

THERMODYNAMICS, KINETICS, AND MICROPHYSICS OF CLOUDS

Climate change has provided a new impetus for research on clouds and precipitation. One of the greatest uncertainties in current global climate models is cloud feedback, arising from uncertainties in the parameterization of cloud processes and their impact on the global radiation balance. In the past two decades, substantial progress has been made in the simulation of clouds using cloud resolving models. However, most of the parameterizations employed in these models have been empirically based. New theoretical descriptions of cloud processes are now being incorporated into cloud models, using spectral microphysics based on the kinetic equations for the drop and crystal size spectra along with the supersaturation equation, and newer parameterizations of drop activation and ice nucleation based on the further development of the classical nucleation theory. From these models, cloud microphysics parameterizations are being developed for use in global weather and climate models.

Thermodynamics, Kinetics, and Microphysics of Clouds reflects this shift to an increasingly theoretical basis for the simulation and parameterization of cloud processes. The book presents a unified theoretical foundation that provides the basis for incorporating cloud microphysical processes in cloud and climate models in a manner that represents interactions and feedback processes over the relevant range of environmental and parametric conditions. In particular, this book provides:

- the closed system of equations of spectral cloud microphysics that includes kinetic equations for the drop and crystal size spectra for regular and stochastic condensation/deposition and coagulation/accretion along with the supersaturation equations;
- the latest theories and theoretical parameterizations of aerosol hygroscopic growth, drop activation, and ice homogeneous and heterogeneous nucleation, derived from the general principles of thermodynamics and kinetics and suitable for cloud and climate models;
- a theoretical basis for understanding the processes of cloud particle formation, evolution, and precipitation, based on numerical cloud simulations and analytical solutions to the kinetic equations and supersaturation equation;
- a platform for advanced parameterizations of clouds in weather prediction and climate models using these solutions; and
- the scientific foundation for weather and climate modification by cloud seeding.

This book will be invaluable for researchers and advanced students engaged in cloud and aerosol physics, and air pollution and climate research.

Vitaly I. Khvorostyanov is Professor of Physics of the Atmosphere and Hydrosphere, Central Aerological Observatory (CAO), Russian Federation. His research interests are in cloud physics, cloud numerical modeling, atmospheric radiation, and cloud-aerosol and cloud-radiation interactions, with applications for climate studies and weather modification. He has served as Head of the Laboratory of Numerical Modeling of Cloud Seeding at CAO, Coordinator of the Cloud Modeling Programs on Weather Modification by Cloud Seeding in the USSR and Russia, Member of the International GEWEX Radiation Panel of the World Climate Research Program, and Member of the International Working Group on Cloud-Aerosol Interactions. Dr. Khvorostyanov has worked as a visiting scientist and Research Professor in the United States, United Kingdom, France, Germany, and Israel. He has co-authored nearly 200 journal articles and four books: *Numerical Simulation of Clouds* (1984), *Clouds and Climate* (1986), *Energy-Active Zones: Conceptual Foundations* (1989), and *Cirrus* (2002). Dr. Khvorostyanov is a member of the American Geophysical Union and the American Meteorological Society.

Judith A. Curry is Professor and Chair of the School of Earth and Atmospheric Sciences at the Georgia Institute of Technology. She previously held faculty positions at the University of Colorado, Penn State University, and Purdue University. Dr. Curry's research interests span a variety of topics in the atmospheric and climate sciences. Current interests include cloud microphysics, air and sea interactions, and climate feedback processes associated with clouds and sea ice. Dr. Curry is co-author of *Thermodynamics of Atmospheres and Oceans* (1999) and editor of the *Encyclopedia of Atmospheric Sciences* (2003). She has published more than 190 refereed journal articles. Dr. Curry is a Fellow of the American Meteorological Society, the American Association for the Advancement of Science, and the American Geophysical Union. In 1992, she received the Henry Houghton Award from the American Meteorological Society.

The Cloud
Percy Bysshe Shelley (1820)

I bring fresh showers for the thirsting flowers,
From the seas and the streams;
I bear light shade for the leaves when laid
In their noonday dreams.
From my wings are shaken the dews that waken
The sweet buds every one,
When rocked to rest on their mother's breast,
As she dances about the sun.
I wield the flail of the lashing hail,
And whiten the green plains under,
And then again I dissolve it in rain,
And laugh as I pass in thunder.

I am the daughter of Earth and Water,
And the nursling of the Sky;
I pass through the pores of the oceans and shores;
I change, but I cannot die.
For after the rain, when with never a stain
The pavilion of Heaven is bare
And the winds and sunbeams with their convex gleams
Build up the blue dome of air,
I silently laugh at my own cenotaph
And out of the caverns of rain,
Like a child from the womb, like a ghost from the tomb,
I arise and unbuild it again.

