



The dynamic fragility and apparent activation energy of bitumens as expressed by a modified Kaelble equation

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ABSTRACT

The temperature dependence of the dynamics of glass-forming liquids can be characterized by the dynamic fragility (m) and apparent activation energy (E_a) at the glass transition temperature T_g . In this study, we derive analytical expressions that allow the calculation of these parameters from a modified Kaelble equation which divides the temperature dependence into two regimes above and below a characteristic temperature T_d . Special emphasis is given to the analysis of the T_d parameter that can be considered as the rheological glass transition temperature. Rheological characterization is performed on twenty-seven bitumens originating from various crude oil sources and refining processes. Their dynamic fragilities and apparent activation energies are calculated at the calorimetric T_g and at T_d . Bitumen can be classified as a strong glass-forming liquid, dynamic fragilities varying in the range of $m(T_g) = 26 \dots 52$ for the individual bitumen samples. The results indicate that $m(T_g)$ and $E_a(T_g)$ are linearly correlated with T_g , and these T_g -dependences are unusually strong in comparison to other classes of glass-forming liquids. However, dynamic fragilities and apparent activation energies evaluated at T_d are nearly independent of the type of bitumen and show only a weak dependence on T_d .

1. Introduction

Petroleum bitumen, a residue of crude oil distillation, is widely used as a binder in asphalt pavements [1]. It is an extremely complex mixture of different molecular constituents that vary in chemical composition and molecular weight [2, 3]. Although mainly composed of low-molecular-weight hydrocarbons, bitumen also contains significant amounts of heteroatoms such as sulfur, nitrogen and oxygen, as well as traces of metals like vanadium and nickel [4]. The physical properties of bitumen are largely governed by complex molecular interactions including dispersive, polar, hydrogen bonding and π - π interactions [5]. In particular, the rheological properties of bitumen have been shown to be heavily influenced by aromatic interactions [5–7] and by the content of carbonyl and sulfoxide functional groups [8]. Moreover, the chemical composition and therefore the physical properties of bitumen depend on the crude oil source and on the refining processes employed in its production [9].

Bitumen is known to be a complex glass-forming liquid [10–12] with a glass transition at around -20°C , the exact glass transition temperature being dependent mainly on the crude oil it originates from [13–17]. Due to its extreme chemical and structural complexity,

bitumen exhibits unusual rheological characteristics as compared to most other glass-forming liquids. Most importantly, a significant broadening of the viscoelastic glass transition is observed [11, 12]. However, although numerous studies have been performed to study the rheological properties of bitumen at low temperatures, no one has yet specifically studied the temperature dependence of these properties at the glass transition.

The temperature dependence of the viscoelastic properties of glass-forming liquids is commonly described by two coupled parameters: dynamic fragility, m , and apparent activation energy, E_a , at T_g [18]. The dynamic fragility, also known as the steepness index [19], characterizes the rapidity with which a liquid's dynamic properties change as the glass transition temperature is approached and is quantified as [20]:

$$m(T_g) = \left[\frac{d \log a_T}{d(T_g/T)} \right]_{T=T_g} \quad (1)$$

where a_T is the time-temperature shift factor. This parameter measures the deviation from the Arrhenius temperature dependence in the vicinity of T_g [21]. When $m(T_g)$ is high, the material exhibits highly non-Arrhenius temperature dependence and we refer to it as a fragile liquid.

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On the contrary, when $m(T_g)$ is low, the material shows (nearly) Arrhenius-type temperature dependence and it is said to be a strong liquid. The apparent activation energy at T_g can be readily calculated from the dynamic fragility:

$$E_a(T_g) = \ln(10)RT_g m(T_g) \quad (2)$$

where R is the universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. Consequently, the dynamic fragility can be understood as a T_g -normalized activation energy.

Traditionally, the temperature dependence of relaxation patterns in the vicinity of T_g is modelled with the Vogel–Fulcher–Tammann (VFT) [22–24] or Williams–Landel–Ferry (WLF) [25] equation. In this case, dynamic fragility and apparent activation energy can be rewritten in terms of VFT and WLF parameters [18]. For the WLF equation:

$$\log a_T = \frac{-c_1(T - T_{ref})}{c_2 + T - T_{ref}} \quad (3)$$

$$m(T_g) = \frac{c_1^g T_g}{c_2^g} \quad (4)$$

$$E_a(T_g) = \ln(10)R \frac{c_1^g T_g^2}{c_2^g} \quad (5)$$

where c_1 and c_2 are the WLF parameters at an arbitrary reference temperature T_{ref} , and c_1^g and c_2^g represent the values of c_1 and c_2 when $T_{ref} = T_g$.

