Topics in Crystal Shape Dynamics

Dissertation
zur Erlangung des akademischen Grades

Doktoringenieur
(Dr.-Ing.)

von: Dipl.-Ing. Christian Borchert
geb. am: 25. April 1983
in: Cloppenburg

genehmigt durch die Fakultät für Verfahrens- und Systemtechnik
der Otto-von-Guericke-Universität Magdeburg

Gutachter: Prof. Dr.-Ing. habil. Kai Sundmacher
Prof. Doraiswami Ramkrishna, Ph.D.
Prof. Dr.-Ing. habil. Heiko Briesen

eingereicht am: 25. April 2012
Promotionskolloquium am: 20. Juli 2012

Forschungsberichte aus dem Max-Planck-Institut
für Dynamik komplexer technischer Systeme

Band 36

Christian Borchert

Topics in Crystal Shape Dynamics

Shaker Verlag
Aachen 2012

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at http://dnb.d-nb.de.

Zugl.: Magdeburg, Univ., Diss., 2012

Printed in Germany.

ISBN 978-3-8440-1526-3
ISSN 1439-4804

Shaker Verlag GmbH • P.O. BOX 101818 • D-52018 Aachen
Phone: 0049/2407/9596-0 • Telefax: 0049/2407/9596-9
Internet: www.shaker.de • e-mail: info@shaker.de

Abstract

The topic of this work is the dynamic modeling and observation of polyhedral, growing crystals. This is motivated by the fact that besides size, shape is an important product property for particulate materials in various industries. Due to the underlying anisotropic molecular crystal structure, growth proceeds at different rates in different directions. Therefore, crystals assume a non-spherical, polyhedral, though, under ideal conditions also a symmetric shape. The work at hand is essentially divided into three major parts. At first, a system-theoretic framework is introduced and applied to describe the evolution of single crystals and of crystal populations. In the second part the extraction of shape information from suspension images is discussed. This data is finally used to determine growth kinetics enabling the description of the conducted experiments with the developed models.

It is shown that models decribing the development of a single crystal exhibit hybrid dynamics if the number of faces changes. In order to transfer this property to the population level, the class of systems that can be captured with population balances is widened to hybrid systems. Such systems are capable of performing switches in their velocity field or jumps in their state space. It is pointed out that different crystal morphologies exist in different parts of the state space, the so called morphology cones. On the bounding elements of the morphology cone hybrid dynamics is induced. It turns out that the morphology cones do not cover the whole state space and thus the computational time for the solution of evolution equations is reduced.

The shape evolution modeling studies are then augmented by the development of a crystal shape observation scheme. 3D shape descriptors of crystal populations cannot be measured directly with current devices. Therefore, an image processing routine is assembled that reduces 2D grayscale images of the crystal suspension so that individual particle projections are extracted. The estimation scheme to obtain the 3D shape is validated against synthetic (in-silico) image data. It is shown that the time-dependent shape distribution function of the synthetic images is reconstructed accurately. Also growth kinetics that control the shape evolution can be extracted from the image data. Since this is successfully tested on synthetic image data, the method is applied to observe the batch cooling crystallization of potassium dihydrogen phosphate. Two experiments are used to determine the supersaturation-dependent, face-specific growth rates. The obtained growth rates are cross-validated against the mass balance and independently conducted experiments.

Employing the developed techniques allows for a rigorous population balance modeling of crystals taking polyhedral shape into account. On the basis of the image-based crystal observation scheme, it is possible to determine face-specific growth rates. The so equipped population balance model can be included in a process model for crystallization and used to reproduce and predict the outcome of crystallization experiments.

Zusammenfassung

Die vorliegende Arbeit behandelt die dynamische Modellierung und Beobachtung wachsender Kristallpolyeder. Da neben der Größe auch die Kristallform eine bedeutende Produkteigenschaft darstellt, ist dieses Thema für Verständnis und Optimierung von Kristallisationsprozessen relevant. Kristalle wachsen aufgrund ihrer anisotropen molekularen Struktur in unterschiedlichen Richtungen mit verschiedenen Geschwindigkeiten. Daher nehmen sie eine nicht-sphärische, polyedrische, und unter idealen Bedingungen dennoch symmetrische Form an. Die vorliegende Arbeit gliedert sich in drei Teile. Zunächst werden systemtheoretische Methoden entwickelt, die zur Beschreibung der Entwicklung von Einzelkristallen und Kristallpopulationen eingesetzt werden. Im zweiten Teil werden Methoden zur Gewinnung quantitativer Forminformationen aus Bildern von Kristallsuspensionen vorgestellt. Die so extrahierten Daten werden dann zur Bestimmung von Wachstumskinetiken herangezogen, die die Beschreibung der durchgeführten Experimente mit Hilfe der entwickelten Modelle ermöglichen.

