

Relationship between viscous dynamics and the configurational thermal expansion coefficient of glass-forming liquids

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ABSTRACT

We propose a model to describe the relationship between the viscosity of a glass-forming liquid and its configurational contribution to liquid state thermal expansion. The viscosity of the glass-forming liquids is expressed in terms of three standard parameters: the glass transition temperature (T_g), the liquid fragility index (m), and the extrapolated infinite temperature viscosity (η_∞), which are obtained by fitting of the Mauro–Yue–Ellison–Gupta–Allan (MYEGA) expression to measured viscosity data. The model is tested with experimental data for 41 different glass-forming systems. A good correlation is observed between our model viscosity parameter, $h(T_g, m, \eta_\infty)$, and the configurational coefficient of thermal expansion (i.e., the configurational CTE). Within a given class of glass compositions, the model offers the ability to predict trends in configurational CTE with changes in viscosity parameters. Since viscosity is governed by glass network topology, the model also suggests the role of topological constraints in governing changes in configurational CTE.

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1. Introduction

It is usually assumed and has recently been experimentally demonstrated that the vibrational and configurational contributions to the coefficient of thermal expansion (CTE) can be expressed as separate terms [1]. Considering the enthalpy landscape description of glass-forming liquids [2], the vibrational and configurational contributions arise from intra- and inter-basin transitions, respectively [3]. The inter-basin transitions are relatively slow such that upon cooling they begin to freeze, starting with those having the highest activation barriers [4,5]. Near the glass transition temperature, the configurational space partitions into a set of metabasins with slow transitions between these metabasins [6,7]. As a result, the glassy state contains primarily vibrational degrees of freedom, whereas the liquid state contains both vibrational and configurational degrees of freedom.

Potuzak et al. [1] have demonstrated that the total CTE of a glass-forming liquid (α_{liq}) can be accurately calculated by $\alpha_{liq} = \alpha_{vib} + \alpha_{conf}$, where the vibrational (α_{vib}) and configurational (α_{conf}) contributions to thermal expansion are determined by independent room temperature measurements on glassy state samples. Specifically, α_{vib} is the room temperature CTE of a glass as determined through standard dilatometry, i.e., strain with respect to change in temperature, and α_{conf} is determined by the strain of the glass with respect to change in

fictive temperature, T_f . Comparing the calculated value of $\alpha_{vib} + \alpha_{conf}$ to an independent measurement of α_{liq} , Potuzak et al. found that these independent measurements of the vibrational and configurational CTEs of a glass at room temperature lead to a highly accurate determination of the total CTE of a glass-forming liquid [1]. This is a technologically useful result because the high-temperature thermal expansion coefficient of a glass-forming liquid is an important parameter for glass processing.

In this paper, we propose and evaluate a new model relating configurational CTE to the viscous dynamics of glass-forming liquids, as determined by fitting the Mauro–Yue–Ellison–Gupta–Allan (MYEGA) equation to measured viscosity data [8]. The model itself is derived by expressing the configurational CTE in terms of the configurational entropy of the glass-forming liquid and relating this to viscosity using the Adam–Gibbs equation (Eq. (3)). Although this simple model does not capture every detail of the composition dependence of configurational CTE, it can be used to predict trends of α_{conf} with composition within a given family of glass compositions.

2. Dynamical dependence of the configurational CTE

We begin with the definition of the configurational CTE, α_{conf} , given by

$$\alpha_{conf}(T) = \frac{1}{3} \left(\frac{\partial \ln V_{conf}}{\partial T} \right)_p, \quad (1)$$

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where T is temperature, P is pressure, and V_{conf} is the configurational volume [9]. Since glass is isotropic, the factor of $1/3$ is included to convert the volumetric changes to a linear strain. Rewriting Eq. (1) in terms of configurational entropy (S_{conf}) and substituting $T \cdot \partial \ln T$ for ∂T , we get

$$\alpha_{conf}(T) = \frac{1}{3} \left(\frac{\partial \ln V_{conf}}{\partial \ln S_{conf}} \right)_P \frac{1}{T} \left(\frac{\partial \ln S_{conf}}{\partial \ln T} \right)_P. \quad (2)$$