*(Poetical Works of Shelley (Cambridge Editions),
by Percy Bysshe Shelley (Author), Newell F. Ford (Introduction).
Publisher: Houghton Mifflin; Revised edition,
January 1975, 704 pages, ISBN-10: 0395184614)*

THERMODYNAMICS,
KINETICS, AND
MICROPHYSICS OF CLOUDS

VITALY I. KHVOROSTYANOV
Central Aerological Observatory, Russia

JUDITH A. CURRY
Georgia Institute of Technology, USA





CAMBRIDGE
UNIVERSITY PRESS

Shaftesbury Road, Cambridge CB2 8EA, United Kingdom

One Liberty Plaza, 20th Floor, New York, NY 10006, USA

477 Williamstown Road, Port Melbourne, VIC 3207, Australia

314–321, 3rd Floor, Plot 3, Splendor Forum, Jasola District Centre, New Delhi – 110025, India

103 Penang Road, #05–06/07, Visioncrest Commercial, Singapore 238467

Cambridge University Press is part of Cambridge University Press & Assessment,
 a department of the University of Cambridge.

We share the University's mission to contribute to society through the pursuit of
 education, learning and research at the highest international levels of excellence.

www.cambridge.org

Information on this title: www.cambridge.org/9781107016033

© Vitaly I. Khvorostyanov and Judith A. Curry 2014

This publication is in copyright. Subject to statutory exception and to the provisions
 of relevant collective licensing agreements, no reproduction of any part may take
 place without the written permission of Cambridge University Press & Assessment.

First published 2014

A catalogue record for this publication is available from the British Library

Library of Congress Cataloging-in-Publication data

Khvorostyanov, Vitaly I.

Thermodynamics, kinetics, and microphysics of clouds / Vitaly I. Khvorostyanov,

Judith A. Curry. — First edition.

pages cm

Includes bibliographical references and index.

ISBN 978-1-107-01603-3

1. Precipitation (Meteorology)—Measurement. 2. Cloud forecasting.

3. Precipitation forecasting. 4. Atmospheric thermodynamics. I. Curry, Judith A. II. Title.

QC925.K47 2014

551.57'6—dc23 2014001806

ISBN 978-1-107-01603-3 Hardback

Cambridge University Press & Assessment has no responsibility for the persistence
 or accuracy of URLs for external or third-party internet websites referred to in this
 publication and does not guarantee that any content on such websites is, or will
 remain, accurate or appropriate.

Contents

<i>Preface</i>	<i>page xv</i>
1. Introduction	1
1.1. Relations among Thermodynamics, Kinetics, and Cloud Microphysics	1
1.2. The Correspondence Principle	2
1.3. Structure of the Book	3
2. Clouds and Their Properties	9
2.1. Cloud Classification	9
2.2. Cloud Regimes and Global Cloud Distribution	13
2.2.1. Large-Scale Condensation in Fronts and Cyclones	16
2.2.2. Sc-St Clouds and Types of Cloud-Topped Boundary Layer	18
2.2.3. Convective Cloudiness in the Intertropical Convergence Zone	19
2.2.4. Orographic Cloudiness	19
2.3. Cloud Microphysical Properties	20
2.4. Size Spectra and Moments	23
2.4.1. Inverse Power Laws	23
2.4.2. Lognormal Distributions	24
2.4.3. Algebraic Distributions	25
2.4.4. Gamma Distributions	26
2.5. Cloud Optical Properties	32
Appendix A.2. Evaluation of the Integrals with Lognormal Distribution	44
3. Thermodynamic Relations	45
3.1. Thermodynamic Potentials	45
3.2. Statistical Energy Distributions	49
3.2.1. The Gibbs Distribution	49
3.2.2. The Maxwell Distribution	51
3.2.3. The Boltzmann Distribution	52
3.2.4. Bose–Einstein Statistics	54
3.2.5. Fermi–Dirac Statistics	55

3.3.	Phase Rules	56
3.3.1.	Bulk Phases	57
3.3.2.	Systems with Curved Interfaces	57
3.4.	Free Energy and Equations of State	59
3.4.1.	An Ideal Gas	59
3.4.2.	Free Energy and the van der Waals Equation of State for a Non-Ideal Gas	62
3.5.	Thermodynamics of Solutions	67
3.6.	General Phase Equilibrium Equation for Solutions	70
3.6.1.	General Equilibrium Equation	70
3.6.2.	The Gibbs–Duhem Relation	72
3.7.	The Clausius–Clapeyron Equation	73
3.7.1.	Equilibrium between Liquid and Ice Bulk Phases	73
3.7.2.	Equilibrium of a Pure Water Drop with Saturated Vapor	74
3.7.3.	Equilibrium of an Ice Crystal with Saturated Vapor	75
3.7.4.	Humidity Variables	78
3.8.	Phase Equilibrium for a Curved Interface—The Kelvin Equation	80
3.9.	Solution Effects and the Köhler Equation	81
3.10.	Thermodynamic Properties of Gas Mixtures and Solutions	82
3.10.1.	Partial Gas Pressures in a Mixture of Gases	82
3.10.2.	Equilibrium of Two Bulk Phases around a Phase Transition Point	83
3.10.3.	Raoult’s Law for Solutions	84
3.10.4.	Freezing Point Depression and Boiling Point Elevation	84
3.10.5.	Relation of Water Activity and Freezing Point Depression	86
3.11.	Adiabatic Processes	88
3.11.1.	Dry Adiabatic Processes	88
3.11.2.	Wet Adiabatic Processes	90
Appendix A.3. Calculation of Integrals with the Maxwell Distribution		95
4.	Properties of Water and Aqueous Solutions	99
4.1.	Properties of Water at Low Temperatures and High Pressures	99
4.1.1.	Forms of Water at Low Temperatures	99
4.1.2.	Forms of Water at High Pressures	101
4.2.	Theories of Water	103
4.3.	Temperature Ranges in Clouds and Equivalence of Pressure and Solution Effects	107
4.4.	Parameterizations of Water and Ice Thermodynamic Properties	108
4.4.1.	Saturated Vapor Pressures	108
4.4.2.	Heat Capacity of Water and Ice	109
4.4.3.	Latent Heats of Phase Transitions	110
4.4.4.	Surface Tension between Water and Air or Vapor	111
4.4.5.	Surface Tension between Ice and Water or Solutions	112

