

# Contents

<b>1</b>	<b>Introduction .....</b>	<b>1</b>
<b>2</b>	<b>States of Aggregation, Thermodynamic Phases, Phase Transformations, and the Vitreous State.....</b>	<b>7</b>
2.1	The Vitreous State: First Attempts at a Classification .....	7
2.2	Basic Thermodynamic Relationships .....	10
2.2.1	The Fundamental Laws of Classical Thermodynamics and Some Consequences .....	10
2.2.2	General Thermodynamic Evolution Criteria, Stability Conditions and the Thermodynamic Description of Non-equilibrium States .....	14
2.2.3	Phases and Phase Transformations: Gibbs's Phase Rule and Ehrenfest's Classification .....	16
2.3	Crystallization, Vitrification and Devitrification of Glass-Forming Melts: Overview on Some Experimental Results.....	24
2.4	The Viscosity of Glass-Forming Melts .....	35
2.4.1	The Temperature Dependence of the Viscosity of Glass-Forming Melts .....	35
2.4.2	Technological Significance of the Viscosity.....	42
2.4.3	Temperature Dependence of Molecular Properties Connected with the Viscosity .....	43
2.5	Thermodynamic Properties of Glass-Forming Melts .....	46
2.5.1	Temperature Dependence of the Heat Capacities .....	46
2.5.2	The Temperature Dependence of the Thermodynamic Functions.....	50
2.5.3	Alternative Methods of Determination of Caloric Properties of Glass-Forming Melts .....	57
2.5.4	The Change of Mechanical, Optical and Electrical Properties in the Transformation Range ...	59
2.6	Conclusions: The Nature of the Vitreous State .....	63

<b>3</b>	<b>Non-equilibrium Thermodynamics and the Kinetics of Glass Transition and Stabilization</b>	<b>69</b>
3.1	The Thermodynamic Description of Non-equilibrium States: Introduction	69
3.2	Structural Order Parameters and Thermodynamic Functions of Vitrified Systems	72
3.3	Thermodynamic Functions of Undercooled Melts: A Simple Thermodynamic Model	77
3.4	Some Simple Geometrical Considerations	82
3.5	Thermodynamic Functions of Vitrified Melts	83
3.6	Thermodynamics and the Kinetics of Vitrification in Terms of Simon's Approximation	85
3.7	Dependence of the Thermodynamic Properties of Glasses on Cooling Rate	89
3.8	The Prigogine-Defay Ratio	92
3.9	Kinetics of Stabilization Processes	95
3.10	Temperature Dependence of the Thermodynamic Driving Force of Stabilization	102
3.11	Experimental Results	105
3.12	Vapor Pressure and Solubility of Glasses	107
3.13	Affinity of Chemical Reactions Involving a Vitreous Reagent	118
3.14	Location of the Vitreous State in the $(p, T)$ -Diagram	120
3.15	Discussion	122
<b>4</b>	<b>General Approaches to the Description of the Structure of Glasses</b>	<b>127</b>
4.1	Introduction	127
4.2	Goldschmidt's Rule	128
4.3	Zachariasen's Criteria for Glass-Formation	129
4.4	Lebedev's Crystallite Hypothesis of Glass Structure	131
4.5	The Bernal-Polk Model	138
4.6	Further Developments: Voronoi Polyhedra, Polymerization and Aggregation	144
4.7	Homogeneous Versus Heterogeneous Models for the Structure of Glasses	148
4.8	Superstructure of Real Glasses	151
4.9	Structure of Organic High-Polymer Glasses	152
4.10	Reconstructive and Non-Reconstructive Crystallization	156
4.11	The Hierarchy of Disorder and the Structure of Glasses	159
4.12	Discussion	162
<b>5</b>	<b>Statistical Physics of Under-cooled Melts and Glasses</b>	<b>165</b>
5.1	Introduction: Summary of Attempts at Modeling the Liquid State	165
5.2	Statistical Physics of Liquids: Basic Equations	167

