Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

Review

Statistical mechanics of glass

John C. Mauro [a,*], Morten M. Smedskjaer [b]

[a] Science and Technology Division, Corning Incorporated, Corning, NY 14831, USA
[b] Section of Chemistry, Aalborg University, DK-9000 Aalborg, Denmark

A B S T R A C T

The field of glass science is quickly maturing from a purely empirical science to one built upon rigorous fundamental physics. These advancements offer an unprecedented level of understanding of the glass transition and the glassy state, as well as the ability to design new glass compositions starting at the atomic level. As a non-equilibrium material, the structure and properties of glass depend not only on its composition, but also on its thermal and pressure histories. Since glass is thermodynamically unstable, it is continually relaxing toward the metastable supercooled liquid state. Owing to this time dependence of glass properties and microstructure, traditional reversible thermodynamics cannot be directly applied to study the glassy state. While some nonequilibrium aspects of the glassy state can be estimated using irreversible thermodynamics, this approach has no microscopic basis and hence cannot offer a rigorous physical description of either the glass transition or glass itself. Alternatively, nonequilibrium statistical mechanics offers a framework in which the macroscopic properties of a glass can be rigorously calculated from its microscopic structure. As such, statistical mechanics has many practical applications in glass science and technology. The objective of this article is to provide an overview of various statistical mechanical descriptions of the glassy state and their practical use in understanding glass physics and in the design of new glass compositions. The relationship among these various descriptions is emphasized to build a single unified picture of glass statistical mechanics synthesizing these various approaches.

1. Introduction

Glass and the glass transition are widely considered as two of the most challenging problems in condensed matter physics [1–3]. Glass is challenging at a microscopic level due to its non-crystalline structure, lacking the long-range order characteristic of crystalline solids [4,5]. At a thermodynamic level, glass is difficult since it is a nonequilibrium material [6,7]. As such, the properties of a glass are not a simple function of composition, temperature, and pressure: the entire thermal history (and pressure history, if applicable) of a glass must be considered [8–10]. Furthermore, the properties of a glass evolve as it continually relaxes toward its corresponding metastable equilibrium liquid state [11–13]. One of the main challenges of glass science is to capture this complicated composition and time dependence of glass properties in a manner that is physically rigorous and quantitatively accurate [14–16].

While the thermodynamics of equilibrium materials is well understood, the same cannot be said for nonequilibrium systems such as glass [17,18]. The field of irreversible thermodynamics seeks to overcome these limitations by introducing one or more additional parameters, called "order parameters," responsible for describing the nonequilibrium state of the glass [19–24]. However, irreversible thermodynamics is phenomenological by design and hence is not rooted in any fundamental physics. Moreover, there is no direct connection to the underlying microscopic physics of the system [25], e.g., the notion of atomic structure plays no role in either reversible or irreversible thermodynamics.

The connection between microscopic and macroscopic physics is provided by statistical mechanics [26,27]. Many processes that occur on the atomic level are stochastic in nature, such as thermal fluctuations and transitions between microstates [28,29]. While in classical mechanics these processes may be considered deterministic, our lack of detailed knowledge of the exact dynamics of each atom in the system requires the use of a statistical approach [30,31]. Statistical mechanics addresses this issue by using probability theory to determine expectation values for macroscopic properties averaged over a suitable ensemble of microstates. However, the application of statistical mechanics to the glassy state is not necessarily straightforward, since most statistical mechanical approaches make an implicit assumption of ergodicity, i.e., the equivalence of time and ensemble averages of the properties of interest. Glass is nonergodic by its very nature and hence requires special care in developing rigorous statistical theory [32–36].

The objective of this review paper is to provide an overview of the statistical mechanics of glass, emphasizing both the underlying physics and the practical application of statistical mechanical techniques toward the design and understanding of new glasses. In this paper we seek to synthesize the various statistical mechanical treatments of the glass transition and the glassy state into one unified picture. For example, the breakdown of ergodicity at the glass transition is fundamentally

* Corresponding author. Tel.: +1 607 974 2185.
E-mail address: mauroj@corning.com (J.C. Mauro).

induced by an onset of rigid constraints as considered in topological constraint theory. Both of these phenomena are intimately connected with the imposition of an experimental observation time that constrains the kinetics of the glass. The authors hope that additional connections among the various statistical descriptions of the glass transition and the glassy state should become apparent to the reader throughout the article.

The particular organization of this paper is meant to guide the reader in this endeavor. We begin in Section 2 with an overview of ergodic theory, since the breakdown of ergodicity is the most fundamental feature of the glassy state. This provides the basis for Section 3, where we review the concept of an enthalpy landscape. By leveraging the broken ergodic nature of glass, enthalpy landscape theory enables the accurate calculation of glass properties and dynamics on long (experimental) time scales. In Section 4 we turn our attention to the statistics of glass structure, which provides the basis for the discussion of topological constraint theory in Section 5. Topological constraint theory allows for the quantitative prediction of the composition and structural dependence of glass properties. In Section 6 we focus on the statistics of glass relaxation, and in particular the stretched exponential decay function, which is shown to be intrinsic to homogeneous glasses. Finally, in Section 7 we draw together some important insights gained from statistical mechanics regarding general glass physics and the use of statistical methods in the design of new glassy materials. Please note that it is not our objective to cover every statistical mechanical approach proposed to describe glasses and glass-forming liquids. Rather we focus our attention on those approaches with the greatest practical utility for designing new industrial glass compositions and processes. Thorough reviews of other statistical mechanical approaches not covered in this paper can be found in several excellent monographs by other authors [37–39].