However, as reviewed by McKenna and Zhao [26], recent theoretical [27–34] and experimental [35–43] studies suggest that time scales actually do not diverge at temperatures above zero Kelvin, i.e. the temperature dependence of viscoelastic properties deviate from the VFT/WLF behavior below T_g . In fact, deviations from the VFT/WLF behavior are often observed even slightly above T_g (typically around $T_g + 10 \text{ K}$), see e.g. Refs. [11, 44–46]. Consequently, $m(T_g)$ and $E_a(T_g)$ values calculated from the VFT/WLF fits (Eqs. (4) and (5)) cannot always be considered reliable. Several modifications have been proposed to the traditional WLF equation to describe the temperature dependence of relaxation processes both above and below T_g by a single relation [47–54]. Most notably, Rowe and Sharrock [55] have proposed the following equation that is commonly known as the modified Kaelble equation:

$$\log a_T = \frac{-c_1(T - T_d)}{c_2 + |T - T_d|} \quad (6)$$

where T_d defines the temperature at which the curvature of the S-shaped $\log a_T$ versus T curve changes from positive to negative. It should be noted that this equation is a modification of the shift factor model initially proposed by Kaelble [54]. The general shape of the modified Kaelble equation is illustrated in Fig. 1. Above T_d , Eqs. (3) and (6) are identical when $T_{ref} = T_d$. Below T_g , Eq. (3) predicts too rapid a rise in $\log a_T$ culminating in a predicted infinite positive value when $T = T_{ref} - c_2$. Conversely, Eq. (6) predicts non-diverging time scales below T_g in a fashion consistent with experimental data. However, it is not straightforward to fit Eq. (6) to data since the form of this equation inherently assumes that the defining temperature and the reference temperature are the same, $T_{ref} = T_d$. This difficulty can be overcome by the addition of a constant term that separates T_d from T_{ref} [55]:

$$\log a_T = -c_1 \left(\frac{T - T_d}{c_2 + |T - T_d|} - \frac{T_{ref} - T_d}{c_2 + |T_{ref} - T_d|} \right) \quad (7)$$

It has been shown that the modified Kaelble equation accurately captures the temperature dependence of various viscoelastic materials both above and below T_g . These materials include different types of asphalt binders and mixtures [11, 55–58], as well as various polymers (e.g. polymethylmethacrylate [54], polystyrene [54, 55], polyisoprene [59] and polyurethane [59]) and commercial damping materials (e.g.

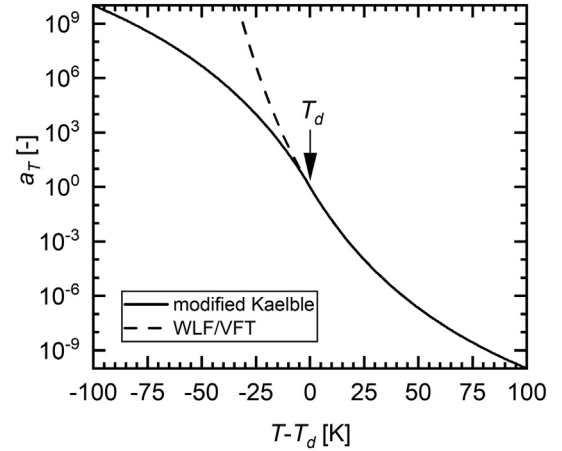


Fig. 1. Schematic representation of the modified Kaelble equation. A curve corresponding to the traditional WLF/VFT equation is shown for comparison purposes.

EAR C-1002 [59] and Hunston [59]). Moreover, we expect that the modified Kaelble equation can accurately describe the temperature dependence of many other viscoelastic materials too, although this needs to be confirmed by further studies.

In this paper, we analytically derive equations that allow the calculation of m and E_a from the fits of the modified Kaelble equation. These equations are used to calculate the m and E_a values of a wide variety of bitumens at T_g and T_d . Furthermore, the T_g -dependences of these parameters are examined and compared with other types of glass-forming liquids.

2. Theory

2.1. Analytical derivation of $m(T_g)$ and $E_a(T_g)$ from the modified Kaelble equation

In this section, we derive analytical equations for calculating $m(T_g)$ and $E_a(T_g)$ using parameter values obtained from the fit of the modified Kaelble equation, Eq. (7). Upon differentiation with respect to T_g/T , the second term of Eq. (7) becomes zero (derivative of a constant). Thus, we can start the derivation of the dynamic fragility from the modified Kaelble equation by considering the form of Eq. (6). When $T \leq T_d$, this equation can be written as follows:

$$\log a_T = \frac{-c_1(T - T_d)}{c_2 - T + T_d} = \frac{-c_1 T_g \left(\frac{T}{T_g} \right) + c_1 T_d}{c_2 - T_g \left(\frac{T}{T_g} \right) + T_d} \quad (8)$$

By substituting

$$u = \frac{T_g}{T} \Leftrightarrow u^{-1} = \frac{T}{T_g} \quad (9)$$

into Eq. (8), the following equation is obtained:

$$\log a_T = \frac{-c_1 T_g u^{-1} + c_1 T_d}{c_2 - T_g u^{-1} + T_d} \quad (10)$$

As described by Eq. (1), the dynamic fragility is defined as the derivative of the time-temperature shift factor with respect to T_g -normalized inverse temperature. Considering the substitution of Eq. (9) and the expression of Eq. (10), Eq. (1) can be rewritten as:

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