<i>Contents</i>	vii
4.4.6. Surface Tension between Ice and Air or Vapor	113
4.4.7. Density of Water	113
4.4.8. Density of Ice	113
4.5. Heat Capacity and Einstein-Debye Thermodynamic Equations of State for Ice	114
4.6. Equations of State for Ice in Terms of Gibbs Free Energy	116
4.7. Generalized Equations of State for Fluid Water	120
4.7.1. Equations of the van der Waals Type and in Terms of Helmholtz Free Energy	120
4.7.2. Equations of State Based on the Concept of the Second Critical Point	122
Appendix A.4. Relations among Various Pressure Units	125
5. Diffusion and Coagulation Growth of Drops and Crystals	127
5.1. Diffusional Growth of Individual Drops	127
5.1.1. Diffusional Growth Regime	127
5.1.2. The Kinetic Regime and Kinetic Corrections to the Growth Rate	129
5.1.3. Psychrometric Correction Due to Latent Heat Release	132
5.1.4. Radius Growth Rate	135
5.1.5. Ventilation Corrections	137
5.2. Diffusional Growth of Crystals	138
5.2.1. Mass Growth Rates	138
5.2.2. Axial Growth Rates	141
5.2.3. Ventilation Corrections	143
5.3. Equations for Water and Ice Supersaturations	144
5.3.1. General Form of Equations for Fractional Water Supersaturation	144
5.3.2. Supersaturation Relaxation Times and Their Limits	147
5.3.3. Equation for Water Supersaturation in Terms of Relaxation Times	149
5.3.4. Equivalence of Various Forms of Supersaturation Equations	151
5.3.5. Equation for Fractional Ice Supersaturation	152
5.3.6. Equilibrium Supersaturations over Water and Ice	154
Liquid Clouds	154
Ice Clouds	154
Mixed Phase Clouds	156
5.3.7. Adiabatic Lapse Rates with Non zero Supersaturations	157
5.4. The Wegener–Bergeron–Findeisen Process and Cloud Crystallization	158
5.5. Kinetic Equations of Condensation and Deposition in the Adiabatic Process	161
5.5.1. Derivation of the Kinetic Equations	161
5.5.2. Some Properties of Regular Condensation	163
5.5.3. Analytical Solution of the Kinetic Equations of Regular Condensation	165
5.5.4. Equation for the Integral Supersaturation	167

viii	<i>Contents</i>	
	5.6. Kinetic Equations of Coagulation	168
	5.6.1. Various Forms of the Coagulation Equation	168
	5.6.2. Collection Kernels for Various Coagulation Processes	170
	Brownian Coagulation	170
	Gravitational Coagulation	171
	5.7. Thermodynamic and Kinetic Equations for Multidimensional Models	171
	5.8. Fast Algorithms for Microphysics Modules in Multidimensional Models	173
6.	Wet Aerosol Processes	181
6.1.	Introduction	181
6.1.1.	Empirical Parameterizations of Hygroscopic Growth	182
6.1.2.	Empirical Parameterizations of Droplet Activation	183
6.2.	Equilibrium Radii	186
6.2.1.	Equilibrium Radii at Subsaturation	187
6.2.2.	Equilibrium Radii of Interstitial Aerosol in a Cloud	193
6.3.	Critical Radius and Supersaturation	197
6.4.	Aerosol Size Spectra	203
6.4.1.	Lognormal and Inverse Power Law Size Spectra	203
6.4.2.	Approximation of the Lognormal Size Spectra by the Inverse Power Law	203
6.4.3.	Examples of the Lognormal Size Spectra, Inverse Power Law, and Power Indices	204
6.4.4.	Algebraic Approximation of the Lognormal Distribution	206
6.5.	Transformation of the Size Spectra of Wet Aerosol at Varying Humidity	211
6.5.1.	Arbitrary Initial Spectrum of Dry Aerosol	211
6.5.2.	Lognormal Initial Spectrum of Dry Aerosol	212
6.5.3.	Inverse Power Law Spectrum	216
6.5.4.	Algebraic Size Spectra	218
6.6.	CCN Differential Supersaturation Activity Spectrum	219
6.6.1.	Arbitrary Dry Aerosol Size Spectrum	219
6.6.2.	Lognormal Activity Spectrum	221
6.6.3.	Algebraic Activity Spectrum	226
6.7.	Droplet Concentration and the Modified Power Law for Drops Activation	230
6.7.1.	Lognormal and Algebraic CCN Spectra	230
6.7.2.	Modified Power Law for the Drop Concentration	231
6.7.3.	Supersaturation Dependence of Power Law Parameters	233
	Appendix A.6. Solutions of Cubic Equations for Equilibrium and Critical Radii	237
7.	Activation of Cloud Condensation Nuclei into Cloud Drops	241
7.1.	Introduction	241
7.2.	Integral Supersaturation in Liquid Clouds with Drop Activation	243
7.3.	Analytical Solutions to the Supersaturation Equation	246
7.4.	Analytical Solutions for the Activation Time, Maximum Supersaturation, and Drop Concentration	250

