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Accumulating evidence for non-diverging time-scales in glass-forming fluids

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ABSTRACT

One perceived important signature of the “ideal” glass transition and of the complex fluid nature of glass-forming liquids remains the apparent divergence of the dynamics at temperatures above zero Kelvin. Recently, however, this perception has been increasingly challenged both through experiment, large scale data analysis, and in some new theories of the dynamics of glass forming systems. Here we summarize early evidence suggesting that time scales actually do not diverge in glasses that are aged into equilibrium, perhaps 15 °C below the conventional glass transition temperature T_g. We then show novel results from an extremely densified glass – 20 million year old Dominican amber – in which we were able to obtain the upper bounds to the relaxation times at temperatures below the glass transition temperature through a step-wise temperature scan in which the stress relaxation response of the amber was measured both below and above the fictive temperature T_f. We find that in the case of the upper bound responses at $T > T_f$, there is a strong deviation of the response from the Super-Arrhenius Vogel–Fulcher–Tammann (VFT) extrapolation and this persists to the fictive temperature which is some 43.6 °C below T_g. Evidence is also presented suggesting that different dynamic properties may deviate from the VFT extrapolation differently and challenges for future measurement are presented.

1. Introduction

In the 1920s the empirical equation, now referred to as the Vogel [1], Fulcher [2], and Tammann [3,4] (VFT) equation (among others [5])[1] was proposed as a means of describing the viscosity of glass-forming liquids above the glass transition temperature T_g. The equation has subsequently been taken as paradigmatic of the nature of glass-forming liquids and suggests that if the viscosity η (or the relaxation time) upon extrapolation to below the T_g will diverge at a finite temperature T_0 often referred to as the VFT temperature. The expression is:

$$\eta = A_0 e^{B/(T-T_0)} \text{ or } \tau = A_1 e^{B/(T-T_0)} \tag{1}$$

where A_0 and A_1 are prefactors, B is a parameter similar to an activation energy in an Arrhenius expression and T is the temperature. This well known behavior is illustrated in Fig. 1 as the viscosity of a polystyrene polymer glass-former both as a function of reciprocal temperature (Fig. 1a) and as a function of temperature (Fig. 1b) [6,7].

The behavior was associated with the observation [8] that dilatometric or calorimetric responses seemed to show thermodynamic signatures reminiscent of a phase transition near to what is now commonly called the glass transition temperature T_g. Some of the earliest work from Tool and Eichlin [8] showing the thermodynamic ‘heat absorption’ of a glass is shown in Fig. 2. Hence, it has become an important area of investigation to determine the origins of the rapid (super-Arrhenius) change of the dynamics (viscosity or relaxation time) with decreasing temperature. Frequently, the explanations depend on the existence of an ideal glass transition temperature that is related to the VFT temperature, though not always. Regardless, it has become important in the theoretical descriptions of the glass transition to know whether or not the dynamics continue to follow the super-Arrhenius type of behavior suggested by the VFT empiricism into the regime where it is extremely difficult to make equilibrium measurements because of the “geological” age [7] or “astronomical” age [9] problem associated with extremely long relaxation times for the materials to achieve equilibrium. While the fundamental questions of glass formation are, of themselves fascinating, as evidenced by the large amount of work that continues in this area, it is also an especially important field for practical applications. Not only does our understanding of glass formation impact processing of items made of glass-forming

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[1] It is of interest to remark that Tammann [3,4] does not seem to have proposed this equation. Rather, he originally [3] cited work from H. Le Chatelier [5] stating that the viscosity could be represented by an equation of the form $\log(\log(\eta)) = P - MT$ which is a form of stretched exponential rather than the modern form of the VFT equation. In the Tammann and Hesse paper [4] the work of Fulcher was correctly cited, hence it is only for historical reasons that we use the terminology of VFT rather than just VF, who seemed to have proposed the equation independently [1,2].

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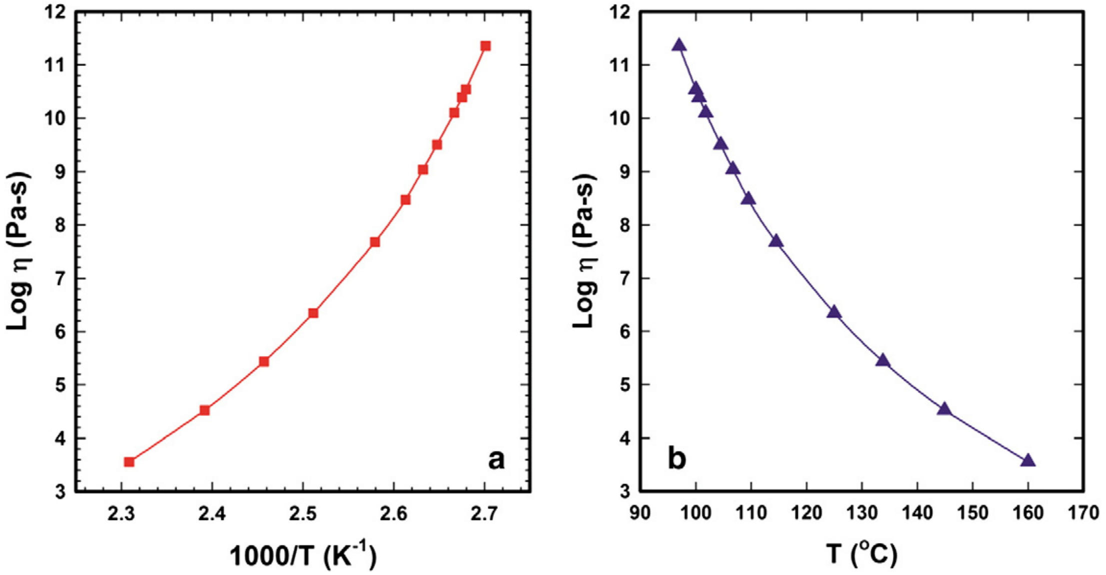