Es wird gezeigt, dass Modelle, die die Entwicklung eines einzelnen Kristalls beschreiben, hybride Dynamik aufweisen, wenn sich die Anzahl der wachsenden Flächen ändert. Um die Dynamik auf die Populationsebene zu übertragen, wird die Systemklasse, die mit populationsdynamischen Modellen beschrieben werden kann, um hybride Systeme erweitert. Diese Systeme können instantane Änderungen im Geschwindigkeitsfeld oder Sprünge innerhalb ihres Zustandsraumes aufweisen. Es wird gezeigt, dass unterschiedliche Kristallmorphologien in verschiedenen konvexen, polyedrischen Kegeln – den sogenannten Morphologiekegeln – des Zustandsraums erzeugt werden und auf ihren begrenzenden Elementen hybride Dynamik erzeugt wird. Die Morphologiekegel decken nicht den gesamten Zustandsraum ab, weshalb das Rechengebiet zur Lösung von Evolultionsgleichungen signifikant reduziert und die Simulation beschleunigt wird.

Die Untersuchungen zur Kristallformdynamik werden dann um einen Algorithmus zur Messung von Kristallformen erweitert. Die 3D Form kann für Kristallpopulationen mit verfügbaren Mitteln nicht direkt gemessen werden. Daher wird eine Bildverarbeitungsvorschrift entwickelt, die 2D Graustufenbilder einer Kristallsuspension so abstrahiert, dass Projektionen einzelner Kristalle extrahiert werden können. Der Schätzalgorithmus zur Bestimmung der 3D Form wird gegen synthetische Bilddaten getestet. Darüberhinaus werden die – die Formentwicklung kontrollierenden – Wachstumskinetiken extrahiert. Da die Methode für Testdaten gute Ergebnisse liefert, wird sie zur Beobachtung einer Batch-Kühlungskristallisation von Kaliumdihydrogenphosphat angewendet. Mit Hilfe von zwei Experimenten werden flächenspezifische Wachstumsraten in Abhängigkeit der Übersättigung bestimmt. Die ermittelten Wachstumsraten halten einer Vergleichsprüfung gegen die Massenbilanz und unabhängigen Experimenten stand.

Die in dieser Arbeit entwickelten Methoden erlauben eine rigorose populationsdynamische Modellierung polyedrischer Kristalle. Auf Basis der ausgearbeiteten Formschätzmethode ist es möglich, flächenspezifische Wachstumsraten aus Experimenten zu bestimmen. Die damit parametrierte Populationbilanz kann in einem Prozessmodell für Kristallisation genutzt werden, um den Verlauf von Experimenten zu beschreiben und vorherzusagen.

Acknowledgements

This work has been taken out from 2007 till 2011 at the Max Planck Institute for Dynamics of Complex Technical Systems in Magdeburg. I would like to thank the Max Planck Society and in the end the German tax payer for establishing and financing this splendid research institute.

Personally, I thank at first Kai Sundmacher for supervising the thesis and creating the framework in which the work has been taken out. It has been a valuable experience to be part of his group, seeing people working on a broad spectrum of problems in process engineering. Since nearly a decade, a great deal of my professional development has been enabled by his guidance and support. Full commitment to the engineering sciences and willingness to move beyond personal boundaries and those of the discipline is the most important lecture I learnt from him.

As a young undergraduate student I met Doraiswami "Ramki" Ramkrishna first in 2006 when I spent nine months at Purdue. Working with him has been a shaping experience in many ways. He has encouraged me to enforce this research direction and to fight the mission through. His confidence in dealing with people and an unambigous though unpretentious attitude of leadership has become an anchor point in my own coordinate system. It was an honor to have him on my committee.

On my first working day as a PhD student at the Max Planck Institute I met Heiko Briesen who launched a research group in population balance systems that day. He has been an important advisor in technical discussions and with regard to professional development. I am glad he could serve on my committee.

Furthermore, I thank Helmut Weiß for being a decent head of the committee.

Over the years I had the luck to meet many brilliant people at the Max Planck Institute. Everyone of them has particular splendid qualities. To my office comrade Michael Fricke I am grateful for being a permanent discussion partner and for being an even-tempered and modest close colleague. To Bianka Stein I am grateful for her creative ideas, dedicated work and good conversations. Richard Hanke-Rauschenbach has been of the utmost influence on me in activating the last and decisive reserves, in leading groups and being always open-minded and keeping a healthy portion of naivety. Peter Heidebrecht is the most dedicated teacher I've had at university. Furthermore, I thank Erik Temmel for proofreading of the manuscript and for an excellent collaboration without which the experimental part of this thesis would not have reached its state. We've had great discussions together with Holger Eisenschmidt who I also thank for proofreading and continuing the work. For being great colleagues I thank also Florian Karst, Sascha Rollié, Janine Holzmann, Kongmeng Ye, Hannsjörg Freund, Andreas Peschel, Andreas Voigt, Anett Raasch, Boris Bensmann, Astrid Bornhöft, Kaidi Gao, Linzhu Gou, Timm Faulwasser, Alexander Zinser, Matthias Eicke. Over the years I've had good discussions with Naim Bajinca, Meenesh Singh, Alexander Reinhold, Martin Behrendt, Martin Dietrich, Heike Lorenz, Luise Borchert and Jayanta Chakraborty.