<i>Contents</i>	ix
7.5. Calculations of CCN Activation Kinetics	254
7.6. Four Analytical Limits of Solution	263
7.7. Limit #1: Small Vertical Velocity, Diffusional Growth Regime	265
7.7.1. Lower Bound	265
7.7.2. Upper Bound	268
7.7.3. Comparison with Twomey’s Power Law	270
7.8. Limit #2: Small Vertical Velocity, Kinetic Growth Regime	273
7.8.1. Lower Bound	273
7.8.2. Upper Bound	275
7.9. Limit #3: Large Vertical Velocity, Diffusional Growth Regime	277
7.9.1. Lower Bound	277
7.9.2. Upper Bound	277
7.10. Limit #4: Large Vertical Velocity, Kinetic Growth Regime	278
7.10.1. Lower Bound	278
7.10.2. Upper Bound	280
7.11. Interpolation Equations and Comparison with Exact Solutions	282
Appendix A.7. Evaluation of the Integrals J_2 and J_3 for Four Limiting Cases	284
8. Homogeneous Nucleation	289
8.1. Metastable States and Nucleation of a New Phase	290
8.2. Nucleation Rates for Condensation and Deposition	293
8.2.1. Application of Boltzmann Statistics	293
8.2.2. The Fokker–Planck, and the Frenkel–Zeldovich Kinetic Equations and the Zeldovich Factor	295
8.2.3. Application of Bose–Einstein Statistics for Condensation and Deposition	299
8.3. Nucleation Rates for Homogeneous Ice Nucleation	300
8.3.1. Nucleation Rates with the Boltzmann Distribution	300
8.3.2. Application of Bose–Einstein Statistics for Freezing	303
8.3.3. Parameterizations of Activation Energy	303
8.4. Semi-empirical Parameterizations of Homogeneous Ice Nucleation	305
8.5. Equations for Water and Ice Supersaturations with Homogeneous Ice Nucleation	311
8.6. Critical Germ Size, Energy, and Homogeneous Freezing Rate	313
8.6.1. Derivation of the Critical Germ Size, Energy, and Nucleation Rate	313
8.6.2. Analysis and Properties of the Solution	319
8.6.3. Comparison with Other Models and Observations	322
8.6.4. The Freezing of Cloud Drops	325
8.7. Critical Freezing and Melting Temperatures of Homogeneous Freezing	328
8.7.1. General Expressions Based on Classical Theory	328
8.7.2. Liquidus Curves	331
8.7.3. Relation of the Freezing and Melting Point Depressions	332
8.7.4. Comparison with Observations	333
8.7.5. Equivalence of Solution and Pressure Effects	339

8.8.	Threshold or Critical Saturation Ratios for Homogeneous Freezing	345
8.8.1.	General Equations	346
8.8.2.	Parameterization of Effective Melting Heat	347
8.8.3.	Derivation from Classical Theory of the Water Activity Shift Method	350
8.8.4.	Effects of Various Factors on the Critical Humidity $S_{w,cr}^{hom}$	353
8.8.5.	Calculations of Critical Relative Humidities over Water and Ice	354
8.9.	Parcel Model Simulations of the Kinetics of Homogeneous Ice Nucleation	357
8.9.1.	Parcel Model Description	357
8.9.2.	Simulation Results	359
8.10.	Analytical Parameterization of Homogeneous Ice Nucleation Kinetics Based on Classical Nucleation Theory	368
8.10.1.	General Features of Homogeneous Ice Nucleation Kinetics	368
8.10.2.	The Freezing Rate and Its Simplification	369
8.10.3.	Separation of Temperature and Supersaturation Dependencies	370
8.10.4.	The Evolution of the Nucleation Rate and Crystal Concentration	373
8.10.5.	Evaluation of the Deposition Integral I_{dep}	377
8.10.6.	Solution of Equations for the Supersaturation and for Crystal Concentration	379
8.10.7.	Particular Limiting Cases	381
	Diffusion Growth Limit	381
	Kinetic Growth and Large Particle Limits	381
8.10.8.	Physical Interpretation	383
8.11.	Temperature Effects and the Homogeneous Freezing of Cloud Drops	387
Appendix A.8.	Evaluation of the Integrals $J_{0i}^{(k)} = \int_0^t r_{c,ef}^{(k)}(t, t_0) \exp(\beta t_0) dt_0$	391
9.	Heterogeneous Nucleation of Drops and Ice Crystals	395
9.1.	Introduction	395
9.2.	Nucleation of Drops by Vapor Deposition on Water-Insoluble Particles	395
9.3.	Modes of Ice Nucleation and Properties of Ice Nuclei	400
9.3.1.	Modes of Ice Nucleation	400
9.3.2.	Properties of Ice Nuclei	401
9.4.	Empirical Parameterizations of Heterogeneous Ice Nucleation	404
9.5.	Nucleation of Crystals in the Deposition Mode on Water-Insoluble Particles	408
9.6.	Ice Nucleation by Deliquescence-Freezing and Immersion	411
9.7.	Critical Radius and Energy of Heterogeneous Freezing	412
9.7.1.	Basic Dependencies of Heterogeneous Freezing	412
9.7.2.	Volume Heterogeneous Freezing	414
9.7.3.	Particular Cases of Critical Radius	419
9.7.4.	Critical Energy of Volume Freezing	421
9.7.5.	Modification of Critical Energy with Active Sites	423

