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Universal behavior of the viscosity of supercooled fragile and polymeric glassformers in different temperature regions

Adriana Andraca [a], Patricia Goldstein [a,*], Luis Felipe del Castillo [b]

[a] Departamento de Física, Facultad de Ciencias Universidad Nacional Autonoma de Mexico, Ciudad Universitaria, 04510, Coyoacán Ciudad de México, Mexico

[b] Instituto de Investigaciones en Materiales Universidad Nacional Autonoma de Mexico, Ciudad Universitaria, 04510, Coyoacán Ciudad de México, Mexico

HIGHLIGHTS

- Two corresponding states laws for fragile supercooled liquids for all temperatures are presented.
- A new empirical equation for the *LSF* for fragile glassformers below T_c is proposed.
- The universal behavior for the *LSF* for honeys may be extrapolated for all fragile glassformers.

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ABSTRACT

The behavior of the viscosity of supercooled liquids with temperature has been extensively studied in different regimes. We present a universal behavior for the Logarithmic Shift Factor for fragile and polymeric glassformers in two temperature regions, above and below the crossover temperature T_c, respectively. We find two different equations, one for each region, that may be represented as master plots which show universal behaviors for both cases.

1. Introduction

The study of the nature of the phenomenology of the glass transition remains still an open issue. The relaxation processes that take place in fragile supercooled liquids have been extensively presented in the literature for temperatures above the glass transition temperature T_g in the range of temperatures between T_g and the melting temperature T_m. It is exactly in this region that the liquid is considered supercooled. The definition of fragility is in the sense of Angell's classification of fragile and strong glasses [1].

As the supercooled liquid approaches T_g, the value of its viscosity η increases drastically with temperature. Experimentally, there is a clear evidence that the dependence of the viscosity with temperature, for fragile glass formers, presents different behaviors varying the temperature range where it is measured. We may find solid proofs that a crossover of regimes is present, below and above a phenomenological crossover temperature, T_c [2–25], which lies within the values $\left(1.15T_g, 1.28T_g\right)$ [26–30]. It is important to point out that this crossover temperature has not the same meaning as the theoretical critical temperature T_c introduced in the Mode Coupling Theory [31–34].

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[*] Corresponding author.
E-mail address: patricia.goldstein@ciencias.unam.mx (A. Andraca).

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The dependence of the Logarithmic Shift Factor (*LSF*),

$$LSF = \log a_T = \log \frac{\eta(T)}{\eta(T_s)} \tag{1}$$

with temperature has been widely discussed in both the two different temperature regions presented above, where T_s is a reference temperature.

The presence of this crossover of regimes became evident when two of the most widely used empirical equations that expressed perfectly well the behavior of the *LSF* with temperature, above the crossover temperature, namely, the Vogel–Fulcher–Tamann (VFT) [35–37] and the Williams–Landel–Ferry (WLF) [38] for fragile supercooled glassformers, failed to describe relaxation processes below T_c.

The VFT equation is given by.

$$\log a_T = A - \frac{B}{T - T_0}. \tag{2}$$

A and B are independent parameters, and T_0 is generally interpreted as the isoentropic temperature, namely, the temperature where the configurational entropy vanishes [39,40].

The WLF equation is written in the form,

$$\log a_T = \frac{C_1(T - T_s)}{C_2 + T - T_s} \tag{3}$$

where, according to first proposal of Williams, Landel and Ferry [38], C_1 and C_2 were universal constants for all glass forming liquids, given an appropriate reference temperature T_s. The WLF has been applied successfully up to the present in the study of the viscosity of glassforming liquids above T_c, although C_1 and C_2 may not have the same values for different systems [41–52].

Since neither the VFT nor the WLF equations describe the viscosity dependence on temperature below T_c, several equations have been proposed to describe the behavior of the *LSF* with temperature within the range (T_g, T_c) [5,7,8,25–28].

In previous works [53,54] we have proposed an equation for this region that satisfies Stickel's derivative analysis [7,8], that may be written as,

$$-LSF = \log \frac{\eta(T_s)}{\eta(T)} = C(T_A - T)^2 - E \tag{4}$$

where C and E are fitting parameters, and the temperature T_A is related to T_0 and T_c. This equation has proved to fit experimental values for the *LSF* for several glassformers [53,54].

Finding corresponding states laws for physical quantities has always represented a desired result in many fields of knowledge. It seems that the first efforts to find a corresponding states law for glass forming liquids began in 1972 [55]. One of the first analysis in order to obtain a corresponding states law for several supercooled fragile glassformers is presented by Rössler [27]. He works with eleven organic supercooled liquids and recognizes two kinds of behaviors between the glass transition and the melting point temperatures.

In another work [28], Rössler and co-workers on one side, and Leon and Ngai [5] on the other, study corresponding states laws using ten glassformers, including strong, polymeric and organic substances, obtaining the possibility of fitting the data in both intervals using different VFT equations, an idea that Stickel et al. [8] had already proposed. A different approach is proposed by Elmatad and coworkers [56,57] and Kivelson and coworkers [26] present corresponding states laws in different intervals of temperature from the ones we are presenting in this work.

In this work, we shall show that, through master plots for each region, corresponding states laws for several fragile glassformers, organic and polymers, may be obtained, using in each case different empirical equations. In Section 2, we present the empirical equations that have successfully been used to make the description for each case. In Section 3, we study the behavior for temperatures above T_c, and we find a corresponding states law with a proposed empirical equation for all the supercooled liquids we have considered. We find that using the same equation for temperatures below T_c, this pattern breaks down. In order to find a corresponding states behavior for this last temperature region, in Section 4, we propose a different empirical equation that results in a master plot for the same liquids, now below T_c. Finally, in Section 5 we present a complete discussion on our results.

2. The empirical equations

2.1. The LSF for temperatures above T_c

As we have already pointed out, one of the most used empirical equation to describe the relaxation processes for temperatures above T_c is the WLF equation (3). In previous works [48,58], we have shown that the WLF equation may