Kacker, S. Dhingra, D. Irimia, M.K. Ghatkesar, A. Stankiewicz, H.J.M. Kramer and H.B. Eral, [Multiparameter Investigation of Laser-Induced Nucleation of Supersaturated Aqueous KCl Solutions](#), *Crystal Growth & Design*, **18** (2018), 312-317.

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- Department of Precision and Microsystems Engineering, 3ME faculty, Delft University of Technology, 2628 CD Delft, The Netherlands (Ghatkesar)
- Van't Hoff Laboratory for Physical and Colloid Chemistry, Debye Institute for Nanomaterials Science, Utrecht University, 3584 CH Utrecht, The Netherlands (Eral)

Various mechanisms have been proposed to explain the nonphotochemical laser-induced nucleation (NPLIN). Identifying the dominant mechanism requires addressing a large set of experimental parameters with a statistically significant number of samples, forced by the stochastic nature of nucleation. In this study, with aqueous KCl system, we focus on the nucleation probability as a function of laser wavelength, laser intensity, and sample supersaturation, whereas the influence of filtration and the laser-induced radiation pressure on NPLIN activity is also studied. To account for the nucleation stochasticity, we used 80–100 samples. The NPLIN probability showed an increase with increasing laser intensity. The results are different from the previous report, as a supersaturation independent intensity threshold is not observed. No dependence of the NPLIN probability on the laser wavelength (355, 532, and

1064 nm) was observed. Filtration of samples reduced the nucleation probability suggesting a pronounced role of impurities on NPLIN. The magnitude and the propagation velocity of the laser-induced radiation pressure were quantified using a pressure sensor under laser intensities ranging from 0.5 to 80 MW/cm². No correlation was found between the radiation pressure and NPLIN at our unfocused laser beam intensities ruling out the radiation pressure as a possible cause for nucleation.

- A.E.D.M. van der Heijden, [Developments and challenges in the manufacturing, characterization and scale-up of energetic nanomaterials – a review](#), *Chemical Engineering Journal*, **350** (2018), 939-948.

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In the domain of energetic nanomaterials, more specifically nano-sized explosives and oxidizers, many small scale production methods have been explored up to now. So far only limited attempts have been made to scale up the production to tens or maximally a few hundreds of grams. This paper provides a review of these small scale production methods as well as characterization techniques for nanometric explosives and oxidizers. As a result of the limited scale-up, the application of energetic nanomaterials in typical propellant and explosive formulations is currently very limited. This might be caused by the fact that a clear and commonly shared view on which energetic nanomaterials and production processes it would be economically beneficial and feasible to invest in is lacking at the moment. Furthermore, a considerable number of technical challenges can be expected regarding the processing of energetic nanomaterials on a composition level. To manage these challenges, this review proposes several technical solutions which may contribute to a better understanding of the benefits, risks and costs involved in the use and scale-up of energetic nanomaterials and, if considered economically feasible, a more widespread application of these nanomaterials in the defense and space domains.

- A.H.J. Engwerda, P. van Schayik, H. Jagtenberg, H. Meekes, F.P.J.T. Rutjes, E. Vlieg, [Deracemization of a racemic compound by using tailor-made additives](#), *Chem. Eur. J.* **24** (2018) 1-6.

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Viedma ripening is a process that combines abrasive grinding of a slurry of crystals with solution-phase racemization, resulting in solid-phase deracemization. One of the major disadvantages of Viedma ripening is that the desired compound needs to crystallize as a racemic conglomerate, accounting for only 5–10 % of all chiral molecules. Herein, we show that use of a chiral additive causes deracemization under conditions, in which the compound normally crystallizes as a racemic compound. Although this concerns a single example, it is envisioned that through this new approach the scope of Viedma ripening can be significantly expanded.