<i>Contents</i>	xi
9.8. Properties of the Deliquescence-Freezing Mode	426
9.8.1. Critical Radius, Energy, and the Nucleation Rate	426
9.8.2. Separation of Temperature, Supersaturation, and Aerosol Dependences of the Critical Energy and Nucleation Rate	429
9.8.3. Separation of Insoluble Fractions between Activated Drops and Unactivated CCN	434
9.8.4. Characteristic Relaxation Times of CCN Size and Solution Concentration	435
9.9. Surface Freezing and Melting	436
9.9.1. Surface Freezing	436
9.9.2. Surface Melting	438
9.10. Nucleation in a Polydisperse Aerosol	440
9.10.1. Freezing of Haze Particles at Water Subsaturation in the DF Mode	440
9.10.2. Simultaneous Freezing in the DF and Immersion Modes at Water Supersaturation	444
9.11. Critical Freezing and Melting Temperatures	446
9.11.1. General Equations	446
Volume Heterogeneous Freezing	446
Surface Quasi-Heterogeneous Freezing	450
Surface Quasi-Heterogeneous Melting	451
Liquidus Curves	452
9.12. Critical Saturation Ratios or Water Activities of Heterogeneous Freezing	452
9.12.1. General Equations	453
9.12.2. Simplifications of Equations for the Heterogeneous Critical Saturation Ratio	454
9.12.3. Derivation from Classical Theory of the Water Activity Shift Method	456
9.12.4. Calculations of Critical Relative Humidities for Heterogeneous Nucleation	458
9.12.5. Comparison of Critical Humidities for Heterogeneous and Homogeneous Nucleation	463
9.13. Parcel Model for a Mixed-Phase Cloud	465
9.13.1. Supersaturation Equation with Nucleation of Drops and Crystals	466
9.13.2. Kinetic Equations for Droplet and Crystal Size Spectra with Particle Nucleation	470
9.14. Parcel Model Simulations of Ice Nucleation Kinetics in Deliquescence-Freezing Mode	470
9.14.1. Introduction	470
9.14.2. Simulation Characteristics	471
9.14.3. Kinetics of Ice Nucleation in the Mixed and Crystalline Clouds with Weak Updrafts	473
9.14.4. Ice Nucleation Effects with Stronger Updrafts	482
9.14.5. Comparison with Homogeneous Nucleation Theory	485

xii	<i>Contents</i>	
	9.15. Comparison of Simulated Crystal Concentrations with Experimental Data and Parameterizations	491
	9.16. Thermodynamic Constraints on Heterogeneous Ice Nucleation Schemes	497
	9.17. Evaluation of Ice Nucleation and Cloud Phase State Parameterizations	501
10.	Parameterizations of Heterogeneous Ice Nucleation	507
	10.1. Analytical Parameterization of Heterogeneous Freezing Kinetics Based on Classical Nucleation Theory (CNT)	507
	10.1.1. Nucleation Rates in a Polydisperse Aerosol	507
	10.1.2. Temporal Evolution of Supersaturation	508
	10.1.3. Heterogeneous Nucleation Rate Derived from CNT and Comparison with the Previous Parameterizations	510
	10.1.4. Temporal Evolution of the Crystal Concentration	514
	10.1.5. Comparison of Crystal Concentrations with Empirical Parameterizations	515
	10.1.6. Parameterization for the Large-Scale Models. Case 1: Large N_a and Crystal Concentrations Limited by Kinetics	516
	10.1.7. Diffusion Growth Limit	520
	10.1.8. The Kinetic Growth Limit, and Small and Large Particle Limits	522
	10.1.9. Parameterization for the Large-Scale Models. Case 2: Small IN Concentration N_a and Crystal Concentration Limited by N_a	524
	10.2. Temperature Effects and Heterogeneous Freezing of Cloud Drops	525
	10.3. Parameterization of Deposition Ice Nucleation Based on Classical Nucleation Theory	529
	10.4. General Properties and Empirical Parameterizations of Contact Nucleation	533
	10.4.1. General Properties	533
	10.4.2. Empirical Parameterizations	535
	10.5. Aerosol Scavenging by Drops	536
	10.5.1. Brownian Diffusion	536
	10.5.2. Thermophoresis	537
	10.5.3. Diffusiophoresis	539
	10.6. Freezing and Scavenging Rates	541
11.	Deliquescence and Efflorescence in Atmospheric Aerosols	547
	11.1. Phenomena of Deliquescence and Efflorescence	547
	11.2. Theories and Models of Deliquescence and Efflorescence	549
	11.3. A Model for Deliquescence of Salt Crystals Based on the Entropy Equation	553
	11.4. Applications of the Deliquescence Model	558
	11.4.1. The Temperature Dependence of Dissolution Heat	559
	11.4.2. The Temperature Dependence of Solubility	559
	11.4.3. The Temperature Dependence of the Deliquescence Relative Humidity	562
	11.5. Phase Diagram of the Solution and Evaluation of the Eutectic Point	563
	11.6. A Model for Efflorescence of Salt Crystals Based on the Entropy Equation	566

