



Research paper

Calculation of thermal expansion coefficient of glasses based on topological constraint theory



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ARTICLE INFO

Article history:

Received 29 June 2016

In final form 1 September 2016

Available online 21 September 2016

ABSTRACT

In this work, the thermal expansion behavior and the structure configuration evolution of glasses were studied. Degree of freedom based on the topological constraint theory is correlated with configuration evolution; considering the chemical composition and the configuration change, the analytical equation for calculating the thermal expansion coefficient of glasses from degree of freedom was derived. The thermal expansion of typical silicate and chalcogenide glasses was examined by calculating their thermal expansion coefficients (TEC) using the approach stated above. The results showed that this approach was energetically favorable for glass materials and revealed the corresponding underlying essence from viewpoint of configuration entropy. This work establishes a configuration-based methodology to calculate the thermal expansion coefficient of glasses that, lack periodic order.

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1. Introduction

The study of thermal expansion of materials is increasingly significant in both scientific and technological fields [1]. Matching thermal expansion between different materials is a matter of considerable interest for technicians [2]. Scientific researchers have been investigating the nature of thermal expansion behavior of materials for decades [3–7]. However, the essence of glasses' TEC still remains to be explored, due to their non-periodic order and complex structures [8–11]. To achieve the prediction of thermal expansion properties of glasses, various early empirical approaches have been explored; for example, the investigation of Demkina established the equation that describes the relationship between the TEC and each component of glass material [12]. Aside from the empirical approaches, the semi-empirical equation deduced by Makishim et al. from the Gruneisen formula is typically used [13]. However, Makishim noted, “Unfortunately, the additive factors vary for each of the authors”. Molecular dynamics approaches have been recently developed to interpret the thermal expansion phenomenon especially for crystalline materials [14–16]. The TEC of crystalline materials can be accurately calculated due to their well-defined periodic order. However, the atomic scale modeling of glasses still remains to be a challenge because of their disordered structures. Moreover, the thermodynamic stability of

glasses is much larger in terms of time and length required, compared to that of crystals [17,18].

Here we present a model to calculate glasses' TEC based on topological constraint theory (TCT), which is established in previous work by Phillips and Thorpe [19]. Recently, Gupta and Mauro derived the equation that upon introducing the entropy into TCT to calculate the glass transition temperature and the liquid fragility of chalcogenide glasses [20,21]. The difference between oxide and chalcogenide glasses is observed in the case of their bond types, particularly that oxide glasses usually contain ionic bonds. Yue et al. [22,23] and Zeng et al. [24,25] proposed that TCT is also applicable to oxide glasses based on their experimental data, which is also validated in this paper. An illustration of the hardness comes from the study of Smedskjaer et al., in which it was shown that the hardness of glasses can be readily calculated from its constraint number using TCT [26].

Following a similar strategy, the thermal expansion behavior of chalcogenide glass systems was studied in the work of Senapati and Varshneya [27] and Hyung et al. [28]. It has been observed that the thermal expansion coefficient of a glass material is proportional to its coordination number. Here, a detailed study on different glass-forming units was performed rather than on average sense. The purpose of this work was to unravel the natural connection between thermal expansion and topological constraints by introducing configuration entropy and to derive the equation to calculate the TEC of glasses.

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In Section 2, the methodology and the derivation details are described. The calculation of TEC using our approach and the results obtained for the silicate and chalcogenide glasses are presented in Section 3. The summary is subsequently given in Section 4.

2. Modelling

A systematic study on thermal expansion behavior, starting from basic thermodynamic formulas to topological constraints calculations, was performed. Glasses have been intensively studied before using various approaches focusing on their micro short and medium-range structures, their macro mechanical, or their thermodynamic properties [29,30]. In essence, bond stretching causes the thermal expansion behavior of materials, glass formers relax with increasing the temperature, which leads to the anharmonic vibration of the system [31]. These investigations served as the basic knowledge for comprehension of glasses' isotropy features, as were adopted in this study. This characteristic allowed for the modelling of the TEC from the statistical thermodynamics point of view and provided the prerequisite of the model. The observation that bulk glasses have fixed thermal expansion coefficient values at different directions further support this idea. Models on crystals cannot be directly applied to glasses, but these approaches gave insight into the treatment of glasses. Summarizing this information about glasses, the basic thermodynamic formula was quoted and the linear correlation of TEC and degrees of freedom was finally obtained.

