

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.

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