<i>Contents</i>	<i>xiii</i>
11.7. Applications of the Efflorescence Model	570
11.7.1. The Temperature Dependence of Efflorescence	570
11.7.2. The Solute Activity and Mole Fraction Dependence of Efflorescence	571
11.7.3. The Joint Phase Diagram	573
12. Terminal Velocities of Drops and Crystals	577
12.1. Review of Previous Theories and Parameterizations	577
12.2. Basic Equations for Fall Velocities	582
12.3. Turbulent Corrections	587
12.4. Asymptotic Values and Applications for Spherical and Nonspherical Particles	588
12.5. Corrections for Temperature and Pressure	591
12.6. Results of Calculations	593
12.6.1. Re-X Relation	593
12.6.2. The Drag Coefficient and “Crisis of Drag”	594
12.6.3. Application to Drops	596
12.6.4. Turbulent Corrections and Their Application to Aggregates	598
12.6.5. Other Crystal Habits	603
12.6.6. Application to Hail	605
12.6.7. Altitude Correction Calculations	606
12.7. Parameterizations for Large-Scale Models	608
12.8. Applications for Remote Sensing, Other Objects and Other Planets	610
13. Broad Size Spectra in Clouds and the Theory of Stochastic Condensation	613
13.1. Introduction	613
13.1.1. Mechanisms and Theories of the Formation of Broad Size Spectra in Clouds	614
13.1.2. Kinetic Equations of Stochastic Condensation	618
13.2. Condensation in a Turbulent Cloud	623
13.2.1. Basic Equations	623
13.2.2. Stochastic Equations	624
13.2.3. Supersaturation Fluctuations	625
13.3. Evaluation of Correlation Functions	628
13.3.1. Expansions of Random Characteristics over the Turbulent Frequencies	628
13.3.2. Supersaturation as a Nonconservative Variable	629
13.3.3. Covariances with Supersaturation	630
13.3.4. Covariances with the Drop Size Distribution Function	631
13.4. General Kinetic Equations of Stochastic Condensation	633
13.5. Assumptions and Simplifications for Analytical Solutions	636
13.6. Approximation Neglecting the Diffusional Growth of Larger Particles	639
13.6.1. Small Particle Solution	640
13.6.2. Large Particle Solution	640
13.6.3. Merged Solution	641
13.6.4. Asymptotic Solutions	643
13.7. Solution Including the Diffusional Growth of Large Particles, Sedimentation, and Coagulation	645

xiv	<i>Contents</i>	
13.8.	Physical Interpretation of the Parameters	647
13.8.1.	Various Forms of Solution Parameters	647
13.8.2.	Solutions in the Form of Gamma Distributions	649
13.8.3.	Solutions in the Form of Inverse Power Laws	654
13.9.	Applications of the Solution for Liquid Clouds	656
13.10.	Comparison with Previous Theories and Observations	661
13.11.	Calculation of Size Spectra for a Crystalline Cloud	665
13.12.	Derivation of the Generalized Stochastic Kinetic Equations	
	from the Fokker–Planck Equation	669
13.12.1.	Chapman–Kolmogorov and Fokker–Planck Equations	669
13.12.2.	Spatially Homogeneous Cloud	673
13.12.3.	Spatially Inhomogeneous Cloud	676
Appendix A.13.	Derivation and Solution of the Kummer Equation in Section 13.6.3	679
Appendix B.13.	Solutions of Kinetic Equation of Section 13.7, Taking	
	into Account Diffusional Growth in the Tail	684
14.	Analytical Solutions to the Stochastic Kinetic Equation for Precipitating Clouds	685
14.1.	Introduction	685
14.2.	Derivation of Kinetic Equations in Continuous Collection Approximations	688
14.3.	Basic Equations and Assumptions for the Large-Size Fraction	692
14.4.	Solutions for the Large-Size Fraction Taking into Account Diffusion	
	Growth and Coagulation	696
14.4.1.	General Solution	696
14.4.2.	Particular Case: Fall Speed as a Linear Function of Particle Size	698
14.4.3.	Particular Case: Coagulation Growth Rate Much Greater	
	than Diffusion Growth Rate	699
14.4.4.	Particular Case: Aerodynamic Regime for the Fall Speed	
	of Large Particles	700
14.4.5.	Solutions for Subcloud Layers	702
14.5.	Interpretation of Solutions	703
14.5.1.	General Analysis of the Parameters	703
14.5.2.	Example Calculations for a Crystalline Cloud	705
14.5.3.	General Interpretation of the Solutions	709
14.6.	Autoconversion and Corrections to the Analytical Solutions	712
14.7.	The Coagulation Equation as the Integral Chapman–Kolmogorov	
	and Differential Fokker–Planck Equations	716
Appendix A.14.	Evaluation of the Integrals in Section 14.4.2 for $v(r) = A_v r$	722
Appendix B.14.	Evaluation of the Integrals in Section 14.4.4 for $v(r) = A_v r^{1/2}$	
	(Aerodynamic Regime of Fall Velocities)	724
<i>References</i>		727
<i>Notations</i>		767
<i>Index</i>		777

Preface

Cloud microphysics is a branch of cloud physics that studies initiation, growth, and dissipation of cloud and precipitation particles. Cloud microphysics is governed by the thermodynamic and kinetic processes in clouds. The field of cloud microphysics has been intensively developed since the 1940s when the first successful experiments on cloud seeding were performed. The field has received additional impetus in recent years from the challenges associated with forecasting precipitation and understanding aerosol-cloud interactions in the context of climate change and feedback processes. Several books on cloud microphysics are available, including Mason (1957), Fletcher (1962, 1970a), Dufour and Defay (1963), Sedunov (1974), Voloshchuk and Sedunov (1975), Voloshchuk (1984), Matveev (1984), Young (1993), Pruppacher and Klett (1997), and Cotton et al. (2011).

