

Advances in Dielectrics

Series Editor

Friedrich Kremer

Aims and Scope

Broadband Dielectric Spectroscopy (BDS) has developed tremendously in the last decade. For dielectric measurements it is now state of the art to cover typically 8–10 decades in frequency and to carry out the experiments in a wide temperature and pressure range. In this way a wealth of fundamental studies in molecular physics became possible, e.g. the scaling of relaxation processes, the interplay between rotational and translational diffusion, charge transport in disordered systems, and molecular dynamics in the geometrical confinement of different dimensionality – to name but a few. BDS has also proven to be an indispensable tool in modern material science; it plays e.g. an essential role in the characterization of Liquid Crystals or Ionic Liquids and the design of low-loss dielectric materials.

It is the aim of “Advances in Dielectrics” to reflect this rapid progress with a series of monographs devoted to specialized topics.

Target Group

Solid state physicists, molecular physicists, material scientists, ferroelectric scientists, soft matter scientists, polymer scientists, electronic and electrical engineers.

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Molecular Dynamics of Glass-Forming Systems

Effects of Pressure

 Springer

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ISSN 2190-930X e-ISSN 2190-9318
ISBN 978-3-642-04901-9 e-ISBN 978-3-642-04902-6
DOI 10.1007/978-3-642-04902-6
Springer Heidelberg Dordrecht London New York

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Cover design: WMXDesign GmbH, Heidelberg, Germany

Printed on acid-free paper

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To the memory of Tadeusz Pakula

Preface

In his Science article of 1995, P.W. Anderson mentioned that “*the deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition. This could be the next breakthrough in the coming decade.*” Today (some 15 years later), we claim that he was right in this prediction. Especially over the last 10–15 years, there has been more progress in our understanding of glass formation than in the previous 40 years.

A unique feature of the molecular dynamics in glass-forming systems is the continuous and dramatic increase in the structural relaxation time, from values on the order of picoseconds up to hundreds of seconds in the vicinity of the glass “transition” temperature. Other transport quantities such as the diffusion constant or viscosity show a similar increase. Another important characteristic is the non-exponential character of the relaxation function. Although cooling a liquid is the method most often employed to induce the liquid-to-glass “transition,” this is not the only root towards the glassy state. Among others, a liquid can be vitrified by increasing pressure under isothermal conditions. This path was first exploited in the 1960s, but due to serious experimental difficulties in performing spectroscopic measurements under elevated pressures, it soon came to a standstill (and hence pressure became the “forgotten” thermodynamic variable). Nevertheless, such experiments are necessary to provide the complete physical description of the vitrification process. In recent years, we have witnessed a major breakthrough in the study of the dynamics of supercooled liquids and of the glass “transition” under elevated pressures, mainly by using dielectric spectroscopy and other methods (photon correlation spectroscopy, rheology, and NMR).

This book provides a comprehensive survey of the recent advances in the study of the effect of pressure on the vitrification process of simple van der Waals liquids, hydrogen-bonded systems, polymers, polymer blends, and biopolymers. We first review the important knowledge attained in the 1960s by the seminal work of G. Williams, Sasabe, and Saito, and proceed to the current understanding of the effects of pressure on the dynamics of glass-forming liquids in the vicinity of the glass “transition.”

Chapter 1 discusses the pressure dependence of the structural relaxation times and the effect of pressure on the glass temperature and fragility. We also address the role played by thermal energy and density in the tremendous slowing down of the structural relaxation dynamics when approaching the glass temperature.

Chapter 2, with the ambitious title “Origin of Glass formation,” discusses in detail the current understanding of the liquid-to-glass transformation and, in particular, the importance of pressure. Identifying the main control parameter that dominates the slow dynamics at the glass temperature has been a point of debate. Theoretical predictions consider thermally activated processes on a constant density “energy landscape” and “free-volume” as extreme cases. However, since changing temperature affects both the thermal energy and the volume (and thus the associated “free volume”), it is impossible to separate the two effects by temperature alone. In order to disentangle the effects of temperature and volume (or better said, the corresponding intensive variable, density) on dynamics, pressure-dependent measurements have been of paramount importance, as pressure can be applied isothermally (affecting only the density) and have been employed to provide a quantitative assessment of their relative importance. We provide two recent approaches that have led to a better understanding of the liquid-to-glass dynamics. The first is based on the newly observed dynamic feature known as “thermodynamic scaling”; the second emphasizes the role of molecular volume and local packing on the glass transition dynamics.

Knowledge of the equation of state is essential in predicting the pressure behavior of fragility and of the glass transition temperature. Chapter 3 discusses the equivalent of an “equation of state” with physically interpretable parameters for the description of the structural relaxation times as a function of temperature and pressure. In this chapter, various canonical models that incorporate both the temperature and pressure dependences of the structural relaxation time are reviewed.

Chapter 4 discusses the latest findings on the dynamics of glass formers. The new results turn out to be nearly universal, present in glass formers of different physical structures and chemical natures, and have not been addressed before and thus have tremendous impact on current concepts and theories of glass “transition.” The results also point out the new physics that have to be included before the problem of glass formation is solved completely.

