Physica A 510 (2018) 787–801

Contents lists available at ScienceDirect

Physica A

journal homepage: www.elsevier.com/locate/physa

Statistical mechanics of topological fluctuations in glass-forming liquids

Katelyn A. Kirchner [a], Seong H. Kim [a,b], John C. Mauro [a,*]

[a] Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA
[b] Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802, USA

HIGHLIGHTS

- We derive the general theory linking statistical mechanics of glass structure with topological constraint theory.
- The full distribution of localized fluctuations in the structure and topology of glass forming systems can be calculated.
- Example calculations are shown to illustrate the interplay between enthalpic and entropic effects.

ARTICLE INFO

Article history:
Received 7 May 2018
Received in revised form 16 June 2018
Available online 17 July 2018

Keywords:
Liquids
Supercooled liquids
Modeling
Statistical mechanics
Topological constraint theory
Glass

ABSTRACT

All liquids are topologically disordered materials, yet the degree of disorder can vary as a result of internal fluctuations in structure and topology. These fluctuations depend on both the composition and temperature of the system. Most prior work has considered the mean values of liquid or glass properties, such as the average number of topological degrees of freedom per atom; however, the localized fluctuations in properties also play a key role in governing the macroscopic characteristics. This paper proposes a generalized approach for modeling topological fluctuations in glass-forming liquids by linking the statistical mechanics of the disordered structure to topological constraint theory. In doing so we introduce the contributions of localized fluctuations into the calculation of the topological degrees of freedoms in the network. With this approach the full distribution of properties in the disordered network can be calculated as an arbitrary function of composition, temperature, and thermal history (for the nonequilibrium glassy state). The scope of the current investigation focuses on describing topological fluctuations in liquids, concentrating on composition and temperature effects.

1. Introduction

Unlike a crystal, where the atomic positions are clearly defined, glass-forming systems have a non-crystalline structure where the details of atomic coordinates and bond configurations must be described in terms of statistical distributions. Due to the role of configurational entropy, liquids have localized fluctuations (or local variations in disorder) inherent in their structure, bonding configurations, and network topology [1–4]. These variations are evident in experimental results, such as in the broadening of absorption peaks or shapes in spectroscopy [5–7]. In multicomponent systems, the fluctuations depend on composition, temperature, and (for the glassy state) thermal history. For example, a hyperquenched glass fiber has a higher entropic contribution to its structure, and hence a greater level of atomic fluctuations, compared to a slowly cooled or annealed sample having the same chemical composition [8,9].

* Corresponding author.
E-mail address: jcm426@psu.edu (J.C. Mauro).

https://doi.org/10.1016/j.physa.2018.07.028
0378-4371/

Localized fluctuations in glass-forming systems are important for many practical applications. For example:

- The attenuation in low-loss optical fibers is dominated by Rayleigh scattering. Rayleigh scattering is a function of density fluctuations, which scale nonmonotonically with the thermal history of the glass [10,11].
- The relaxation behavior in glass is comprised of a variety of different relaxation modes operating over a range of time scales. This spectrum of relaxation modes relates directly to atomic scale fluctuations in the glass structure, with some structural motifs having shorter relaxation times. This behavior is critical for glasses used in high performance display applications [12–15].
- Nucleation and phase separation are likely to be governed by localized fluctuations in bonding, since over-constrained regions of the network create localized stresses that can be relieved through crystallization. Compositional inconsistencies can also serve as a precursor to larger scale phase separation [16–19].
- Localized fluctuations in bonding and topology play a governing role in the mechanical properties and fracture behavior of glasses. Cracks propagate preferentially through regions where the glass network is under-constrained, since there are fewer bonds to break. As a result, the toughness and damage resistance of glass can potentially be enhanced through tailoring the localized bond fluctuations [20].

Despite the scientific and technological importance of compositional and topological fluctuations in glasses, very few studies have been conducted to elucidate this subject. To date, most studies of glass composition–structure–property relationships have focused primarily on *mean-field* descriptions, averaging over the fluctuation effects and making the connection between average values of structural features and the resulting macroscopic properties of the system [21–26]. However, as non-crystalline materials, glass-forming systems have inherent atomic scale fluctuations, i.e., distributions in their structure and bonding. These inconsistencies play a key role in determining many of their thermophysical properties, including the details of their mechanical properties and relaxation behavior [7,13,27].

This paper presents a general modeling approach describing structural and topological fluctuations in the metastable equilibrium supercooled liquid state. By linking statistical mechanics with topological constraint theory, we analyze the factors governing modifier speciation. We then present several model calculations demonstrating the effects on the properties of the liquid network, including details of its topological degrees of freedom. The physics of the statistical and topological constraint approaches are linked through the strength of bonding in the glass-forming network. By calculating the probability density associated with the number of atomistic constraints in the network, we describe the structural and bonding characteristics of the localized and network glass-forming system as a function of composition and temperature. Whereas most prior work in the field has focused on the average number of constraints per atom, this paper extends constraint theory by incorporating localized fluctuations in rigidity, consistent with the statistical mechanical model of the underlying atomic structure.

2. Statistical mechanics of glass-forming structures

Composition and temperature govern the atomic structure and resulting macroscopic properties of a glass-forming system [28–30]. Glass-forming systems are typically composed of network formers, which are strongly bonded atoms that form the main backbone of the network, and network modifiers, which are weakly bonded atoms that alter the structure and topology of the network [31]. The presence of modifiers affects the microscopic coordination number of the nearest neighbor network formers, which has a large influence on the macroscopic structural properties of the system [1]. An additional challenge in glass physics is that the system is continuously relaxing toward its metastable equilibrium liquid state [32–40]. Statistical mechanical approaches allow us to capture this time dependent relaxation and connect the microscopic and macroscopic physics [41,42].

Diffraction experiments and atomistic simulations (e.g., molecular dynamics) have provided information regarding the statistics of glass structure, such as the probability distributions of atomic positions and the time evolution of the material [43–45]. While molecular dynamics simulations aid in the understanding of structural and energetic properties, such as the energies associated with various types of bond constraints, these simulations are unable to capture all of the material's features due to time and length scale restrictions. Thus, they are too computationally intensive to be applied for thorough compositional studies [46–49].

Ab initio simulations offer more accurate descriptions but at a higher computational cost, making them impractical for large systems or long time scales [50–54]. In order to circumvent the problems associated with traditional atomic scale simulations, Mauro [1,3] developed a statistical mechanical model based on a hypergeometric distribution of site occupancies. In this approach, a network modifier (such as an alkali or alkaline earth ion in an oxide glass) occupies a network forming site based on a relative probability. Once an association is made, that site is no longer available for further occupation (i.e., bonding) [1]. In order to simplify our model, we are disregarding nearest neighbor effects for the surrounding network formers once this modifier occupation occurs. This statistical mechanical approach is an effective method for capturing the distribution of structural motifs in a glass-forming network [55].

Statistical mechanics can be used to describe the inherent disorder in glass-forming systems and calculate the macroscopic properties associated with a suitable ensemble of microscopic states [40,46,56–65]. The approach for implementing statistical theory must be addressed carefully due to the nonequilibrium and nonergodic nature of glass [2,66–69]. Here, we