Thermodynamics, Kinetics, and Microphysics of Clouds extends the subject of cloud microphysics beyond these previous treatments. The goals and contents of this book are formulated to:

- Present in compact form the major thermodynamic relations and kinetic equations required for theoretical consideration of cloud microphysics;
- Review the currently known states of water in liquid, crystalline, and amorphous forms, and the conceptual modern theories of water and equations of state for water in various states;
- Formulate a closed system of equations that describe the kinetics of cloud microphysical processes and is suitable both for analytical studies and for inclusion in numerical models;
- Derive from theory generalized analytical parameterizations for aerosol deliquescence, hygroscopic growth, efflorescence, and drop activation and ice nucleation in various modes;
- Demonstrate that these theoretical parameterizations generalize and unify previous parameterizations and include them as particular cases; express previous empirical parameters via atmospheric and aerosol parameters and theoretical quantities;
- Derive the kinetic equations of stochastic condensation and coagulation and obtain their analytical solutions that reproduce the observed drop and crystal size spectra; express parameters of empirical distributions from theory; and
- Outline a path for future generalizations of the kinetic equations of cloud microphysics based on the Chapman–Kolmogorov and Fokker–Planck equations.

Using the general principles of thermodynamics and kinetics, a closed system of equations is formulated that includes kinetic equations for the drop and crystal size spectra along with the supersaturation equations. Using these equations and further developing classical nucleation theory, theories are

developed of aerosol hygroscopic growth, drop activation, and ice homogeneous and heterogeneous nucleation. Analytical expressions are obtained for the particle concentration, critical radii and energies of nucleation, nucleation rates that are expressed as functions of temperature, saturation ratio, pressure, and aerosol concentration simultaneously and in factorized form. It is shown that the new theoretical expressions generalize previous empirical parameterizations, can reduce to them in some particular cases, and their empirical parameters are expressed via the aerosol parameters and physical constants. The validity of these new theoretical expressions is verified in comparison with experimental data, previous empirical and semi-empirical parameterizations, and parcel model simulations. A similar theory is developed for the aerosol deliquescence and efflorescence. This allows for the first time calculation from the theory of a unified phase diagram for solutions that are in agreement with experimental phase diagrams.

Various analytical solutions to the kinetic equations and supersaturation equations are obtained for adiabatic and non-adiabatic processes. These solutions are suitable both for analytical studies of condensation and for inclusion in the numerical models. This system of equations, including kinetic equations for drops and crystals and integral supersaturation equations, is generalized for the turbulent atmosphere and multidimensional models. A fast algorithm for a numerical solution based on the splitting method is described. Spectral bin microphysical method was applied for many years in various 1D, 2D, and 3D models for various cloud types, and its applicability in the models of various scales and dimensions is discussed.

The kinetic equations of stochastic condensation in a turbulent atmosphere are derived and generalized taking into account the coagulation and accretion processes. Various analytical solutions to these stochastic equations are obtained, whose functional forms are similar to the gamma distributions and to exponential and inverse power laws that have been observed in clouds and precipitation. The solution parameters are expressed via the atmospheric characteristics and physical constants, and the solutions are verified through comparison with experimentally observed size spectra. These solutions provide explanations of various empirical parameterizations and a platform for their refinement.

In addition to advancing our basic understanding of cloud microphysical processes, the theoretical approach employed in this book supports the explanation and interpretation of laboratory and field measurements in the context of instrument capabilities and limitations and motivates the design of future laboratory and field experiments. In the context of models that include cloud processes, ranging from small-scale models of clouds and atmospheric chemistry to global weather and climate models, the unified theoretical foundations presented here provide the basis for incorporating cloud microphysical processes in these models in a manner that represents the process interactions and feedback processes over the relevant range of environmental and parametric conditions. Further, the analytical solutions presented here provide the basis for computationally efficient parameterizations that include the relevant parametric dependencies. The methods of cloud simulation using spectral bin microphysics described here are especially suitable for modeling of weather modification by cloud seeding since these methods are almost always based on modification of cloud microstructure and phase state. These methods are also convenient for studies of inadvertent cloud modification by anthropogenic and natural pollutions and for studies of cloud-radiation interactions.

This book incorporates the heritage of Russian cloud physics that introduced and developed the kinetic equations for drop and crystal diffusion growth, the fast numerical algorithms for their

solutions, and the stochastic approach to cloud microphysical processes. This Russian heritage is combined with the best knowledge of cloud microphysics acquired and described in the Western literature over the past several decades. A large amount of the material presented in this book is based on original work conducted jointly by the authors over almost two decades. Some of this research has been published previously in journal articles, but a large portion of this material is being published here in this book for the first time, notably the parameterization of heterogeneous ice nucleation and the theory of aerosol deliquescence and efflorescence.

