Contents

1. Introduction 1

2. Acoustic Spectroscopy of Ideal Solutions 7
2.1 Density 8
2.2 Viscosity 8
2.3 Ultrasound Velocity, Compressibility, and Heat Capacity 12
2.4 Ultrasonic Absorption 14

3. Phase-Separating Solutions 23
3.1 Hydrogen Bonds in Solutions with Lower Phase-Separation Critical Point 23
3.2 Phase Diagrams of Phase-Separating Solutions. Order Parameter 25
3.3 Phase Diagrams of Binary Solutions with One Critical Point . 27
3.4 Binary and Ternary Solutions with Closed Phase-Separation Region 27

4. Dynamics of States Close to Critical 37
4.1 Low Frequency Acoustic Spectroscopy of Weakly Absorbing Liquids 37
4.2 Acoustic Spectroscopy of Critical Solutions with Low Sound Absorption 39
4.3 Acoustic Perturbation and Correlation Radius of Fluctuations in the Vicinity of a Critical Point 43
4.4 Chemical Reactions in Near-Critical States 45
4.5 Kinetics of Mono- and Bimolecular Reactions Close to a Phase-Separation Critical Point 46

5. Physics of Solutions with Double Critical Point 53
5.1 Theory of Solutions with Double Critical Point 54
5.2 Rayleigh Scattering of Light 55
5.3 Dynamics of Near-Critical States of Solutions with a DCP . . . 62
5.4 Shear Viscosity 63
5.5 Sound Propagation 67

6. Micellization as a Phase Transition 71
6.1 Conceptual Experiments 71
6.2 Electronic Structure of Hydrocarbon Chains of Molecules 75
6.3 Fluctuon Model of Micellization 77
6.4 Green Function Method 80
6.5 Huckel's Method of Molecular Orbitals 81
6.6 Critical Micellization Concentration 84
6.7 Micellization as a Phase Transition of Finite Type 88
6.8 Phase Transitions at Micellization in Solutions of Ionic Molecules 90
6.9 Kinetics of Micellar and Pre-micellar Associations 93
6.10 Micellization Under Intensification of Molecular Mass Transfer 101
6.11 Micellization in the Electric Field of Charged Admixtures ... 105

7. Fluctuation Mechanism of Forced Spinodal Decomposition 113
7.1 Spinodal Decomposition as a Model for Microemulsion Formation 113
7.2 Non-equilibrium States in Phase-Separating Binary Liquids and External Perturbations 119
7.2.1 Variable Electric Field 121
7.2.2 Ultrasound 122
7.2.3 Thermal Action 122
7.2.4 Optothermal Influence 123
7.2.5 Noise Field 123
7.2.6 Turbulence 124
7.2.7 Shear Flow 124
7.2.8 Centrifugal Forces 125
7.2.9 Stirring 126
7.3 External Perturbation and Spinodal Decomposition 128
7.3.1 Heating of a System Without Stirring 129
7.3.2 Heating of a System by Stirring 131
7.4 Statistical Account of an External Stirring Field 133

8. Weak Stirring and Absolute Instability Phenomena 139
8.1 Singularity in the Heat Capacity in Forced Spinodal Decomposition 139
8.2 Extending the Region of Absolute Instability 142
8.3 Initial Stage Kinetics of Forced Spinodal Decomposition 145

9. Microheterophase Relaxation State 147
9.1 Relaxation State Near the Boundary of Absolute Instability Under Weak Perturbation 147

9.2 Surface Tension Energy and Heat Absorption Effect 150
9.3 Thermal Relaxation Effects in the Cellular Structure 152

10. Transition from Emulsion to Microemulsion 155
10.1 Microemulsion Structure 155
10.2 Polychronal Relaxation Processes and Dispersion on the Interface 158
10.3 Stable Microheterophase State on the Interface of Weakly Dissolved Liquids 161
10.4 Conclusion 166

References 169