



## Tracer diffusion in glassforming liquids

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### ARTICLE INFO

#### Article history:

Received 15 May 2007

Received in revised form 28 March 2008

Available online 8 April 2008

#### Keywords:

Tracer diffusion

Stokes–Einstein relation

Glass forming liquids

Time–temperature superposition principle

### ABSTRACT

In the last decades, a wide collection of experimental evidence has been found in the study of supercooled glassformers on the existence of a crossover between two dynamical regimes at a temperature  $T_c$ . We discuss the validity of the Vogel–Fulcher–Tammann in both regions. The breakdown of the Stokes–Einstein relation below  $T_c$  is presented, indicating that the diffusion coefficient of a tracer becomes decoupled from the viscosity through an exponent  $\xi$ , and the diffusion process is intensified. We verify that a temperature shift on the diffusion coefficient introduces the same effect as the Stokes–Einstein breakdown equation. We present the dependence of this exponent on the ratio between the radii of the tracer and the host liquid molecule.

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### 1. Introduction

Relaxation processes that take place in supercooled liquids in the vicinity of the glass transition temperature  $T_g$ , have been extensively studied in the last two decades. One of the most significant features of a liquid approaching the glass transition is the rapid increase of the viscosity. Theoretically, many efforts have been undertaken to study the temperature dependence of the viscosity and other thermodynamic properties.

One of the most important empirical equations that deals with the behavior of the viscosity as the system approaches  $T_g$  is the Vogel–Fulcher–Tammann (VFT) equation, namely [1–3],

$$\log \eta = A - \frac{B}{T - T_0}, \quad (1)$$

where  $A$  and  $B$  are independent parameters and  $T_0$  may be interpreted as the isoentropic temperature, namely, the temperature where the configurational entropy vanishes. The relaxation phenomena described by the VFT equation correspond to the very slow  $\alpha$ -relaxation processes. One may find, however, that fast relaxation processes occur in the vicinity of  $T_g$ , namely the  $\beta$ -relaxation processes [4–14]. Relaxation and diffusion mechanisms present drastic changes around a cross-over temperature  $T_c$  which lies within the interval  $[1.15T_g, 1.28T_g]$  [15–34]. There are two important aspects that characterize this cross-over region. The VFT equation does no longer describe the experimental results for the viscosity below  $T_c$ , and, furthermore, the diffusion mechanisms undergo changes.

The Stokes–Einstein (SE) equation establishes that the diffusion coefficient of a sphere of radius  $a$  in a fluid whose viscosity is  $\eta$ , is given by

$$D = \frac{k_B T}{6\pi a \eta}, \quad (2)$$

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where  $k_B$  is Boltzmann's constant. In the case of a glassformer at temperatures above  $T_c$ , the SE equation works. However, for temperatures below  $T_c$ , the SE equation breaks down, and the diffusion process is enhanced. In this region, the influence of the viscous relaxation upon the diffusion coefficient may be expressed in terms of the relation

$$D \propto \eta^{-\xi}, \quad (3)$$

where

$$0 < \xi < 1.$$

In fact, both experimental [35–47] and theoretical [48–56] results have indicated that as a supercooled glass forming liquid is cooled towards  $T_g$ , its dynamics becomes increasingly heterogeneous presenting magnified diffusion mechanisms. For temperatures below  $T_c$ , one may assume a dynamic heterogeneity consisting of two different mobile domains, more mobile domains that govern the translational molecular displacement and less mobile domains that determine structural relaxation [35]. In this case, the diffusion decouples from the viscosity ( $\xi < 1$ ) due to the so-called microviscosity effect [48] that considers that the viscosity around a small tracer is rather different from that of the bulk due to size effects. The single particle dynamics of the tracer and the collective dynamics of the supercooled liquid, as it is taken towards lower temperatures, occur on different time and length scales, and  $\xi$  increases with increasing size of the tracer.

In this work, we present the enhancement of the diffusion coefficient of small tracers in glass formers in the region below the crossover temperature  $T_c$  taking into consideration that the VFT equation is not valid for this region. In Section 2 we give a brief presentation of an empirical equation for the viscosity in the temperature range between  $T_g$  and  $T_c$ . In Section 3, we present the behavior of different tracers in supercooled liquids and we obtain the SE equation breakdown below  $T_c$ . We discuss the effect of a temperature shift on the diffusion coefficient by means of the time-temperature superposition principle [35]. In addition, we find different values for the exponent  $\xi$  in terms of the ratio between the radius of the tracer and that of the host and the dependence of the exponent with the glass transition temperature of the host. Finally, we present in Section 4 some conclusions,

## 2. The viscosity

One strong evidence of the crossover of the regimes is that a single VFT equation cannot fit the data for the viscosity in the whole range of temperatures from  $T_g$ , the glass transition temperature, to  $T_m$ , the fusion temperature [5–7,13,21,26–30,57–60]. As we have already discussed these two regimes are separated by the temperature  $T_c$ . It has been proven that the experimental data for the viscosity for temperatures above  $T_c$  may always be fitted by a VFT equation. In the literature one may find different proposals to fit the data for the viscosity for temperatures below  $T_c$ . Some authors propose that a different VFT, namely one with different parameters of those of the VFT fit above  $T_c$ , may fit the data below  $T_c$  [5,13,26–30,60]. Another empirical equation that is also used to fit the viscosity data is the well known Williams–Landel–Ferry (WLF) equation [61] which actually also fits nicely the data for the viscosity above  $T_c$ . One may find proposals where a different WLF equation may also fit the data below  $T_c$  [6,7]. There is also strong evidence that the data below  $T_c$  must be fitted using different equations, as for example those given in references [13,26,27,56–59]. Stickel's derivative analysis [26,27] provides an excellent way to prove which is the right answer to this question. This method consists of the study of a given equation used to fit the data below  $T_c$  in terms of the temperature derivative analysis for the quantities,

$$x = \left\{ f/\text{Hz}, \sigma_{dc}\epsilon_0/s^{-1}, \eta^{-1}/\text{poise}^{-1} \right\}, \quad (4)$$

where  $f$  is the frequency of the peak of the loss function, the imaginary part of the complex dielectric function,  $\sigma_{dc}$  is the dc conductivity, and  $\eta$  the viscosity. The method consists on the evaluation of three derivatives of a given empirical form for  $\log x$ ,

$$\left[ \frac{d \log x}{dT} \right]^{-1/2} \quad (5)$$

$$\frac{d}{dT} \left[ \left( \frac{d \log x}{dT} \right)^{-1/2} \right] \quad (6)$$

$$\Theta = \frac{\frac{d \log x}{dT}}{\frac{d^2 \log x}{dT^2}} \quad (7)$$

and the comparison of the values of the derivatives for the given form and the VFT equation, finding whether experimental data fit VFT or not.

In this work, we propose an empirical form for the viscosity for the  $T < T_c$  region which has already been discussed in a previous work [56], namely,

$$\log \frac{\eta(T^*)}{\eta(T)} = C(T_A - T)^2 + E \quad (8)$$

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