

Kinetic Analysis of Food Systems

Alejandro G. Marangoni

Kinetic Analysis of Food Systems

 Springer

Alejandro G. Marangoni
Department of Food Science
University of Guelph
Guelph
Ontario
Canada

ISBN 978-3-319-51291-4 ISBN 978-3-319-51292-1 (eBook)
DOI 10.1007/978-3-319-51292-1

Library of Congress Control Number: 2017932900

© Springer International Publishing AG 2017

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made.

Printed on acid-free paper

This Springer imprint is published by Springer Nature
The registered company is Springer International Publishing AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

*Dedicated to my colleagues who remind
me that the scientific endeavor is a privilege
and an honor.*

Introduction: Trials and Tribulations in the Study of Complex, Multicomponent, Multiphasic, Nonequilibrium Systems

The computer model is to the mind what the telescope and microscope are to the eye.
(Heinz Pagels)

Food systems encompass anything from whole organisms and living tissue to nanostructured soft materials: potatoes to cheese. One characteristic all these systems share is complexity. All food materials are multicomponent, multiphasic, and mostly nonequilibrium systems, while living matter is ephemeral. It is thus very difficult to use a thermodynamic approach to predict system behavior. However, at the same time, this makes food systems amenable to kinetic analysis, where researchers try to catch a fleeting glimpse at the dynamics of living processes, structure formation, structure breakdown, state transformations, and the energetics involved in these processes. At the end of the exercise, we talk about free energies of activation, partition functions, orders of processes, and rate constants instead of free energy, enthalpy, and entropy of standard states.

The complexity of a food system might discourage some; however, many of these complex systems are amenable to “coarse-graining,” which means that structural or functional averages of ensembles of molecules, higher-order structural units, or entire metabolic pathways can be used to model whole system behavior – a mean field approach. Engineers have known this for a while and carry out phenomenological finite-element and finite-difference analysis; however, there are many approaches available, limited only to the imagination and skill of the researcher. Here is where art meets science, where creativity is key. How do we succeed in describing the behavior of a complex system?

Should we use a deterministic or a stochastic approach? Deterministic processes (cause-effect) follow an exact mathematical rule, while in stochastic processes, the time evolution of a system is represented by a variable whose change is subject to random variation. Deterministic modeling utilizes the tools of differential equations, assuming that the time evolution of a system can be modeled exactly. According to Laplace, “The state of the world at a given instant is defined by an infinite number of parameters, subject to an infinite number of differential equations. If some ‘universal’ mind could write down all these equations and integrate

them, it could then predict with complete exactness the entire evolution of the world in the infinite future.” Features common to all deterministic mathematical formulations include that the system is completely defined by mathematical entity ω (can be a set of real numbers, one or more functions, etc.) and that values of ω in the future $t > t_0$ are uniquely determined by ω_0 , the initial state of ω , namely, $\omega = F(t_0, \omega_0, t)$. For phenomena described by differential equations, the process of finding their solution involves the integration of these differential equations with the initial conditions $\omega = \omega_0$ and $t = t_0$. Such formulations are exact and direct expressions of the deterministic character of the actual phenomena, of the physical principle of causation. However, this quantitative infinity is coarse compared to the qualitatively inexhaustible character of the real world, and this approach sometimes does not adequately represent the infinite complexity of actual events.

Stochastic modeling, on the other hand, uses probabilities to analyze the time evolution of a system. A Markov chain is probably the most famous example of stochastic modeling, aside from random walks. In a time-discrete Markov process, the probability of each event depends only on the state attained in the previous event in time. Interestingly, most deterministic modeling deals with nonlinear functions, while probabilistic modeling relies on first- and higher-order polynomial functions. This is a consequence of the mathematics used in either approach. Is the world nonlinear and deterministic or linear and probabilistic?

Regardless of the approach, the art of an investigation consists in finding a very simple space Ω (i.e., a set of values of ω or different possible states of the system) such that if we replace the actual process by varying the point ω in a determinate way over this space, we can include all the *essential* aspects of the actual process. In the words of *J.W. Gibbs*, “One of the principal objects of theoretical research in any department of knowledge is to find the point of view from which the subject appears in its greatest simplicity.”

At this point, we should discuss other considerations in the modeling process. Are we going to adopt a reductionist view or a wholistic view of the system? A reductionist approach would attempt to describe the behavior of a system from the behavior of the smallest structural unit in that system. In this bottom-up approach, whole system behavior can be predicted from the behavior of ensembles of the smallest structural units. A wholistic approach would seek to describe the behavior of the whole system as a unit, separate from its individual building blocks. In this top-down approach, correlations would be established between macroscopic behavior and particular length scales in a system in an attempt to correlate function to biological or physical structure and their interactions. The approach could also be mechanistic or phenomenological in nature. Mechanistic approaches are based on theory that describes the physical and chemical behavior of a system. A phenomenological approach just utilizes a convenient function which describes system behavior without addressing the reason for that behavior. Finally, I would like to mention the difference between interpolation and extrapolation. A simple phenomenological modeling exercise such as obtaining a least squares estimate of a straight line by linear regression generates a function which can only predict unknown values within the bounds of the data set. It should never be used outside these limits.