A basic thermodynamic formula describes the relation between internal energy and entropy: $dU = TdS - pdV$, where T is temperature, S is the entropy, U is the internal energy, p is the pressure, and V is the volume. The heat energy absorbed by glasses transforms into two parts: first is the entropy increase, and the rest corresponds to the volume work due to the expansion of glasses. For a homogeneous system in which the internal energy is $U = U(T, V)$ [32], the differential form is given by Eq. (1). It includes the treatment which has the objective to disintegrate the internal energy into two parts, the first part is isochoric heat capacity, and the second part is related to the functions in terms of isothermal compressibility and the volume expansion coefficient. Theoretically, Eq. (1) introduces a method of obtaining the thermodynamic functions related to the volume expansion coefficient.

$$\begin{aligned} dU &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_V dT + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] dV \\ &= C_V dT + \left[-T\frac{a}{K_T} - p\right] dV \end{aligned} \quad (1)$$

where a is the volume expansion coefficient, and K_T is the isothermal compressibility coefficient. K_T is determined by the composition of the materials [33]. It represents the quantity with the same standard compressibility properties, and indicates the thermodynamic stability defined by the second derivative of the changes in volume. With the value of $0 \leq K_T \leq \infty$, the thermodynamic equilibrium of a system can be characterized.

$$a = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p, \quad K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T \quad (2)$$

Combining the basic thermodynamic formula with Eq. (2) gives:

$$TdS = C_V dT - T \frac{a}{K_T} dV \quad (3)$$

Naumis provided an approach to introduce thermodynamics into the topological constraint theory [34]. According to Naumis, the total entropy of a glass material is composed of the floppy modes and the different configurations of the system. Note that the

entropy is mainly composed of floppy modes near the softening temperature; this contribution was accordingly calculated as the main entropy. Its contribution to the configurational entropy could be expressed as:

$$S = Nk_B \ln \Omega_1^f \quad (4)$$

where f is the degree of freedom, N is the number of atoms, k_B is the Boltzmann constant, and Ω_1 is the thermodynamic probability. The TEC of the glasses remains slightly changed under its softening temperature. The average thermal expansion coefficient was calculated for engineering applications. The temperature range is $T_0 \sim T$ (between the room and softening temperature). Integrating the entropy in the range of $T_0 \sim T$ gives:

$$\int_{T_0}^T dS = Nk_B \ln \Omega_1 \times \int_{T_0}^T df. \quad (5)$$

here $Nk_B \ln \Omega_1 = \zeta$, so $dS = \zeta df$, Eq. (3) can therefore be rewritten as:

$$\zeta df = C_V d \ln T - \frac{a}{K_T} dV \quad (6)$$

There is only one independent variable in Eq. (6), since the volume is dependent on temperature; therefore, $dV = \alpha V dT$. So Eq. (6) can be transformed into:

$$\zeta df = C_V d \ln T - \frac{a^2 V}{K_T} dT \quad (7)$$

Using the Gruneisen equation gives:

$$a = \frac{rC_V}{K_0 V} \quad (8)$$

where r is the Gruneisen constant, and K_0 is the bulk elastic modulus. Thermal expansivity is one extremely important thermal parameter, and it is accounted for the Gruneisen's law of thermodynamics [35]; Gruneisen's law of thermodynamics has been expressed by many researchers in various forms such as Mitra and Mishra [36], Tolapadi [37]. Here r and K_0 are dependent on the material nature. $r = -(\ln v / \ln V)$, where v is the frequency of vibration of the system. Eq. (7) can be rewritten as:

$$df = \frac{aK_0 V}{\xi r T} dT - \frac{a^2 V}{\xi K_T} dT \quad (9)$$

The reference volume is V_0 at temperature T_0 , so the glass volume V at temperature T is $V = V_0 + \alpha V_0 (T - T_0)$, then

$$\begin{aligned} df &= \frac{aK_0 V_0}{\xi r T} dT + \frac{a^2 K_0 V_0}{\xi r} dT - \frac{a^2 K_0 V_0 T_0}{\xi r T} dT - \frac{a^2 V_0}{\xi K_T} dT \\ &\quad - \frac{a^3 V_0 T}{\xi K_T} dT + \frac{a^3 V_0 T_0}{\xi K_T} dT \end{aligned} \quad (10)$$

Integrating Eq. (10) gives:

$$\begin{aligned} f - f_0 &= \frac{aK_0 V_0}{\xi r} \ln \frac{T}{T_0} + \frac{a^2 K_0 V_0}{\xi r} (T - T_0) - \frac{a^2 K_0 V_0 T_0}{\xi r} \ln \frac{T}{T_0} \\ &\quad - \frac{a^2 V_0}{\xi K_T} (T - T_0) - \frac{a^3 V_0}{2\xi K_T} (T^2 - T_0^2) + \frac{a^3 V_0 T_0}{\xi K_T} (T - T_0) \end{aligned} \quad (11)$$

Eq. (11) describes the relationship between the degree of freedom and the TEC. The TEC of glasses is of 10^{-6} magnitude, so the square term and the cubic term are much smaller than the linear term, which gives:

$$f \cong f_0 + a \frac{K_0 V_0}{\xi r} \ln \frac{T}{T_0} \quad (12)$$

$K_0 V_0 (\ln(T/T_0)) / \xi r$ can be treated as constant, since the experiments were carried out under the same measurement conditions. From Eq. (12), the value of f can be calculated if a and T are known. a can be determined from the slope of the linear plot of the thermal

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