The second term in Eq. (2) can be rewritten in terms of measurable parameters. Using the Adam–Gibbs relation [10],

$$\eta(T) = \eta_{\infty} \exp\left(\frac{B}{T \cdot S_{conf}(T)}\right), \quad (3)$$

where B is a constant, and Angell's definition of liquid fragility m [11],

$$m \equiv \left. \frac{\partial \log \eta(T)}{\partial (T_g/T)} \right|_{T=T_g}, \quad (4)$$

we obtain the result of Gupta and Mauro [12],

$$\left. \frac{\partial \ln S_{conf}(T)}{\partial \ln T} \right|_{T=T_g} = \left(\frac{m}{(12 - \log \eta_{\infty})} - 1 \right). \quad (5)$$

In Eq. (5) the shear viscosity (η) is understood to be in units of Pa s, $\log \eta_{\infty}$ is the base-10 logarithm of the viscosity extrapolated to infinite temperature, and the constant 12 arises directly from Angell's definition of the glass transition temperature T_g as the temperature at which the shear viscosity of the liquid is equal to 10^{12} Pa s.

Substituting Eq. (5) into Eq. (2) gives the relationship

$$\alpha_{conf}(x) = \frac{1}{3} \left(\frac{\partial \ln V_{conf}}{\partial \ln S_{conf}} \right)_{P,T=T_g} \cdot \frac{1}{T_g(x)} \left(\frac{m(x)}{(12 - \log \eta_{\infty}(x))} - 1 \right). \quad (6)$$

Here, the dynamical dependence is expressed in terms of the three viscosity parameters, T_g , m , and η_{∞} , which can be obtained by fitting the MYEGA model [8] to measured viscosity data. The parameter x represents composition. For simplicity, we group the measurable parameters in a single term h and rename the configurational volume derivative term as A ,

$$A = \left(\frac{\partial \ln V_{conf}}{\partial \ln S_{conf}} \right)_{P,T=T_g} \quad \text{and} \quad h(T_g, m, \eta_{\infty}) = \frac{1}{T_g} \left(\frac{m}{(12 - \log \eta_{\infty})} - 1 \right), \quad (7)$$

so that we obtain the final relationship,

$$\alpha_{conf}(x) = \frac{1}{3} A \cdot h(T_g, m, \eta_{\infty}), \quad (8)$$

between the viscosity term h and the configurational CTE, α_{conf} . The model thus offers prediction of the scaling of α_{conf} based on changes in the viscosity parameters used to obtain h .

3. Temperature dependence of the prefactor A

Since we will use the MYEGA expression [8],

$$\log_{10} \eta(T, x) = \log_{10} \eta_{\infty}(x) + \frac{K(x)}{T} \exp\left(\frac{C(x)}{T}\right), \quad (9)$$

where K and C are constants, to fit viscosity data and obtain h from Eq. (7), we use the same definition of configurational entropy that was used in the derivation of the MYEGA equation directly in our CTE model. From Ref. [8] we have

$$S_{conf}(x, T) = 3 \exp\left(-\frac{C}{T}\right) Nk \ln \Omega, \quad (10)$$

where $C = H(x)/k$. $H(x)$ is the energy difference between intact and broken network constraints in a simple two-state system, N is the number of atoms, k is Boltzmann's constant, and Ω is the number of degenerate configurations per floppy mode [13,14]. Hence, Eq. (10) relates the configurational entropy to topological degrees of freedom per atom [13–16]. The MYEGA model therefore establishes a direct link between viscosity and the number of topological constraints in a glass-forming liquid.

Taking the natural logarithm and differentiating with respect to $\ln T$, we get

$$\left(\frac{\partial \ln S_{conf}}{\partial \ln T} \right)_P = \frac{C}{T}. \quad (11)$$

Substituting Eq. (11) into Eq. (2), we obtain

$$\alpha_{conf}(x, T) = \left(\frac{\partial \ln V_{conf}}{\partial \ln S_{conf}} \right)_P \cdot \frac{1}{T^2} \cdot C, \quad (12)$$

where $C = T_g \left(\frac{m}{(12 - \log \eta_{\infty})} - 1 \right)$. Note that if we set $T = T_g$, Eq. (12) becomes Eq. (6).