This is interpolation. A more sophisticated mechanistic modeling exercise should be able to predict unknown states of the system beyond the data set used to create such model. This is true prediction and constitutes extrapolation from the experimental data set.

In my experience, the modeling process of a complex system involves the following necessary steps for maximum impact:

1. *Write down all the variables that you believe affect the behavior of your system.*
2. *Design the experiment properly, with particular attention to replication. The experiment has to have at least three determinations of three replicates. They are not the same thing!*
3. *Try to control or monitor as many variables as possible during experiments.*
4. *Carry out proper statistical analysis. Any proposed effects or trends need to be statistically significant at least at the 5% level. Determine which variables significantly affect the system and which ones do not; i.e., is the variability attributed to a treatment greater than the one attributed to random experimental error?*
5. *Model the system's behavior using a mechanistic or phenomenological model and test its validity.*
6. *Attribute mechanistic significance to the parameters derived from the model.*

Any discussion about modeling eventually digresses into the realm of the philosophy of carrying out research. Research is the systematic search for new knowledge, while scientific research takes place when research involves a testing step of carefully formulated ideas. Types of research include (a) fact finding, information gathering not intended to derive generalizations or solve problems; (b) critical interpretation, arriving at conclusions through logical reasoning (critical reviews), which is not scientific research; and (c) complete research, solving problems and arriving at generalizations after a thorough search for existent pertinent facts, analysis and logical classification of these facts, and development of a reasonable case using inductive reasoning. The scientific method is a form of complete research plus the development of a hypothesis and controlled experimentation. An essential element of the scientific method includes model building, which has to do with the creation of a hypothesis. Models are central to the scientific method and complete research. Models allow us to explain and create understanding and maybe even predict behavior. These days there is way too much information and not enough knowledge created in research. Moreover, nobody has time to look back and possibly accumulate wisdom (and share it) gathered from new and old knowledge.

This book takes a “stream of consciousness” approach to the subject and is not meant to be exhaustive by any stretch of the imagination. Section 1 is an introduction to the topic of kinetic analysis assuming no prior knowledge of the subject. Section 2 includes nine examples of kinetic modeling that illustrate many techniques and approaches to problems such as color loss, oil migration, biodiesel manufacture, crystallization, nucleation, and protein aggregation. The examples

provide a practical handle on how to carry out kinetic analysis, while each chapter is designed to cover a major mathematical technique such as Fourier series analysis and solutions to coupled ordinary differential equations. Examples include both phenomenological and mechanistic modeling. The book is also meant to be a standard reference in the use of the specific models presented for research. The student of modeling should always remember that a model is “entertained” since it is just an attempt to catch a glimpse at the workings of nature. Experimental evidence must always be gathered, which will support or not support the model in the long term. A model is a sophisticated hypothesis.

I finish this brief introduction with two of my favorite quotations which are very relevant to modeling and scientific research, one by a famous scientist and one by a famous wilderness adventurer:

If nature were not beautiful it would not be worth knowing, and if nature were not worth knowing life would not be worth living. (Henri Poincare)

Only those who have had the experience can know what a sense of physical and spiritual excitement comes to one who turns his face away from men and towards the unknown. (Bill Mason)

Alejandro G. Marangoni
Guelph, ON, Canada
November 1, 2016

Contents

Part I Kinetic Modelling Basics

1	Fundamentals of Kinetics	3
1.1	Generalities	3
1.2	Basic Definitions	4
1.2.1	The Rate Equation	5
1.2.2	Integrated Rate Equations	7
1.3	Dependence of Reaction Rates on Temperature	13
1.3.1	Theoretical Considerations	13
1.3.2	Energy of Activation	16
1.4	Theory of Reaction Rates.	17
1.5	Reaction in Solution.	19
1.6	Diffusion Controlled Reactions	20
1.7	Experimental Determination of Reaction Order and Rate Constants.	21
1.7.1	Differential Method (Initial Rate Method).	21
1.7.2	Integral Method	23
1.8	Modeling Complex Reaction Pathways.	24
1.8.1	Exact Analytical Solution (Non-steady State Approximation).	25
1.8.2	Exact Analytical Solution (Steady State Approximation)	25
1.8.3	Numerical Integration and Regression.	26
1.9	Enzyme Kinetics	34
1.9.1	Enzyme Catalyzed Reactions.	34
1.9.2	Characterizing Enzyme Activity	34
1.9.3	The Equilibrium Catalysis Model	37
1.9.4	The Steady-State Catalysis Model.	39
1.9.5	The Initial Velocity vs [S] Plot.	39
1.9.6	Determining Parameters of an Enzyme Kinetic Model: Method 1	41

- 1.9.7 Determining Parameters of an Enzyme Kinetic Model: Method 2 42
- 1.9.8 Kinetic Effects of Reversible Inhibition 43
- 1.10 Food Science-Specific Kinetic Analysis: D and Z Values 49
- Bibliography 51