5.3	Cell or Lattice Models of Liquids .....	172
5.4	Lattice-Hole Models of Simple Liquids .....	178
5.4.1	General Characterization .....	178
5.4.2	The Classical Lattice-Hole Model .....	179
5.4.3	Incorporation of the Melt-Crystal Transition into Lattice-Hole Models of Liquids.....	186
5.4.4	Discussion of Some Further Developments .....	188
5.5	Statistical Models of Polymer Glass-Forming Systems .....	189
5.5.1	Introductory Remarks .....	189
5.5.2	Lattice-Hole Models of Polymer Liquids .....	192
5.6	Configurational Statistical Determination of the Zero-Point Entropies of Glasses .....	200
5.6.1	Comparison of Theoretical and Experimental Results and the Correlation of the Entropy with the Structure of Glasses.....	200
5.6.2	Further Attempts.....	204
5.7	Specific Heats of Glasses at Ultra-low Temperatures .....	209
5.8	Atomistic Approach to the Kinetics of Stabilization .....	211
5.9	Model Statistical Treatments of Vitrification .....	214
5.10	Conclusions.....	216
<b>6</b>	<b>Kinetics of Crystallization and Segregation: Nucleation in Glass-Forming Systems .....</b>	<b>219</b>
6.1	Kinetics of Phase Formation and Its Relevance for Glass Science and Technology.....	219
6.2	Thermodynamics and Nucleation Phenomena .....	221
6.2.1	Thermodynamics of Heterogeneous Systems .....	221
6.2.2	The Origin of Metastability: Critical Clusters.....	224
6.2.3	General Expression for the Thermodynamic Driving Force of First-Order Phase Transformations .....	231
6.2.4	Size Dependence of the Thermodynamic Properties of Small Clusters .....	235
6.3	Kinetics of Homogeneous Nucleation.....	242
6.3.1	Classical Nucleation Theory .....	242
6.3.2	Analysis of Important Special Cases .....	249
6.3.3	Problems, Generalizations and Improvements: An Overview .....	254
6.3.4	General Description of the Time Evolution of the Cluster Size Distribution: The Zeldovich-Frenkel Equation .....	257
6.3.5	Transient Nucleation: Time Dependence of the Nucleation Rate and the Number of Supercritical Clusters .....	265
6.3.6	The Time-Lag in Transient Nucleation .....	271

6.3.7	Nucleation in Processes of Reconstructive Crystallization: Nucleation of Chain-Folding Polymers .....	275
6.3.8	Atomistic Approach to Nucleation .....	280
6.3.9	Thermal and Athermal Nucleation .....	283
6.3.10	General Scenario for the Overall Course of First-Order Phase Transformations in Finite (Closed) Systems: Conclusions from a Thermodynamic Analysis .....	285
<b>7</b>	<b>Catalyzed Crystallization of Glass-Forming Melts .....</b>	<b>289</b>
7.1	Introductory Remarks: Ways to Induce Nucleation .....	289
7.2	Heterogeneous Nucleation: Basic Thermodynamic Relationships .....	290
7.3	The Kinetics of Heterogeneous Nucleation: Basic Equations .....	294
7.4	Activity of Foreign Substrates in Induced Crystallization .....	297
7.5	Homogeneous Nucleation Catalysis: The Influence of Surfactants .....	300
7.6	Nucleation on Charged Particles and in Electromagnetic Fields .....	304
7.7	Surface Induced Crystallization of Glasses .....	308
7.7.1	Inhibition of Bulk Crystallization by Elastic Strains .....	308
7.7.2	Elastic Strains and the Catalytic Effect of Planar Interfaces .....	312
7.7.3	The Influence of Surface Roughness on Crystallization of Glasses .....	317
7.7.4	Crystallization of Glass Powders and Elastic Strains .....	322
7.8	Kinetics of Nucleation and Induced Crystallization of Glass-Forming Melts: Experimental Evidence .....	323
<b>8</b>	<b>Theory of Crystal Growth and Dissolution in Under-cooled Melts: Basic Approaches .....</b>	<b>333</b>
8.1	Introduction .....	333
8.2	The Normal or Continuous Mode of Growth and Dissolution: The Transition Frequency .....	335
8.3	Crystal Growth Determined by Two-Dimensional Nucleation .....	340
8.4	Screw Dislocations and Crystal Growth .....	346
8.5	Further Developments of the Basic Models: Diffusive Melt-Crystal Interfaces, Transient Effects in Two-Dimensional Nucleation and Crystal Growth .....	348
8.6	Modes of Crystal Growth in Chain-Folding Polymer Melts .....	351
8.7	Experimental Investigations on the Mechanisms of Crystal Growth in Glass-Forming Melts .....	353