If we consider α_{conf} to be independent of temperature and if we assume that Eq. (10) correctly captures the temperature dependence of S_{conf} , then the scaling factor A from Eq. (7) should have a quadratic dependence on temperature. However, in our study of α_{conf} , we need only the single value of A at the glass transition temperature. Since a direct measurement of A is not possible, we will determine this value empirically by fitting our measured α_{conf} data, as depicted in Fig. 1.

4. Experimental overview

In order to validate our model described in Eq. (8), we compare the scaling of α_{conf} obtained from thermal expansion measurements with values of $h(T_g, m, \eta_{\infty})$ obtained from MYEGA fits of viscosity measurements. We consider 41 different silicate glass-forming systems belonging to four distinct compositional families: alkali titanosilicates, barium aluminosilicates, sodium aluminosilicate, and sodium borosilicates. Measurement of high-temperature thermal expansion is described in detail in Ref. [1]. The details of the viscosity measurements and use of the MYEGA model for fitting viscosity data are described in Ref. [8]. Measured viscosity data are included from beam bending, parallel plate, and high-temperature concentric cylinder techniques for all compositions under study.

5. Results

Fig. 1 shows the correlations between linear configurational CTE (α_{conf}) and $h(T_g, m, \eta_{\infty})$ for the four families of silicate glass compositions under study. We find that there is generally a good correlation between our model viscosity parameter, $h(T_g, m, \eta_{\infty})$, and the configurational CTE, with $R^2 > 0.7$ for each compositional family. The optimized value of the parameter A in Eq. (7) is on the order 10,000 ppm but varies somewhat among the different families of glass, as indicated by the different slopes shown in Fig. 1.

While a direct measurement of A is not possible in the laboratory, it is interesting to note that the average value of 10,000 ppm is in good agreement with that calculated using an *ab initio*-derived