Part II Kinetic Modeling of Complex Processes in Food Systems

- 2 Chlorophyll Degradation in Green Tissues: Olives, Cabbage and Pickles 55**
 - 2.1 Chlorophyll Pigments 55
 - 2.2 Chlorophyll Degradation 56
 - 2.3 A Kinetic Model of Chlorophyll Degradation 57
 - 2.3.1 Coleslaw by Heaton et al. 60
 - 2.3.2 Pickles by White et al. 60
 - 2.3.3 Olives by Minguez-Mosquera et al. 62
 - 2.3.4 Relating Kinetic Parameters to Degradation Mechanisms 62
 - Bibliography 63
- 3 Oil Migration Through Cocoa Butter: The Solubilization-Recrystallization-Diffusion (SRD) Model 65**
 - 3.1 Oil Migration in Confectionery Products 65
 - 3.2 Proposed Oil Migration Mechanisms 65
 - 3.3 Fickian Diffusion. 66
 - 3.4 Capillary Forces 67
 - 3.5 Other Considerations 69
 - 3.6 Solubilization-Recrystallization-Diffusion Model. 70
 - Bibliography 76
- 4 Low-Temperature Sweetening in Potato Tubers 79**
 - 4.1 Potato Sprouting. 79
 - 4.2 The Kinetics of Cold Sweetening 81
 - 4.3 Relating Kinetic Parameters to Mechanism. 84
 - 4.4 The Impact of Starch Availability on Cold Sweetening. 87
 - 4.5 Numerical Simulations. 88
 - Bibliography 89
- 5 Modelling Sucrose Oscillations in Cold-Sweetened Potato Tubers using a Statistical Approach to Fourier Analysis 91**
 - 5.1 The Fourier Series 91
 - 5.2 A Periodic Function. 91
 - 5.3 The Mathematics of a Fourier Series. 92
 - 5.4 Modelling Sucrose Levels Oscillation Using a Statistical Approach to Fourier Analysis 92

5.5	A “How-To” Analytical Toolbox for the Study of Instabilities and Oscillations in Complex Systems	100
	Bibliography	101
6	Biodiesel Synthesis via Transesterification of Soybean Oil with Methanol	103
6.1	The Need for Alternative Fuel Sources	103
6.2	Biodiesel	103
6.3	Biodiesel Production	104
	6.3.1 Blending	104
	6.3.2 Derivatization	104
	6.3.3 Pyrolysis	105
	6.3.4 Transesterification	105
6.4	A Kinetic Model of Chemical Transesterification	107
	6.4.1 Relating Kinetic Data to Reaction Mechanism	109
	Bibliography	112
7	Kinetics of Crystal Growth Using the Avrami Model and the Chemical Potential Approach	113
7.1	Introduction	113
7.2	Derivation of the Avrami Model	115
7.3	Spherical Growth with Instantaneous Nucleation	117
	7.3.1 Spherical Growth with Sporadic Nucleation	119
	7.3.2 Plate-Like Growth with Instantaneous Nucleation	120
7.4	Plate-Like Growth with Sporadic Nucleation	120
	7.4.1 Rod-Like Growth with Instantaneous Nucleation	121
	7.4.2 Rod-Like Growth with Sporadic Nucleation	121
7.5	Transformation and Use of the Model in Experiments	122
7.6	An Alternative to the Avrami Model: the Chemical Potential Approach	125
	Bibliography	134
8	Steady-State Nucleation Kinetics: The Fisher Turnbull Model	135
8.1	Nucleation	135
8.2	Energy of Activation for Nucleation (the Gibbs-Thomson Equation)	136
8.3	The Fisher-Turnbull Equation	141
8.4	Other Applications of the Fisher-Turnbull Model	144
	Bibliography	144
9	Non-isothermal Nucleation Kinetics in Fats	145
9.1	Non-isothermal Nucleation	145
9.2	Formulation of the Time-dependent Supercooling Parameter	147
9.3	A Probabilistic Approach to Modeling Non-isothermal Nucleation Kinetics	148

9.4	Determining the Energy of Activation for a Non-isothermal Process	150
9.5	Special Case When β Is Very Small	151
9.6	Determination of the Induction Time	152
9.7	Determination of the Melting Point	152
9.8	Determination of the Nucleation Rate	154
	Bibliography	160
10	Implementation of the van Smoluchowski Model for Protein Aggregation Kinetics: Cold-Gelation of Heated Whey Protein Isolate	161
10.1	Introduction	161
10.2	van Smoluchowski's Theory of Rapid Coagulation (Physical Gels)	162
10.3	Polyfunctional Condensation Model (Chemical Gels)	166
10.4	Aggregation of Whey Protein Isolate	167
10.5	Aggregation Kinetics Example: The van Smoluchowski Model Implemented	168
	Bibliography	172



<http://www.springer.com/978-3-319-51291-4>

Kinetic Analysis of Food Systems

Marangoni, A.G.

2017, XIV, 173 p. 89 illus., Hardcover

ISBN: 978-3-319-51291-4