- E.R. Townsend, W.J.P. van Enckevort, J.A.M. Meijer, E. Vlieg, [Amides as anticaking agents for sodium chloride: is a triple branched variant necessary?](#) *Cryst. Eng. Comm.* **20** (2018) 334-339

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Amides are well known for their potential as anticaking agents for sodium chloride. We have investigated what is the ideal structure for an amide based anticaking agent and what features lead to effective anticaking. Through a series of experiments, we have found that a triple-branched structure, with the three branches radiating from the same nitrogen centre, is the only effective compound for preventing caking for sodium chloride. We conclude that this is likely due to bonding between the atoms of the amide functional group and the ions of sodium chloride, with an extra bond from the central nitrogen giving a strong attachment to the surface, thus leading to blocking of growth. We have also outlined a list of four categories, of which a compound must obey all of in order to act as an effective anticaking agent.

- W. de Poel, P.T. Tinnemans, A.L.L. Duchateau, M. Honing, F.P.J.T. Rutjes, E. Vlieg, R. de Gelder, [Racemic and enantiopure camphene and pinene studied by the crystalline sponge method](#), *Cryst. Growth Des.* **18** (2018) 126-132

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The use of an achiral metal–organic framework for structure determination of chiral compounds is demonstrated for camphene and pinene. The structure of enantiopure β -pinene can be resolved using the crystalline sponge method. However, α -pinene cannot be resolved using enantiopure material alone because no ordering of guest molecules takes place in that case. Interestingly, enantiomeric pairs order inside the channels of the host framework when impure (+)-camphene is offered to the host, which is also the case when a racemic mixture of α -pinene is used. A mixture of (+)- α -pinene and (–)- β -pinene also leads to ordered incorporation in the host, showing the influence of the presence of an inversion center in the host framework. We further show that powder X-ray diffraction provides a direct view on incorporation of ordered guest molecules. This technique, therefore, provides a way to determine the optimal and/or minimal soaking time. In contrast, color change of the crystal only demonstrates guest uptake, not ordering. Moreover, we show that color change can also be caused by guest-induced host degradation.

- M.H.M. Smets, M.B. Pitak, J. Cadden, V.R. Kip, G.A. de Wijs, E.R.H. van Eck, P. Tinnemans, H. Meekes, E. Vlieg, S.J. Coles, H.M. Cuppen, [The rich solid-state phase behavior of DL-aminoheptanoic acid: five polymorphic forms and their phase transitions](#), *Cryst. Growth Des.* **18** (2018) 242-252

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The rich landscape of enantiotropically related polymorphic forms and their solid-state phase transitions of dl-2-aminoheptanoic acid (dl-AHE) has been explored using a range of complementary characterization techniques, and is largely exemplary of the polymorphic behavior of linear aliphatic amino acids. As many as five new polymorphic forms were found, connected by four fully reversible solid-state phase transitions. Two low temperature forms were refined in a high Z' crystal structure, which is a new phenomenon for linear aliphatic amino acids. All five structures consist of two-dimensional hydrogen-bonded bilayers interconnected by weak van der Waals interactions. The single-crystal-to-single-crystal phase transitions involve shifts of bilayers and/or conformational changes in the aliphatic chain. Compared to two similar phase transitions of the related amino acid dl-norleucine, the enthalpies of transition and NMR chemical shift differences are notably smaller in dl-aminoheptanoic acid. This is explained to be a result of both the nature of the conformational changes and the increased chain length, weakening the interactions between the bilayers.

- M.A.R. Blijlevens, E.R. Townsend, W.J.P. van Enckevort, J.A.M. Meijer, E. Vlieg, [Additive induced pseudo-homoepitaxy of nanoneedles on NaCl crystals](#), *J. of Cryst. Growth* **498** (2018) 43-50

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Additives and impurities often strongly influence the growth and shape of crystals, sometimes in an unexpected way. Heteroepitaxial growth of 3D guest crystals on different substrate crystals leads to a variety of surface patterns as has commonly been reported. Homoepitaxial growth, on the other hand, generally proceeds by layer by layer growth and leads to flat surfaces with steps. In our study we found that applying a droplet of ethanol with traces of triamide additive on a (0 0 1) NaCl substrate surface results in a 3D pseudo-homoepitaxial pattern comprising of ultrathin NaCl needles ordered in a "Mondriaan-like" arrangement. This is a consequence of small amounts of water in the ethanol, absorbed from the ambient, dissolving NaCl from the substrate, followed by poisoning the substrate surface by additive adsorption, which inhibits NaCl regrowth later on. At the last phase of droplet evaporation the NaCl supersaturation becomes very high and epitaxial crystal needles develop, starting from several oriented 3D nuclei on the poisoned substrate surface. This leads to a network of epitaxial NaCl needles each pointing toward one of the four perpendicular $\langle 1\ 0\ 0 \rangle$ directions on the (0 0 1) NaCl substrate. This peculiar phenomenon of 3D pseudo-homoepitaxy results from a subtle interplay between crystal dissolution, additive blocking and final growth at high supersaturation.