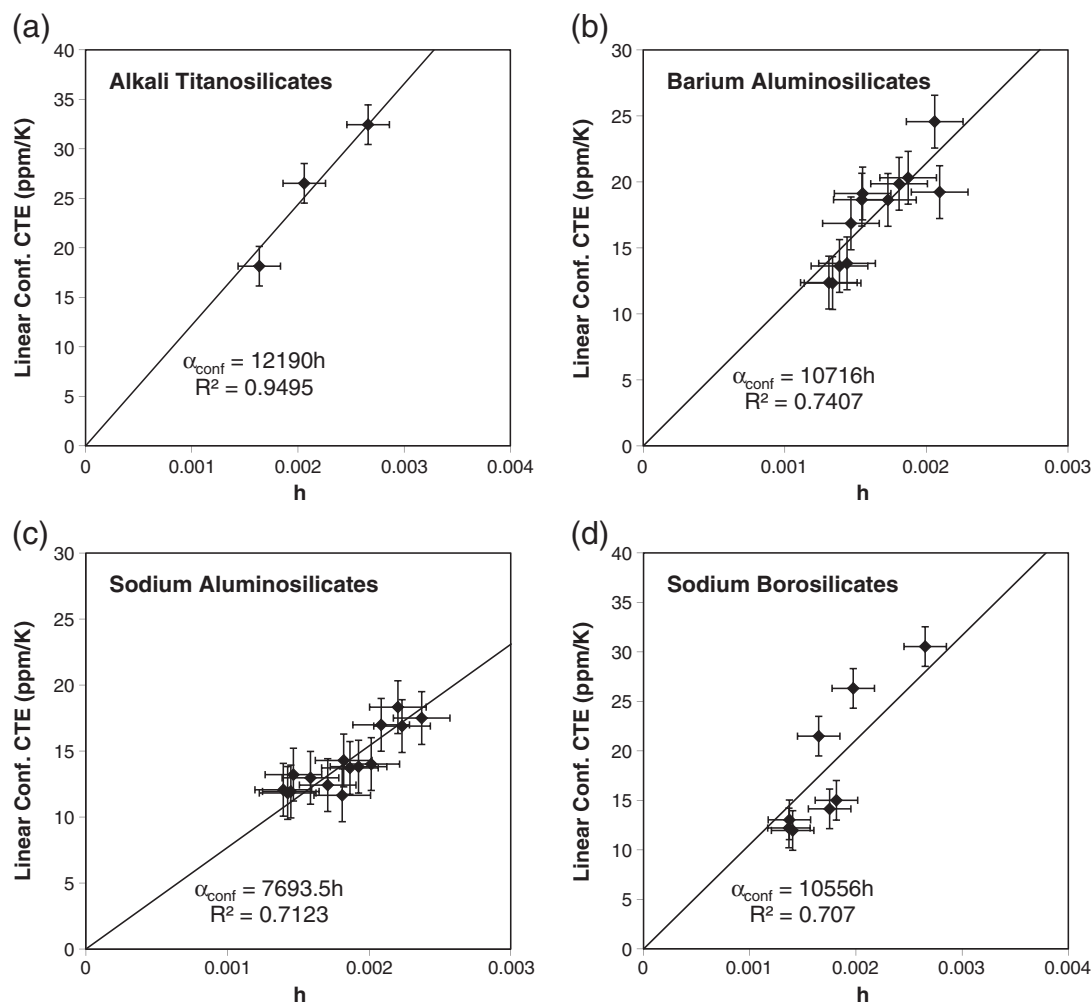


Fig. 1. Correlations between linear configurational CTE (α_{conf}) and the h parameter of Eq. (7) for four different families of glass-forming liquids: (a) alkali titanosilicates (three compositions), (b) barium aluminosilicates (twelve compositions), (c) sodium aluminosilicates (eighteen compositions), and (d) sodium borosilicates (eight compositions). In each case, a good correlation is observed between α_{conf} and h . However, the particular value of the slope A in Eq. (7) varies among the different glass families.

enthalpy landscape model for selenium glass, where Eq. (7) for A can be evaluated directly [17]. Based on this model, the plausible values of A at the glass transition are calculated to be in the range of ~5000 to 15,000 ppm. This is surprisingly good agreement considering that the chemistry of selenium is completely different from that of the silicate glasses considered in our measurements. This good agreement between silicate and chalcogenide glasses indicates that the values of A may also be similar across other types of glass families.

6. Discussion

To our knowledge, there has been only one previous investigation of the dependence of configurational CTE on composition, viz., the pioneering study of Senapati and Varshneya [18] who found a direct connection between α_{conf} and the underlying topology of the glass network. Specifically, Senapati and Varshneya have demonstrated a minimum in configurational CTE in chalcogenide glasses about the Phillips–Thorpe rigidity percolation threshold [19–21], where the number of degrees of freedom in the glass network is equal to the number of atomic bond constraints. In our previous research [8,12,15,16], we have also shown that both the temperature and composition dependence of viscosity can be accurately modeled in terms of topological constraint theory. The results presented in our current paper thus show a direct link between viscous dynamics and configurational CTE. Since viscosity is governed by the underlying topological constraints in the glass network, through our current model in

Eq. (8), the composition dependence of configurational CTE can also be explained as a result of constraint theory. The model presented in our current paper therefore provides the missing link between viscous flow and configurational CTE and clarifies the topological underpinnings of the compositional dependence of configurational CTE. Further information on the calculation of viscosity curves from topological constraint theory can be found in the recent review article by Mauro [21] or in Smedskjaer et al. [22].

7. Conclusions

We have proposed a model for the configurational thermal expansion coefficient of glass-forming liquids that captures the composition dependence in terms of changes in viscous flow dynamics. We have evaluated the model for 41 different silicate glass-forming systems in four different compositional families, and we find that the model accurately captures the scaling of configurational CTE within each family of composition. We find that more than 70% of the composition dependence of configurational CTE can be attributed to changes in the viscous flow parameters, as predicted by our model. The proportionality constant A connecting the configurational CTE with the viscous dynamics varies somewhat among the different compositional families but is in good agreement with that calculated using an enthalpy landscape model of glassy selenium. The success of our model points to a direct link between configurational CTE and topological constraint theory.

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