## **TEUBNER-TEXTE zur Physik** · Band 17

Herausgeber/Editors: Werner Ebeling, Berlin Wolfgang Meiling, Dresden Armin Uhlmann, Leipzig Bernd Wilhelmi, Jena

Heinz Ulbricht / Jürn Schmelzer / Reinhard Mahnke Frank Schweitzer

## Thermodynamics of Finite Systems and the Kinetics of First-Order Phase Transitions

Phase transitions between different states of matter occur in many equilibrium and nonequilibrium systems. The kinetics of thesephase changes are studied mainly in the case of condensation of a single vapour in a supersaturated state by homogeneous nucleation. Based on thermodynamic investigations of heterogeneous systems the stochastic and deterministic theory of nucleation and growth of the new phase is derived. The emphasis lies on finite-size-effects which lead to a depletion of the vapour. The results are mainly explained in terms of clusters (droplet model) and enlarged to the influence of external fields. Numerous computer simulations are presented.

1

## <u>Contents</u>

Foreword

~

1.	Introduction /	
1.1.	Types and Classification of Phase Transitions	7
1.2.	Thermodynamic and Experimental Conditions for Supersaturated Vapour States	12
1.3.	Outline of Classical Nucleation Theory	19
1.3.1.	The Classical Droplet Model	19
1.3.2.	Kinetic Assumptions of Classical Nucleation Theory	23
1.3.3.	Modifications of Classical Nucleation Theory	27
1.4.	Nucleation in a Lattice Gas Model	31
2.	Thermodynamics of Heterogeneous Systems	
2.1.	Thermodynamic Premises of Classical Nucleation Theory	39
2.2.	Gibbs' Theory of Heterogeneous Systems	40
2.3.	Curvature Dependence of Surface Tension	45
2.4.	Heterogeneous Systems in Non-Equilibrium States and the Principle of Inner Equilibrium	53
3.	Thermodynamics and Nucleation in Finite Systems	5.0
3.1.	The Work of Formation of Clusters	28
3.2.	Equilibrium States and the Conditions for Stability of the Clusters	63
3.3.	Critical Thermodynamic Parameters for Nucleation in Finite Systems	67
3.4.	The Work of Formation of Critical Clusters	72
3.5.	Parameters of the Critical Cluster in Dependence on the System Size	76
3.6.	Formation of a Droplet Ensemble in Finite Systems	80
4	Kinetics of Phase Transitions in Finite Systems - A Stochastic Approach	
4.1.	Free Energy of the Cluster Distribution	86
4.2.	Kinetic Assumptions and Master Fouation	92
4.3.	Results of Computer Simulations	98
4.3.1.	Stochastic Dynamics Technique	98
4.3.2	Evolution of a Single Cluster	100
4.3.3	Evolution of the Cluster Distribution	105
4.4.	Probability Distribution and Mean First Passage Time	111
4.5.	Mean Values for the Number of Clusters – Fokker-Planck Equation	117

-

3

5.	<u>Kinetics of Growth of a New Phase -</u> A Deterministic Description	
5.1.	General Scenario of First-Order Phase Transition in Finite Systems	124
5.2.	Nucleation in Finite Systems - The Quasi-Steady-State- Approximation	126
5.3.	Deterministic Growth Equations	128
5.3.1.	Diffusion Equation Approach	128
5.3.2.	Derivation of a General Growth Equation for Clusters of a New Phase	131
5.4.	Simultaneous Description of Nucleation and Growth	133
5.5.	Curvature Dependence of Surface Tension and the Scenario of First-Order Phase Transitions	138
5.6.	Further Applications	140
6	Theory of Ostwald Ripening	
6.1.	Basic Equations	144
6.2.	The Lifshitz-Slyozov Theory	147
6.3.	Thermodynamic Aspects of Ostwald Ripening in Solids and Liquid Solutions	149
6.4.	A New Method of Kinetic Description of Ostwald Ripening	152
6.5.	Ostwald Ripening and the Relations to the Theory of Self-Organization	158
7	Growth of Bubbles in Finite Systems	
7.1.	The Model	168
7.2.	Thermodynamic Analysis	169
7.3.	Kinetic Description of Nucleation and Growth of Bubbles	170
7.4.	Applications to Liquid-Gas Solutions and Multicomponent Systems	174
8.	Nucleation and Growth in Elastic and Viscoelastic Media	
8.1.	Derivation of a Growth Equation for Clusters in Elastic Media	176
8.2.	Models for the Calculation of Elastic Strains	178
8.2.1.	Elastic Strains of Nabarro Type	179
8.2.2.	Elastic Strains in Segregation Processes in Elastic Media	183
8.2.3.	The Influence of Viscous Properties of the Matrix on the Development of Elastic Strains	184
8.3.	Formation and Growth of Single Clusters in Elastic Media	188
8.4.	Ostwald Ripening in Elastic and Viscoelastic Media	190

References

195

l