<b>9</b>	<b>Growth of Clusters and of Ensembles of Clusters: Ostwald Ripening and Ostwald's Rule of Stages</b>	367
9.1	Introductory Remarks: General Observations	367
9.2	Diffusion-Limited Segregation	370
9.3	Growth of Ensembles of Clusters: The Lifshitz-Slezov-Wagner Theory	372
9.4	Modifications and Generalizations	376
9.5	Growth of Clusters with Different Structures and Ostwald's Rule of Stages	379
9.5.1	Introduction	379
9.5.2	The Classical Kinetic Treatment of Ostwald's Rule of Stages	381
9.5.3	Influence of Non-Steady State Effects and Sticking Coefficient Differences	384
9.5.4	Further Developments and Applications	386
9.5.5	Ostwald's Rule of Stages and the Formation of Vitreous Condensates	388
9.5.6	Discussion	392
<b>10</b>	<b>Kinetics of Overall Crystallization: Kinetic Criteria for Glass-Formation</b>	395
10.1	Introduction	395
10.2	The Kolmogorov-Avrami Equation	396
10.3	Generalization Accounting for Non-steady State Nucleation Kinetics	402
10.4	The Kinetics of Overall Crystallization: Experimental Results	405
10.5	Kinetic Criteria for Glass-Formation: Time-Temperature-Transformation (TTT) Diagrams	407
10.6	Kinetic, Bond Energy and Structural Criteria for Vitrification: A Comparison	413
<b>11</b>	<b>Liquid Phase Separation in Glass-Forming Melts</b>	417
11.1	Introduction	417
11.2	Kinetics of Spinodal Decomposition	418
11.3	Liquid-Phase Separation Versus Crystallization	422
11.4	On the Effect of Primary Liquid-Phase Separation on Crystallization	423
<b>12</b>	<b>Rheology of Glass-Forming Melts</b>	425
12.1	Introduction	425
12.2	Phenomenological Rheology of Glass-Forming Melts in its Linear Approximation	428
12.3	Analysis of Special Cases	431
12.4	Non-Newtonian Flow Models	433
12.5	Linear (Maxwellian) and Non-Maxwellian Kinetics of Relaxation	435

12.6	Molecular Models of Viscous Flow .....	437
12.7	Molecular Models of Flow of Liquids Under Stress.....	439
12.8	Kinetics of Nucleation and Growth in Viscoelastic Media.....	441
<b>13</b>	<b>Concluding Remarks</b> .....	<b>443</b>
<b>14</b>	<b>Brief Overview on Some New Developments</b> .....	<b>447</b>
14.1	Glasses and the Glass Transition .....	448
14.1.1	Generic Phenomenology of the Glass Transition and the Thermodynamic Properties of Glasses .....	448
14.1.2	Glasses and the Third Law of Thermodynamics .....	459
14.1.3	The Prigogine-Defay Ratio.....	461
14.1.4	Kinetics of Vitrification at Variable Rates of Change of Control Parameters .....	465
14.1.5	On the Dependence of the Properties of Glasses on Cooling and Heating Rates: Some Results of Numerical Computations .....	466
14.1.6	The Viscosity of Glass-Forming Systems Described in Terms of the Generic Phenomenological Approach: The Activated State Model of Viscous Flow .....	472
14.1.7	Thermodynamic and Kinetic Fragility of Glass-Forming Systems: Thermodynamic and Kinetic Structural Coefficients .....	475
14.2	Phase Formation Processes in Glass-Forming Systems .....	480
14.2.1	Generalized Gibbs' Approach to the Thermodynamics of Heterogeneous Systems and the Kinetics of First-Order Phase Transitions .....	480
14.2.2	Some Comments on the Skapski-Turnbull Rule .....	499
14.2.3	Cluster Growth and Coarsening in Segregation Processes, Crystallization of Glasses and Elastic Stresses .....	501
14.2.4	Catalyzed Crystallization of Glass-Forming Melts: Activity of Nucleants .....	509
14.2.5	Some Further New Results in the Kinetic Description of Phase Formation Processes .....	511
14.3	Concluding Remarks .....	514
	References to Chapter 14 .....	515
	<b>References</b> .....	<b>525</b>
	<b>Index</b> .....	<b>551</b>