Fig. 1. Logarithm of viscosity of a polystyrene glass-former as a function of a) reciprocal temperature and b) temperature. Lines represent fits of Eq. (1) to the data. Original data from Plazek [6]. Plots modified from McKenna [7].

systems but also the increasing use of organic polymers in structural applications makes the understanding of their performance in the non-equilibrium glassy state a matter of material performance for long term applications where public safety may be involved. This aspect is increasingly being appreciated and one reason is that polymeric resins are generally used at very high proportions of their glass transition temperatures [7] and when new materials with higher T_gs are developed, they tend to be used near to those higher glass transition temperatures. Furthermore, current models [10–17] of the aging or structural recovery of materials are only reasonable first order approaches to behavior [7, 18–21] and part of the problem may be related to the correct description [22] of the equilibrium state of the glass below the T_g.

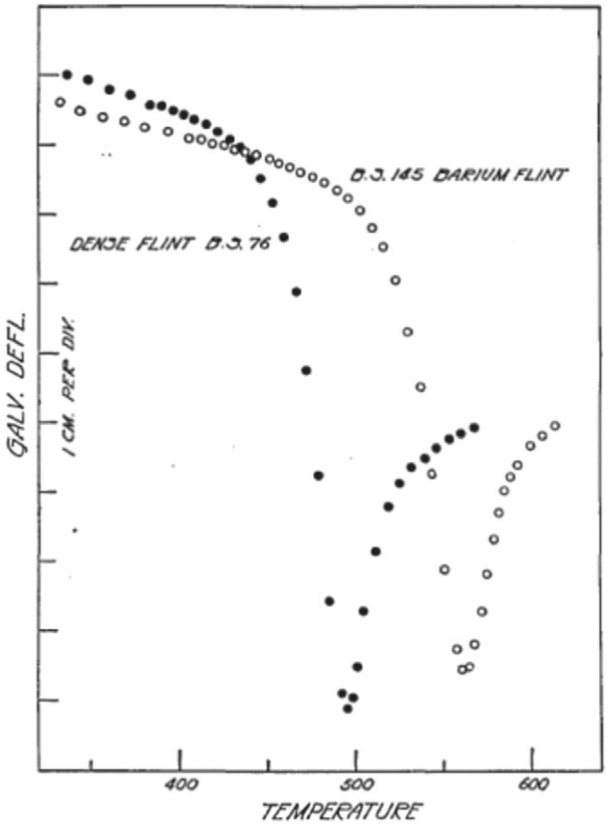

Fig. 2. Heat absorption upon increasing temperature in two flint glasses showing behavior that looks like a phase transition. Galvanic deflection from differential temperature measurements. From A.Q. Tool and C.G. Eichlin, J. Optical Soc. America, 4, 340–365 (1920) [8].

Prior to going into the major thrust of the manuscript, we acknowledge a significant amount of theoretical and, more recently, simulation work that address the origins of and the nature of the glass transition [9, 23–43]. However, the purpose of the present article is not to review this literature, but rather it is to develop a perspective into the experimental situation which relates to the predictions of relaxation times or viscosities as a function of temperature as one goes below the conventional glass transition temperature. Reference [9] provides an excellent recent perspective on the theoretical situation and general reviews on the glass transition [18–21,44–48] also provide perspective. We now turn to the issue of the experimental evidence for a breakdown of the VFT extrapolation to below the glass transition temperature.

2. Evidence for non-diverging time-scales

Fig. 1a and b show the apparent divergence of the viscosity as temperature is reduced to below the nominal glass transition temperature of 100 °C in polystyrene. The question of testing how the equilibrium response can be determined when one is below the glass transition has been little investigated simply because experiments tend to take extremely long times for the material to come into equilibrium. Perhaps the first attempt to look at the problem systematically was a study carried out by O'Connell and McKenna [49] on a polycarbonate polymer that was aged into equilibrium at a series of temperatures following the classic aging protocol of Struik [50]. To understand the approach used in that study, we first give a brief background on structural recovery and physical aging.

2.1. Background on structural recovery and physical aging

For simplicity, we present in Fig. 3 a volume (or enthalpy) vs. temperature schematic for a glass-forming liquid chosen such that it cannot crystallize (as is the case for many polymers) hence the supercooled liquid line of the non-crystallizable glass-former is also the equilibrium state line. Then, in Fig. 3 we see that the dashed line that is of the greatest slope defines the equilibrium response as a function of temperature. The solid line with arrows depicts an arbitrary