- E.R. Townsend, S.J.T. Brugman, M.A.R. Blijlevens, M.H.M. Smets, W. de Poel, W.J.P. van Enkevort, J.A.M. Meijer, E. Vlieg, [The structure of PbCl₂ on the {100} surface of NaCl and its consequences for crystal growth](#), *J. of Chem. Physics* **148** (2018) 144703-1 – 144703-5

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The role that additives play in the growth of sodium chloride is a topic which has been widely researched but not always fully understood at an atomic level. Lead chloride (PbCl₂) is one such additive which has been reported to have growth inhibition effects on NaCl {100} and {111}; however, no definitive evidence has been reported which details the mechanism of this interaction. In this investigation, we used the technique of surface x-ray diffraction to determine the interaction between PbCl₂ and NaCl {100} and the structure at the surface. We find that Pb²⁺ replaces a surface Na⁺ ion, while a Cl⁻ ion is located on top of the Pb²⁺. This leads to a charge mismatch in the bulk crystal, which, as energetically unfavourable, leads to a growth blocking effect. While this is a similar mechanism as in the anti-caking agent ferrocyanide, the effect of PbCl₂ is much weaker, most likely due to the fact that the Pb²⁺ ion can more easily desorb. Moreover, PbCl₂ has an even stronger effect on NaCl {111}.

- S. Pinteau, W. de Poel, A.E.F. de Jong, R. Felici, E. Vlieg, [Solid-Liquid Interface Structure of Muscovite Mica in SrCl₂ and BaCl₂ Solutions](#), *Langmuir* **34** (2018) 4241-4248

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The structure of the solid-liquid interface formed by muscovite mica in contact with two divalent ionic solutions (SrCl₂ and BaCl₂) is determined using in situ surface X-ray diffraction using both specular and non-specular crystal truncation rods. The 0.5 monolayer of monovalent potassium present at the surface after cleavage is replaced by approximately 0.25 monolayer of divalent ions, closely corresponding to ideal charge compensation within the Stern layer in both cases. The adsorption site of the divalent ions is determined to be in the surface ditrigonal cavities with minor out-of-plane relaxations that are consistent with their ionic radii. The divalent ions are adsorbed in a partly hydrated state (partial solvation sphere). The liquid ordering induced by the presence of the highly ordered crystalline mica is limited to the first 8-10 Å from the topmost crystalline surface layer. These results partly agree with previous studies in terms of interface composition, but there are significant differences regarding the structural details of these interfaces.

- S.J.T. Brugman, E.R. Townsend, M.M.H. Smets, P. Accordini, E. Vlieg, [Concentration-Dependent Adsorption of CsI at the Muscovite–Electrolyte Interface](#), *Langmuir* **34** (2018) 3821–3826

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The interfacial structure of muscovite in contact with aqueous CsI solutions was measured using surface X-ray diffraction for several CsI concentrations (2–1000 mM). At CsI concentrations up to 200 mM, Cs⁺ adsorption is likely hindered by H₃O⁺, as both cations compete for the adsorption site above the muscovite hexagonal cavity. Above this concentration, more Cs⁺ adsorbs than is required to compensate the negatively charged muscovite surface, which means that coadsorption of an anion takes place. The I[–] anion does not coadsorb in an ordered manner. Moreover, the hydration ring and water layers do not change significantly as a function of the CsI concentration.