2. Ergodic theory

In statistical theory, the term *ergodic* refers to an equivalence of the time and ensemble averages of the properties of a system. Ergodicity is a common assumption in equilibrium statistical mechanics. However, for nonequilibrium systems such as glass, the ensemble average of certain thermodynamic properties can be different from the corresponding time average. For example, an ensemble average includes frozen-in fluctuations that may not be present in a time average of the same property [35,36]. For any experiment, the question of ergodicity is really a question of time scale. Specifically, there are two relevant time scales of interest: an internal relaxation time scale (τ_{int}) on which the system loses memory of its preceding states, and an external observation time scale (τ_{ext}) on which properties are measured. Reiner [40] defined the ratio of these two time scales as the "Deborah number" of the experiment,

$$D = \frac{\tau_{int}}{\tau_{ext}}, \tag{1}$$

named in honor of the prophetess Deborah, who in the Old Testament sings "…the mountains flowed before the Lord…" (Judges 5:5). While a theological interpretation of this statement is outside the scope of the current article, from a physics perspective this passage underscores the importance of time scale in measurement. For a human observer, mountains are essentially static ($\tau_{int} \gg \tau_{ext}$ or $D \gg 1$). However, on a geological time scale inaccessible to direct measurement by a human being, the mountains do indeed flow. The human observer therefore sees just a small subset of the phase space, i.e., a frozen-in configuration of mountains.

A Deborah number greater than unity implies a nonergodic system, since there is insufficient time for the system to equilibrate during the time of measurement. On the other hand, $D < 1$ indicates that the system has sufficient time to relax to equilibrium during the observation time window, implying that the condition of ergodicity can be satisfied. The

fundamental difference between a liquid and its corresponding glass is that the liquid is ergodic ($D < 1$) while the glass is inherently nonergodic ($D > 1$). As indicated in Fig. 1, the glass transition occurs at $D = 1$ and constitutes a transition from an ergodic liquid state to a nonergodic glassy state. Such breakdown of ergodicity is a type of *partitioning process* [41] and results in no change in the enthalpy or volume of a system, i.e., it is not a first-order thermodynamic phase transition. However, the loss of ergodicity does entail a loss of configurational entropy since the observation time constraint restricts the system to a subset of the configurational phase space. In other words, the macrostate of a nonergodic glass is determined by a fewer number of microstates compared to that of an ergodic liquid system.

The inverse of the glass transition is structural relaxation, which involves a restoration of ergodicity as a glass spontaneously approaches the liquid state. This spontaneous relaxation process is termed a *unifying process* and entails a net increase in entropy as the observation time constraint is lifted [41].

Please be aware that the question of ergodicity is sometimes confused with the so-called *ergodic hypothesis*, an assumption stating that a system becomes ergodic in the limit of infinite time [42]. A glassy system is inherently nonergodic, but it obeys the ergodic hypothesis since in the limit of long time it explores all of phase space as it relaxes to the liquid state. However, the physics of the glassy state itself must be described in terms of nonergodic statistical mechanics: it is *never* a reasonable assumption to treat the solid glass with $D > 1$ as identical to the ergodic liquid state in the limit of infinite observation time (i.e., $D \rightarrow 0$).

2.1. Broken ergodicity

The statistical mechanics of nonergodic systems were originally derived by Palmer [43], who introduced the concept of *broken ergodicity*.
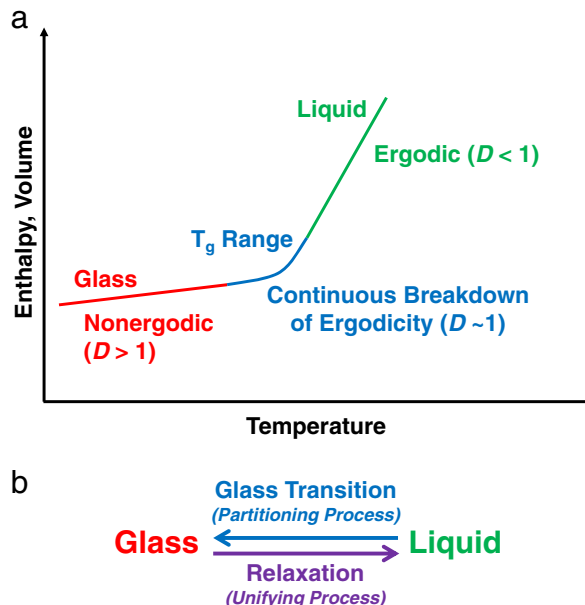

Fig. 1. (a) The glass transition can be observed by cooling a liquid to a sufficiently low temperature, provided that crystallization is avoided. The Deborah number, D, is defined in Eq. (1). The glass transition involves a continuous breakdown of ergodicity as the ergodic liquid at high temperature becomes trapped in a subset of configurational phase space in the nonergodic glassy state at low temperatures. (b) The glass transition is termed a partitioning process since configurational degrees of freedom are lost as the system becomes kinetically trapped in the nonergodic glassy state. The opposite process, structural relaxation, involves the spontaneous lifting of this kinetic constraint, allowing the system to explore additional configurational degrees of freedom. This is termed a unifying process.