To my parents Willi and Brigitte and my brothers Matthias and Johannes I want to express my deepest thankfulness for unconditional support and just being there.

I dedicate this work to the memory of my beloved aunt Helga Vaske, 1959-2008.

Contents

Notation

Latin Symbols

a_I	relative weight of current image	
a_B	relative weight of previous background image	
A	area of crystal surface	m^2
A	area of crystal projection	m^2
b	number of conditions	
b	exponent in the nucleation law for B	
B	nucleation rate	#/s
$\hat{\mathbf{b}}$	outer unit normal on the boundary of Ω	
$\mathbf{b}_j$	j-th discrete coordinate of projection boundary	m
$\mathcal{B}$	boundary of $\mathcal{P}$	
$\mathbf{B}$	boundary matrix of morpholgoy cone	
$\mathbf{B}$	discretized boundary of particle projection	m
$B_{x,y}$	intensity level of background image	
C	circularity	
$\mathbf{d}$	descriptor vector	
$\hat{\mathbf{d}}$	estimated descriptor vector	
$\mathbf{d}_i$	ith row of $\mathbf{D}$	
D	circle-equivalent diameter	
$\mathbf{D}$	velocity delimiter matrix	
$e_{jk,\mathrm{est}}$	relative error of the estimation for the j-th particles with regard to k-th quantity	
$E_{x,y}$	intensity level of enhanced image	
$\mathcal{E}_{ij}$	edge between faces i and j	
$\mathcal{E}_{ij,kl}$	$\mathcal{E}_{ij}$ bounded by faces k and l	
$\mathcal{E}_{ij,kl}^{i\to\varnothing}$	$\mathcal{E}_{ij,kl}$, whose disappearance involves the disappearance of face i	
$\mathcal{E}_{ij,kl}^{\frown}$	$\mathcal{E}_{ij,kl}$, whose disappearance is followed by the appearance of an edge between k and l	
f	number density	#/[**x**]
$\hat{f}$	estimated number density	
$\mathbf{f}_\mathrm{descr}$	function to obtain descriptor vector from shape and orientation	
$\mathbf{f}_\mathrm{est}$	function to obtain the shape vector from descriptor vector	
$\mathbf{F}$	velocity function for mesh equilibration	
$\mathcal{F}$	ith crystal face	
g	grayscale level	
g_i	growth exponent of the growth law for G_i	
G_i	growth rate of face i and ith component of $\mathbf{G}$	
$\mathbf{G}$	growth vector	
h	production density	#/s/[**x**]
h_i	distance of the ith face to the crystal center	m
$\mathbf{h}$	geometrical state vector	m
$\mathbf{h}_{ijk}$	vector with three components of $\mathbf{h}$	m
$\mathbf{h}_\mathrm{nuc}$	nucleation state	m
$\mathbf{H}$	bandwidth matrix	