- W. de Poel, J.A. W. Münninghoff, J.A.A.W. Elemans, W.J.P. van Enckevort, A.E. Rowan, E. Vlieg [Surfaces with controllable topography and chemistry used as a template for protein crystallization](#), *Cryst. Growth Des.* **18** (2018) 763–769

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Surfaces with controllable topography and chemistry were prepared to act as substrates for protein crystallization, in order to investigate the influence of these surface properties on the protein crystallization outcome. Three different methods were investigated to deposit 1,3,5-tris(10-carboxydecyloxy)benzene (TCDB) on a muscovite mica substrate to find the best route for controlled topography. Of these three, sublimation worked best. Contact angle measurements revealed that the surfaces with short exposure to the TCDB vapor (20 min or less) are hydrophilic, while surfaces exposed for 30 min or longer are hydrophobic. The hydrophilic surfaces are flat with low steps, while the hydrophobic surfaces contain macrosteps. Four model proteins were used for crystallization on the surfaces with controlled topography and chemistry. Hen egg white lysozyme crystals were less numerous on the surface with macrosteps than on smoother surfaces. On the other hand, insulin nucleated faster on the hydrophobic surfaces with macrosteps, and therefore, the crystals were more abundant and smaller. Bovine serum albumin and talin protein crystals were more numerous on all TCDB functionalized surfaces, compared to the reference clean muscovite mica surfaces. Overall, this shows that surface topography and chemistry is an important factor that partly determines the outcome in a protein crystallization experiment.

- M.M.H. Smets, G. Baaklini, A. Tijink, L. Sweers, C.H.F. Vossen, C. Brandel, H. Meekes, H. M. Cuppen, G. Coquerel, [Inhibition of the Vapor-Mediated Phase Transition of the High Temperature Form of Pyrazinamide](#), *Cryst. Growth Des.* **18** (2018) 1109-1116

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Tailor-made additives can prove an effective method to prolong the lifetime of metastable forms of pharmaceutical compounds by surface stabilization. Pyrazinamide (PZA) is a pharmaceutical compound with four polymorphic forms. The high temperature γ form, which can be produced by spray drying or sublimation growth, is metastable at room temperature and transforms within days when produced by spray drying, and within several months up to years for single crystals produced by sublimation. However, when PZA is cospray dried with 1,3-dimethylurea (DMU), it has been reported to remain in its γ form for several years. Scanning electron microscopy (SEM) images reveal that the phase transition from γ -PZA to the low temperature forms involves a vapor-mediated recrystallization, while the reverse phase transition upon heating is a nucleation-and-growth solid–solid phase transition. The lifetime-extending effect of DMU on spray-dried PZA has been investigated in more detail and compared with high-energy ball milling of sublimation-grown γ -PZA crystals. Co-ball milling of PZA and DMU is found to extend the lifetime of the high temperature form of PZA to a few months, while separate ball milling leads to an extension of merely a few weeks. DMU acts as an additive that most likely stabilizes the surface of γ -PZA, which would reduce the vapor pressure of PZA, thereby reducing the transition rate. Alternatively, DMU could prevent nucleation of low temperature forms of PZA.

- E.R. Townsend, W.J.P. van Enckevort, P. Tinnemans, M.A.R. Blijlevens, J.A.M. Meijer, E. Vlieg, [Additive Induced formation of ultrathin sodium chloride needle crystals](#), *Cryst. Growth Des.* **18** (2018) 755-762

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A multitude of ultrathin crystal needles are formed during the evaporation of saturated aqueous NaCl solution droplets in the presence of amide containing additives. The needles are as small as 300 nm wide and 100–1000 μm in length. Heating experiments, X-ray diffraction, and energy dispersive X-ray spectroscopy showed that the needles are cubic sodium chloride crystals with the needle length direction pointing toward [100]. This shape, not expected for the 43m point group symmetry of NaCl, has been explained using a model, based on tip formation by initial morphological instability followed by time dependent adsorption of additive molecules blocking the growth of the needle side faces. The latter also suppresses side branch formation, which normally occurs for dendrite growth.