Integration of Russian and Western perspectives on cloud physics was facilitated by the 1972 bilateral treaty between the U.S. and USSR on Agreement and Cooperation in the Field of Environmental Protection, specifically under Working Group VIII – The Influence of Environmental Change on Climate. Its regular meetings and exchanges of delegations and information promoted international collaboration, provided the foundation for long-term cooperation, and outlined proposals for joint research. With the advent of the World Climate Research Programme (WCRP) in 1980, both Khvorostyanov and Curry subsequently became members of the WCRP Working Group on Radiative Fluxes, which later became the Radiation Panel of the Global Water and Energy Exchange Experiment (GEWEX). The GEWEX Radiation Panel had regular annual meetings (where the authors participated and met), which initiated the collaboration that has lasted for almost two decades, resulted in more than 30 joint publications, and culminated in this book.

This book bridges Russian and Western perspectives of cloud physics. Khvorostyanov's involvement in the evolution of the Russian school of cloud physics includes development of cloud models with spectral bin microphysics and applications to cloud seeding and cloud-radiation interactions. Curry's early cloud microphysics research focused on aircraft observations of cloud microphysics and the development of parameterizations for cloud and climate models. Over the past 18 years, Khvorostyanov and Curry have collaborated on a range of cloud microphysical topics of relevance to understanding and parameterizing cloud processes for cloud and climate models, that integrate the Russian perspectives on cloud microphysics into the broader community, and that combine Eastern and Western approaches to cloud microphysics. In addition to summarizing and integrating these perspectives and the broad body of recent research in cloud microphysics, throughout the book a number of new results are included, as well as extensions and generalizations of existing ones.

This monograph is intended to provide a source of information for scientists engaged in teaching and research in cloud physics and dynamics, aerosol physics, air pollution, and weather modification. The book can be used as a textbook to provide graduate-level students with the theoretical foundations of cloud microphysics. Researchers and students should have a basic background in physics and thermodynamics and mathematical physics before using this book. Beyond this basic background, the authors have made every effort to make the book as self-inclusive as possible. Formal derivations and analytical solutions are emphasized, with every effort made to make the mathematical steps easy to follow, including additional details in the appendices. A comprehensive bibliography is provided that references seminal material in the primary literature and previous textbooks and monographs.

The authors gratefully acknowledge support from the DOE Atmospheric Radiation Measurement Program and numerous NASA projects. Many basic concepts and views described in this book were accumulated in multiyear fruitful collaboration with Prof. Mikhail Buikov, Prof. Kirill Kondratyev, and Prof. Kenneth Sassen, to whom the authors are thankful. The authors also greatly appreciate the

numerous useful discussions over many years on multiple aspects of cloud and climate studies with Drs. Al Arking, Stefan Bakan, Neville Fletcher, Steve Ghan, Hartmut Grassl, Olaf Hellmuth, Peter Hobbs, Paul Mason, Hugh Morrison, Leonid Matveev, Anna Pirnach, Bill Rossow, Yuri Sedunov, Robert Schiffer, Victor Smirnov, Alexander Stepanov, Graeme Stephens, Vladimir Voloshchuk, and many of our colleagues and co-authors who helped clarify various aspects of cloud microphysics.

In addition, the authors would like to thank Dr. Vladimir Chukin, Dr. Paul DeMott, and Dr. Hitoshi Kanno for their useful discussions on ice nucleation and for providing experimental data. Dr. Osamu Mishima and Dr. Thomas Koop are also thanked for their permission to adapt and use their conceptual current schemes of the water states and phase diagrams. The authors are also grateful to Mrs. Sylvaine Ferrachat from the group of Prof. Ulrike Lohmann at the Institute for Atmospheric and Climate Science, Zurich, Switzerland, for preparing and providing the figure of the observed climatic global cloud field based on the ISCCP data. They would also like to thank Dr. Yuxin Yun from the group of Prof. Joyce Penner at the University of Michigan for providing the figure of the global cloud field simulated with the climate model. Useful discussions with, and help from, Prof. Stephen Warren and Dr. Ryan Eastman in preparing the figures of the global cloud field are greatly appreciated. Thanks also to Drs. Vladimir Chukin, Olaf Hellmuth, and Vladimir Nikulin for their help in preparing some of the figures.

This book was greatly facilitated and supported by the editors at Cambridge University Press: Dr. Matt Lloyd, Ms. Sarika Narula, and Mrs. Shari Chappell; Ms. Saradha Chandrahasan (Project Manager at S4Carlisle); and Mr. Michael McGee (Copy Editor). The authors greatly appreciate their excellent organizational and editorial work. The authors are grateful to the Art Team of the S4Carlisle Publishing Services who carefully and skillfully created the artwork, preparing the figures for publication. Lastly, the authors gratefully acknowledge the permission granted them for reproducing figures from published articles by the American Meteorological Society, the American Geophysical Union, John Wiley & Sons, and the American Chemical Society.

Vitaly I. Khvorostyanov, Moscow, Russia
Judith A. Curry, Atlanta, Georgia, USA