$I_{x,y}$	intensity level of original image	
I_{thres}	threshold grayscale value	
J	jacobian	
k	index	
k_i	kinetic coefficient in the growth law for G_i	m/s
k_{nuc}	kinetic coefficient in the nucleation rate law	$\#/m^3/m^3/s$
K	kernel function	
$L_{x,y}$	logical image	
m	mass	kg
m	number of C-morphologies	
$\mathcal{M}$	joint morphology cone	
$\mathcal{M}_\lambda$	morphology cone of λth C-morphology	
$\mathcal{M}_{\lambda,j}$	j S- or T- morphology of $\mathcal{M}_\lambda$	
$\mathcal{M}'_{\lambda,j}$	projection of $\mathcal{M}_{\lambda,j}$	
n	number of faces	
n_{lut}	number of entries in lookup table	
$n_{\text{lut},\mathbf{h}}$	number of variations of the $\mathbf{h}$-vector in lookup table	
$n_{\text{lut},\boldsymbol{\psi}}$	number of variations of the $\mathbf{h}$-vector in lookup table	
n_{nuc}	number of pivots for nucleated crystal population	
$n_{\mathcal{P}}$	number of projected crystal vertices that make up the convex hull	
n_{seed}	number of pivots for seed crystal population	
$\hat{\mathbf{n}}$	unit normal on a surface in state space	
$\mathbf{n}_i^{\mathrm{T}}$	ith row of $\mathbf{N}$, unit normal of ith face	
O	convexity	
N	number of particles	
$\dot{N}$	number flux	
$\mathbf{N}$	matrix with face normals (rows)	
$\mathbf{N}_{ijk}$	matrix with rows ijk of $\mathbf{N}$	
$\mathbf{p}$	node for the mesh generation	
$\hat{\mathbf{p}}$	velocity direction vector of unit length	
$\mathbf{p}_j$	projection of crystal vertex	
P	perimeter	m
$\mathbf{P}$	joint projection and rotation matrix	
$\mathcal{P}$	projection of $\mathcal{S}$	
r	distance between centroid and boundary of the particle projection	m
r_1	side-length of the quadratic pyramid's base plane of KDP	m
r_2	distance between the pyramid's apices of KDP	m
r_i	component of $\mathbf{r}$	
$\mathbf{r}$	3-D space coordinate	
$\mathbf{r}$	vector of distances of the discretized boundary of the crystal projection	m
R	fixed region in Ω	
R_j	j-th Fourier coefficient	
s	surface function σ solved for x_n	
S	fixed surface in Ω	
S	solidity	

$\mathcal{S}$	crystal polyhedron	
t	time	s
$t_{\text{cross},k}$	instant when k-th nucleation pivot leaves circle around $\mathbf{h}_{\text{nuc}}$	
T	temperature	K
$\mathbf{v}_j$	coordinates of j-th vertex	m
$\mathbf{v}_{ijk}$	coordinates of $\mathcal{V}_{ijk}$	m
V	volume in property state space or physical space	
$\mathcal{V}_{ijk}$	vertex formed by faces ijk	
$\mathbf{w}_{ij,kl}$	computed weights of the edge $\mathcal{E}_{ij,kl}$	
w	mass ratio between solute and solvent in fluid phase	
x	first component of $\mathbf{x}$ (coord. on proj. plane)	m
x	sample point	
x_i	i-th component of teh property vector	
$\mathbf{x}$	property vector	
$\mathbf{x}$	coordinate on projection plane	m
$\mathbf{x}'$	vector with $n-1$ components of the property vector$\mathbf{x}$	
$\dot{X}_i$	i-th component of the velocity field in $\mathbf{x}$-space	
$\dot{\mathbf{X}}$	velocity field in $\mathbf{x}$-space	
y	second component of $\mathbf{x}$ (coord. on proj. plane)	m
Y_i	i-th component of the environmental state vector	
$\mathbf{Y}$	environmental state vector	
$\mathbf{z}$	surface-intrinsic coordinate system in Σ	
$\dot{\mathbf{Z}}$	velocity in surface coordinates	

Greek Symbols

α	angle
α_j	weight of j-th vertex
Γ	spatial domain
δ	Dirac delta
ϵ_{nuc}	numerical parameter controlling the distance between nucleation pivots
θ	angle
θ	Euler angle
$\boldsymbol{\mu}$	vector of mean values
ν	number of preliminary nodes
ρ	density
σ	indicator function defining Σ
σ	standard deviation
Σ	surface domain in property state space
λ	weight
λ	morphology index
Λ	material control volume in state space
ξ	jump function
ϕ	Euler angle
ψ	Euler angle
Ω	domain in property state space

Superscripts

T	transpose
Σ	quantity on Σ
$\varnothing$	disappearance of a face
$\curvearrowright$	transition to new edge-configuration
$<$	inequality (less than zero)
$\mathbf{0}$	equality (equal zero)
$-$	quantity related to that part of the state space where $\sigma < 0$
$+$	quantity related to that part of the state space where $\sigma > 0$

Subscripts

0	initial value
$\{hkl\}$	related to crystallographic forms $\{hkl\}$
$[hkl]$	related to crystallographic direction $[hkl]$
c	centroid
cry	crystal/crystalline
cry, pop	crystal population
dis	dissolved
est	estimation/estimated value
H_2O	quantity related to water
i, j	indices
j	jump
KDP	quantity related to KDP (potassium dihydrogen phosphate)
lut	lookup table
mod	model
nuc	nucleation/nucleated particles
particles	particles/all particles
P	Projection
S	related to surface S
sat	saturation
sc	scaled
seed	quantity related to the seed crystals
ss	steady state
true	true value
$\mathbf{x}'$	function given in $\mathbf{x}'$-coordinates
$\mathbf{z}$	function given in $\mathbf{z}$-coordinates
Λ	quantity related to Λ
Σ	quantity related to Σ
$\boldsymbol{\psi}$	vector of Euler angles
$\varnothing$	disappearance of a face