# Contents


**1. Introduction** ..... 1

**2. Description of the Phenomenon** ..... 11
2.1 The Classical Picture. No Serious Problems ..... 11
2.1.1 Viscosity ..... 11
2.1.2 Linear Response ..... 16
2.1.3 Dynamic Glass Transition ..... 26
2.1.4 Thermal Glass Transition. Glass Temperature. Partial Freezing ..... 34
2.1.5 Structural Relaxation. Landscape. Nonlinearity ..... 49
2.1.6 Final Remarks ..... 65
2.2 Serious Problems ..... 66
2.2.1 Crossover Region and $\beta$ Process ..... 66
2.2.2 How to Find the 'Right Questions' for Glass Transition Problems? ..... 78
2.2.3 Different Transport Properties ..... 79
2.2.4 Nonexponentiality ..... 88
2.2.5 Dynamic Heterogeneity. Characteristic Length. Cooperatively Rearranging Regions CRR ..... 94
2.2.6 Glass Structure ..... 104
2.2.7 Fischer Modes ..... 110
2.2.8 Similarity in Different Substances ..... 117
2.3 High Frequency Relaxation. Not as Simple as Expected ..... 121
2.3.1 Giga-to-Terahertz Results ..... 122
2.3.2 Götze's Mode-Coupling Theory (MCT) ..... 129
2.3.3 Colloidal Glass Transition ..... 137
2.3.4 Computer Simulations ..... 138
2.4 Long-Running Issues ..... 149
2.4.1 Glass Transition and Flow Transition in Polymers ..... 149
2.4.2 Hindered Glass Transition in Confining Geometries ..... 157
2.4.3 Tunnel States at Low Temperatures ..... 161
2.4.4 Mixed Alkali Effect ..... 170
2.4.5 Relaxation Tails. No Deserts Between Dispersion Zones. Logarithmic Gaussian Distribution ..... 175

2.4.6 Glass Formation ..... 182
2.5 A Preliminary Physical Picture in 1999 ..... 185
2.5.1 Thermodynamic Approach. No Ideal Glass Transition? 191
2.5.2 Dynamic Approach: Strategy ..... 206
2.5.3 Molecular Pictures ..... 210
2.5.4 Tables ..... 218

**3. Theoretical Framework** ..... 227
3.1 Representative Freely Fluctuating Subsystems ..... 228
3.2 Gibbs Fluctuations and Thermodynamic Fluctuations ..... 240
3.2.1 Gibbs Treatment of Statistical Mechanics ..... 241
3.2.2 Von Laue Treatment of Thermodynamics ..... 244
3.2.3 Differences and Relationships Between the Two Treatments ..... 247
3.3 Linear Response ..... 250
3.4 Fluctuation–Dissipation Theorem FDT ..... 269
3.4.1 Correlation Function and Spectral Density ..... 272
3.4.2 Van Hove Correlation Functions for Dynamic Scattering ..... 275
3.4.3 Differential and Integral Forms of the FDT ..... 278
3.4.4 Equilibrium or Nonequilibrium? ..... 278
3.4.5 $\omega$ Identity of the FDT ..... 279
3.4.6 Mathematical Background ..... 280
3.4.7 Stochastic Derivation of the FDT ..... 283
3.4.8 Quantum Aspects ..... 288
3.4.9 Thermodynamic Consequences: Subtleties of the Second Law ..... 290
3.5 Discussion of Functional Independence ..... 293
3.6 Levy Distribution ..... 297

**4. Slowing Down Mechanisms** ..... 313
4.1 Mode Coupling ..... 314
4.2 Activated Rate Processes ..... 321
4.3 Fluctuating Free Volume. Glarum–Levy Defects ..... 326
4.4 Fischer Modes ..... 344
4.5 Modifications Due to Partial Freezing-in ..... 350
4.5.1 Preparation Time, Glass Frequency, and Vitrification Rate ..... 350
4.5.2 Narayanaswamy Mixing ..... 355
4.5.3 Example: Kovacs Expansion Gap ..... 360
4.5.4 Struik Law of Physical Aging ..... 362

**5. Epilogue** ..... 367
5.1 Ten Questions ..... 367
5.2 Control of $T_g$ ..... 371



**6. Conclusion** ..... 377

**A. Synonyms** ..... 381

**B. List of New Concepts** ..... 383

**C. Acronyms** ..... 387

**References** ..... 389

**Index** ..... 411