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# Systematic broadening of the viscoelastic and calorimetric glass transitions in complex glass-forming liquids

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## ABSTRACT

In this experimental study, we explore the broadening of the glass transition in chemically and structurally complex glass-forming liquids (CGFLs) by means of thermal and rheological characterization techniques. Petroleum fluids with different levels of chemical and structural complexity are used as model materials. Thermal characterization by temperature-modulated differential scanning calorimetry (TMDSC) reveals a systematic increase in the width of the glass transition region  $\Delta T_g$  with increasing chemical and structural complexity. The broadening of the glass transition is also strongly reflected in the linear viscoelastic properties that are measured by small-diameter parallel plate rheometry. Most notably, this is observed as the broadening of the relaxation time spectrum at long times. The recently proposed broadened power-law spectrum model is used to describe the constitutive behavior of the investigated petroleum fluids. In this model, the stretching parameter  $\beta$  serves as a quantitative measure of the spectral broadening. A strong power-law correlation is found between  $\Delta T_g$  and  $\beta$ , manifesting a relationship between the broadness of the calorimetric and viscoelastic glass transition in CGFLs.

## 1. Introduction

As documented by several excellent review articles [1–5], the dynamics of supercooled glass-forming liquids (GFLs) have been a subject of intense research over the past five decades or so. For example, a lot of research has been devoted to the study of non-exponential relaxation in GFLs [6,7]. Although experimental techniques such as rheology [8] and dielectric spectroscopy [9] have provided extensive information on glassy dynamics, the underlying theory remains relatively obscure [10–12]. In particular, the dynamics of chemically and structurally complex glass-forming liquids (CGFLs) are still largely unexplored and poorly understood [13].

In terms of rheological properties, the glass transition manifests itself as a rapid increase in the relaxation time  $\tau$  and in the viscosity  $\eta$  upon cooling. Indeed, in many glass-forming systems, this increase is observed to be > 15 orders of magnitude over a relatively narrow temperature range. It is particularly notable that the extreme temperature dependence of GFLs poses a major challenge to their rheological characterization. At low temperatures – i.e. near and below the glass transition temperature ( $T_g$ ) – GFLs are extremely stiff, in which case measurement errors due to torsional instrument compliance may

become an issue [14,15]. To overcome this experimental difficulty, sophisticated measurement techniques such as small-diameter parallel plate (SDPP) rheometry have been developed. To accurately measure the high stiffness values of a glassy material, the SDPP technique relies on minimizing the instrument compliance errors by decreasing the diameter of a parallel plate measurement geometry and by applying instrument compliance corrections [16].

With the help of improved measurement techniques, the linear viscoelastic data of GFLs have become increasingly available during the past decade. This has allowed more comprehensive constitutive models to be developed for GFLs. Particularly, special attention has been recently paid to the modeling of the relaxation time spectra  $H(\tau)$  of GFLs. Winter and coworkers [17,18] discovered that the  $H(\tau)$  of selected colloidal and molecular glass formers can be described by a power-law function that is cut off at the longest relaxation time  $\tau_\alpha$ :

$$H(\tau, \varepsilon) = n_\alpha G_c \left( \frac{\tau}{\tau_\alpha(\varepsilon)} \right)^{n_\alpha}, \quad \text{for } \tau < \tau_\alpha(\varepsilon) \text{ and } n_\alpha \geq 0 \quad (1)$$

where  $\varepsilon$  is the distance from the glass,  $n_\alpha$  is a positive-valued exponent that originates from the mode coupling theory (MCT), and  $G_c$  is the

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plateau modulus of the  $G'$  data. Notably, Eq. (1) is identical to the Baumgaertel-Schausberger-Winter (BSW) model [19] without contributions from the  $\beta$ -relaxation. In a more recent study by the authors [13], it was shown that Eq. (1) is valid only for chemically and structurally simple glass-forming liquids (SGFLs). On the contrary, the relaxation time spectrum of bitumen – a material that can be considered as a model material for CGFLs [13] – exhibits a significantly different shape. Specifically, the bitumen spectrum is characterized by a broad distribution of long relaxation times. This spectrum can be described by a power-law function with a stretched exponential cut-off [13]:

$$H(\tau) = n_\alpha G_c \left( \frac{\tau}{\tau_\alpha} \right)^{n_\alpha} \exp \left[ - \left( \frac{\tau}{\tau_\alpha} \right)^\beta \right], \quad \text{for } \beta < 1 \text{ and } 0 < n_\alpha \leq 1 \quad (2)$$

where  $\beta$  is a stretching parameter that describes the broadening of the relaxation time spectrum at long relaxation times.

In this broadened power-law spectrum model, the stretched exponential function,  $\exp(-t^\beta)$  with  $\beta < 1$ , is used in a way which significantly differs from its common use in the modeling of the glass transition. The stretched exponential function is able to describe decaying processes, which occur more slowly than a regular exponential function ( $\beta = 1$ ) would predict. Conventionally, in the context of the glass transition dynamics, the broadening of stress relaxation has been expressed by a relaxation modulus of stretched exponential format [20,21]. Here, using a different property of the stretched exponential, the stretched exponential function is multiplied into the BSW powerlaw relaxation spectrum with the purpose of broadening the cut-off at the longest relaxation time. For a large  $\beta$  value ( $\beta = 10$ , for instance), the sudden cut-off of the BSW spectrum is preserved. However, for a small  $\beta$  value, the cut-off is broadened as needed for expressing the glassy relaxation of CGFLs. This  $\beta$  parameter is solely used for the broadening of the relaxation time spectrum but is unrelated to the conventional KWW relaxation modulus. In our previous paper [13], the broadened shape of the relaxation time spectrum was attributed to the broad distribution of glass transition temperatures. A schematic representation of the empirical constitutive models of Eqs. (1) and (2) and their associated parameters is given in Fig. 1.