The important role of pressure in the miscibility of polymer mixtures has been realized only recently, as it has direct applications to processing as well as to new syntheses that involve the use of environment-friendly supercritical fluids. Chapter 5 reviews the recent progress made in understanding the effects of pressure on the thermodynamics (i.e., the critical temperature for phase separation) and dynamics of polymer blends.

Chapter 6 reviews recent efforts to investigate the hierarchical self-assembly and dynamics in an important class of biomaterials: polypeptides. Polypeptides play a vital part in the molecules designed for use in drug delivery of gene therapy and thus have been the subject of intensive studies. However, their dynamic response has only recently been explored. In the first part, we discuss the origin

of the dynamic arrest at the glass “transition”. In this respect, pressure again plays a decisive role, as it is used to identify structural and dynamic defects (i.e., *solitons*). Subsequently, and as a direct consequence of the first part, we discuss that contrary to expectation and common belief, helices in concentrated polypeptide solutions are objects of low persistence. In the third part, we address the effect of confinement in controlling the type, persistence, and dynamics of secondary structures.

We would like to acknowledge the many instructive comments and suggestions for improvement of Graham Williams. George Floudas further acknowledges his coworkers at the UoI (A. Gitsas, P. Papadopoulos, K. Mpoukouvalas) who participated in parts of this work. Contributions at the University of Ioannina were cofinanced by the E.U.-European Social Fund (75%) and the Greek Ministry of Development-GSRT (25%) in the framework of the programs PENED 2001 (No 529) and PENED2003 (No 856). Contributions of M. Paluch and A. Grzybowski to this book were made as a part of the research project “From Study of Molecular Dynamics in Amorphous Medicines at Ambient and Elevated Pressure to Novel Applications in Pharmacy,” operated by the Foundation for Polish Science Team Program that is cofinanced by the EU Regional Development Fund within the framework of the Innovative Economy Operational Program. This support is highly appreciated. M. Paluch and A. Grzybowski would like to further thank their coworker K. Grzybowska at the University of Silesia for her help in preparing this book. The work at NRL was supported by the Office of Naval Research.

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Contents

1	The Glass “Transition”	1
1.1	Introduction	1
1.2	Pressure Dependence of the Structural (α -) Relaxation Time	5
1.3	The Glass Transition Temperature	17
1.4	The Concept of Fragility	20
1.5	Relative Importance of Thermal Energy and Density	23
	References	34
2	Origin of Glass Formation	39
2.1	Thermodynamic Scaling of Molecular Dynamics in Viscous Systems	39
2.1.1	A General Idea of Thermodynamic Scaling	39
2.1.2	A New Measure of the Relative Temperature–Volume Influence on Molecular Dynamics	42
2.1.3	The Relaxation Time Description in Accordance with Thermodynamic Scaling	47
2.1.4	Thermodynamic Scaling on Isothermal Conditions and Its Consequences	52
2.1.5	Doubts About the Thermodynamic Scaling Universality	55
2.2	The Role of Monomer Volume and Local Packing on the Glass-Transition Dynamics	61
	References	64
3	Models of Temperature–Pressure Dependence of Structural Relaxation Time	67
3.1	The Generalized Vogel–Fulcher–Tammann Equation	67
3.2	The Adam–Gibbs Model	68
3.3	The Avramov Model	71
3.4	Cluster Kinetics Model	75
3.5	Defect Diffusion Model	79

3.6 Dynamic Lattice Liquid Model	84
References	87
4 New Physics Gained by the Application of Pressure in the Study of Dynamics of Glass Formers	89
4.1 Dynamics Under Pressure	89
4.2 General Dynamic Properties of Glass Formers Discovered by Applying Pressure	90
4.2.1 Coinvariance of τ_α and Width of Dispersion to Changes in P and T	90
4.2.2 Crossover of T or P Dependence of τ_α (or η) at the Same τ_α (or η) Independent on T , P , and V at the Crossover	93
4.2.3 An Important Class of Secondary Relaxations Bearing Strong Connection to the α -Relaxation	98
4.3 Conclusions	115
References	116
5 Pressure Effects on Polymer Blends	121
5.1 Theoretical Background	121
5.2 Effect of Pressure on the Dynamics of Miscible Polymer Blends: Dynamic Heterogeneity	123
5.2.1 Athermal Polymer Blends/Copolymers (PI-PVE, PMMA/PEO)	125
5.2.2 Miscible But Not Athermal Polymer Blends (PS/PMPS, PS/PVME, and PCHMA/PaMS)	131
5.2.3 Polymer Blends with Strong Specific Interactions	140
5.3 Effect of Pressure on Nanophase Separated Copolymers	141
5.3.1 PMVE- <i>b</i> -PiBVE	142
5.3.2 pODMA- <i>b</i> -ptBA- <i>b</i> -pODMA	144
References	146
6 Polypeptide Dynamics	149
6.1 Introduction	149
6.2 Polypeptide Liquid-to-Glass “Transition” and its Origin	150
6.3 Correlation Length of α -Helices	159
6.4 Effects of Nanoconfinement on the Peptide Secondary Structure and Dynamics	162
6.4.1 “Soft” Confinement: Confinement Within the Nanodomains of Block Copolypeptides	162
6.4.2 “Hard” Confinement: Confinement Inside Nanoporous Anodic Aluminum Oxide	163
6.5 Conclusion	166
References	167
Index	169