- W.J.P. van Enkevort, W.L. Noorduyn, S. Graswinckel, P. Verwer, E. Vlieg, [Epitaxy of anthraquinone on \(100\) NaCl: a quantitative approach](#), *Cryst. Growth Des.* (2018), published online

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A growth cell suitable for microscopic in situ observation of well-controlled crystal growth from the vapor phase is used to study the heteroepitaxial growth of anthraquinone crystals on a (100) NaCl substrate. In this, the morphology, orientation, nucleation, and growth rate of the crystals is studied as a function of driving force, $\Delta\mu/kT$. At the lowest $\Delta\mu/kT$, the crystals are block-shaped and show no preferential orientation with respect to the substrate. Increasing the driving force leads to the growth of oriented block- and needle-shaped crystals, which nucleate from macrosteps on the substrate. At the highest $\Delta\mu/kT$, crystals nucleate on the flat surface areas or at monatomic steps on the substrate, resulting in a dramatic increase in epitaxial needle density. Growth rate measurements show an exponential behavior as a function of $\Delta\mu/kT$. In all cases, the supply of growth units proceeds via surface diffusion over the NaCl substrate surface toward the anthraquinone crystals. At the lowest $\Delta\mu/kT$, growth is partly limited by integration of the growth units at the crystal surfaces. At intermediate driving force, kinetic roughening sets in, leading to rounded needle tips. At the highest supersaturation, growth is completely governed by the supply of growth units via surface diffusion, leading to tip splitting as a consequence of morphological instability.

PhD theses

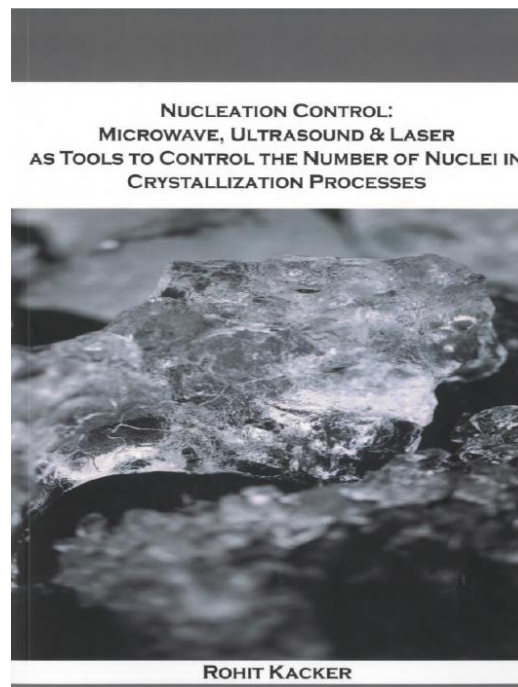
- Rohit Kacker, [Nucleation Control: Microwave, Ultrasound and Laser as Tools to Control the Number of Nuclei in the crystallization process](#)

PhD defense: 8 May 2018, TU Delft

Promotor: Prof.dr.ir. A. Stankiewicz

Copromotor: Dr. H.B. Eral

Supervisor: Dr.ir. H.J.M. Kramer



The principal objective of the research focuses on the intensification of the batch and continuous crystallization processes through enhanced nucleation control, proper plug flow conditions in continuous tubular crystallizers and development of advanced image analysis based PAT tool for process monitoring. Nucleation control is addressed through manipulation of the number of crystals in the crystallizer; by either controlling the rate of nuclei formation or through dissolution of the excess nuclei to limit the nucleation overshoot or through continuous seeding in case of flow crystallizer to suppress nucleation in the tubes. The following topics are addressed: 1. The efficiency of the Direct Nucleation Control (DNC) strategy using microwave heating. 2. Induction of high nucleation rates at low supersaturation by the application of laser or ultrasound energy. 3. Combination of the ultrasound assisted internal seed generation in the continuous tubular crystallizer, under plug flow conditions. 4. Characterization of nucleation and the crystal properties through development of in-situ imaging based PAT technology.

- Mireille Smets, Exploring the mechanism of solid-state phase transitions in molecular crystals
 PhD defense: 28 Sep 2018, Radboud Universiteit, Nijmegen

Promotoren: Prof.dr. H.M. Cuppen and Prof.dr. Elias Vlieg

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