Thermal properties of glass-forming materials are often characterized by differential scanning calorimetry (DSC) or temperature-modulated differential scanning calorimetry (TMDSC) [22]. The main advantage of TMDSC over conventional DSC is that it allows a

quantitative separation between heat capacity-related (reversing) and kinetic (non-reversing) thermal events [23]. From an application point of view, TMDSC has proven to be a particularly powerful technique in the characterization of CGFLs, such as bitumen and its fractions [24,25] and naphthenic and paraffinic oils [26]. Masson et al. [25,27] showed, for example, that TMDSC can detect multiple glass transitions in bitumen and quantify time-dependent changes in its microstructure. Moreover, the reversing heat flow in TMDSC allows accurate determination of glass transition temperatures without interference from non-reversing thermal events such as enthalpy relaxation and cold crystallization; this will be demonstrated later on in Section 3.1.

In this study, we investigate the rheological and thermal properties of CGFLs near and below the glass transition. The main objective is to evaluate the effect of chemical and structural complexity on the broadening of the glass transition. To investigate this, we selected petroleum liquids as model materials for CGFLs. They are obtained from the distillation of crude oil and can be considered as highly complex mixtures of different types of hydrocarbons with small amounts of heteroatoms such as sulfur, oxygen, nitrogen and organic metals [28]. The distillation process separates the crude oil into different fractions based on boiling point ranges. The resulting petroleum fractions exhibit a wide spectrum of chemical and physical properties [28,29]. Low-boiling point fractions of crude oils are mostly composed of paraffinic and naphthenic hydrocarbons that are of relatively low molecular weight and contain only minute traces of heteroatoms [28]. The physical properties of these liquids are mainly governed by the London dispersive interactions that are the dominating type of molecular interaction in non-polar hydrocarbons [30]. Upon increasing boiling point, petroleum fluids become more complex in terms of chemical composition and molecular structure [31,32]. This evolution is often accompanied by an increase in the molecular weight and the molecular weight distribution [33]. Furthermore, aromatic and polar interactions start to play a role with increasing heteroatom content [28]. In the asphaltene fraction, which is the highest molecular weight and most polar component of crude oil and its derivatives, poly-condensed aromatic compounds are believed to form  $\pi$ - $\pi$  stacked structures [34]. Consequently, heavy petroleum products such as vacuum residue and bitumen are best described as extremely complex mixtures of different molecular species exhibiting various forms of molecular interactions [35]. Importantly for the purposes of this study, the varying chemical and structural properties of different petroleum fluids result in vast differences in their rheological behavior [36].

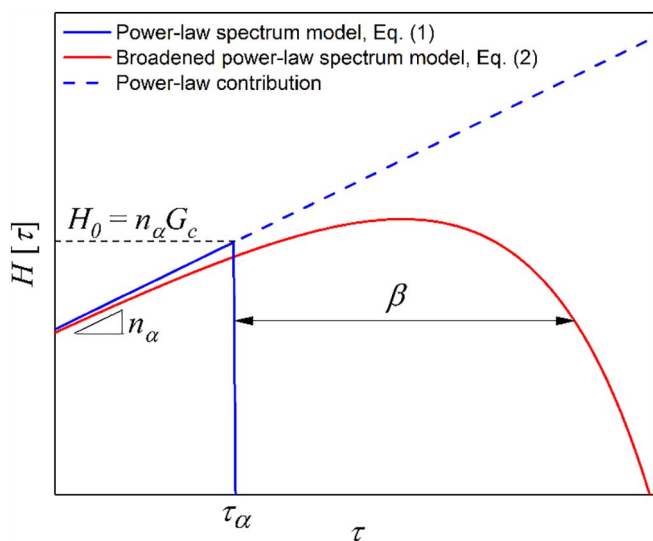


Fig. 1. Schematic representation of the constitutive models described by Eqs. (1) and (2).  $n_\alpha$  describes the slope of the relaxation time spectrum at short relaxation times,  $\tau_\alpha$  is the longest relaxation time in the power-law spectrum model of Winter [17,18], and  $\beta$  defines the width of the broadened power-law spectrum at long relaxation times [13]. The dashed line shows the contribution of the power-law term  $H(\tau) = n_\alpha G_c (\tau/\tau_\alpha)^{n_\alpha}$ .

## 2. Experimental

### 2.1. Materials

Five petroleum fluid samples were investigated in this study. A summary of the basic properties of these samples is given in Table 1. The chemical and structural complexity – of the petroleum fluids increases in the following order, as evidenced by increasing density and molecular weight: NPO1 < NPO2 < NPO3 < SVR < BIT. The average molecular weights reported in Table 1 were measured by gel permeation chromatography (GPC). It needs to be emphasized, however, that these molecular weights are only directional as the GPC of petroleum fluids is prone to experimental artifacts e.g. due to molecular associations and the tendency of asphaltenes to adsorb on the column wall [37,38]. Table 1 also shows the mean molecular polarizability  $\alpha$  of the petroleum fluids. This parameter characterizes the magnitude of the London dispersion forces that are the most important molecular interactions for the physical properties of petroleum hydrocarbons [30]. The polarizability is defined as [39,40]:

$$\alpha = \left( \frac{3}{4\pi N_A} \right) \left( \frac{M}{\rho} \right) \left( \frac{n^2 - 1}{n^2 + 2} \right) \quad (3)$$

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