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A measure of cooperativity in non-Arrhenius structural relaxation in terms of the bond strength–coordination number fluctuation model

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ABSTRACT

In order to understand the non-Arrhenius structural relaxation in a systematic way, a measure of cooperativity is employed, which is based on the bond strength–coordination number fluctuation model developed by the authors. In our model, the cooperativity is described by the temperature-dependent number of structural units N_b involved in the structural relaxation, which increases from unity at the high temperature limit up to of the order of 100 near the glass transition temperature T_g . This is comparable to that estimated by the Donth formula, but is much larger than that obtained from the Adam–Gibbs model. At higher temperature region a characteristic temperature T_x is extracted from the cooperativity analysis, which could be associated with the transition temperature T_A across which the relaxation behavior changes from Arrhenius-like to non-Arrhenius-like. In the polymer melts and molecular liquids investigated, the characteristic temperature ratio T_x/T_g is found to be 1.67–1.81, which agrees with the typical T_A/T_g values reported. The extracted temperature T_x enables the characterization of the high-temperature relaxation behavior in a new way that differs from other methods. A possible interpretation of T_A is given in terms of the cooperativity onset.

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1. Introduction

The mechanism behind the non-Arrhenius temperature dependence of relaxation property in glass-forming liquids is yet to be completely elucidated [1–3]. Especially in fragile systems whose relaxation behaviors are often described by the empirical Vogel–Fulcher–Tammann (VFT) equation [4–6], the rapid slowing down in the atomic mobility occurs in a narrow temperature range as temperature drops to the glass transition temperature T_g . The mechanism operating in such process is attributed to the increase of molecular cooperativity [7–12]. Among the theoretical models proposed, the Adam–Gibbs (AG) model [13] is the most well-known. The AG model postulates a configurational entropy S_c inversely proportional to the activation energy, and relates it to the cooperatively rearranging region (CRR) in glass-forming liquids. The CRR is defined as [13] “a subsystem of the sample which, upon a sufficient fluctuation in energy (or more correctly, enthalpy), can rearrange into another configuration independently of its environment.” Since the proposal of AG model, a great number of studies have been carried out to account for the glass-transition phenomena in terms of the entropy-based AG model and the rise

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of CRR [7–11,14–19]. Nowadays, the CRR provides a key perspective to explain the glass formation of a liquid and the material property of amorphous substances [7–10,12,20–22]. In fact, different expressions have been used to estimate the cooperativity size from various points of views, e.g., the thermodynamic fluctuation approach [11,23–25], the spatially correlated length scale described by four-point dynamic susceptibilities $N_{\text{corr},4}$ [25,26], the thermodynamic cooperativity [27], etc.

In many studies regarding the cooperativity, the central concept of CRR is based on the conventional one proposed in AG model. However, some researchers have cast doubt on the AG model [24,28]. There, it is stressed that the AG model does not explain the proper size of the cooperativity [12,24,29]. Regarding this point, Huth et al. [24] have argued the inconsistency of the AG model by presenting an expression for estimating the size of CRR [7,8,10,11,23,30],

$$N_x = RT^2 \Delta(1/C_V) / \delta T^2 M_0, \quad (1)$$

where $\Delta(1/C_V)$ is the step of the reciprocal specific heat capacity at constant volume, δT is the mean square temperature fluctuation of the CRR, M_0 is the molecular mass defined simply as a particle, and R is the gas constant, respectively. Eq. (1), or the so called the Donth formula [23], estimates the number of monomeric units of an order of 100 at temperatures close to T_g [24,29]. This value is typical for the cooperativity in fragile glass-forming substances [8,11,24–26,31]. On the other hand, the number of monomer units estimated based on the AG model is about $z(T_g) \sim 4\text{--}10$ [16,17,24], which is much lower than $N_x(T_g)$ over one order of magnitude.

The study that aims to bridge the gap between the conceptive and quantitative descriptions of cooperativity would be significant. In the present study, to achieve this aim and understand the non-Arrhenius structural relaxation in a systematic way, we employ a measure of the cooperativity defined in terms of the bond strength–coordination number fluctuation (BSCNF) model [32–37] proposed by the present authors. According to the BSCNF model, the cooperativity degree is evaluated by the number of structural units N_B defined as

$$N_B = E_a / (E_0 Z_0), \quad (2)$$

where E_a is the activation energy for structural relaxation. E_0 and Z_0 are the parameters of the BSCNF model: E_0 is the mean value of the bond energy and Z_0 is the coordination number of the structural units that form the melt. Initially, the cooperativity N_B was defined for viscosity [33,35], whereas Eq. (2) is written for the relaxation time. This replacement is valid as long as the Maxwell relation $\eta = G_\infty \tau$ is obeyed, where G_∞ is the infinite frequency shear modulus. In Eq. (2), $E_0 Z_0$ means physically the average binding energy per structural unit. Hence, the quantity N_B as defined in Eq. (2) gives intuitively the number of structural units that move cooperatively when one structural unit decouples the local constraints formed by its neighboring structural units.

In the following we focus on the growth of molecular motion cooperativity in polymer melts and molecular liquids. Usually, both those materials are classified as fragile systems, typically showing a VFT-like behavior in the low temperature region. The objective of the present study is to show that a specific expression of the cooperativity is obtained from the definition of Eq. (2), and that it can be used as an indicator to understand the relaxation property of undercooled liquids in a wide temperature range. Specifically in Section 2, after giving a brief background of the BSCNF model, the temperature-dependent cooperativity $N_B^*(T)$ is derived. Following that, we discuss the growth of the cooperativity $N_B^*(T)$ in the polymer melts, 1,4-poly(isoprene) (PI), 1,4-poly(butadiene) (PB) and poly(dimethylsiloxane) (PDMS) [38]. As will be indicated later, the expression $N_B^*(T)$ is derived under the condition,

$$\frac{|\Delta E|}{E_0} = \frac{|\Delta Z|}{Z_0}. \quad (3)$$

Here, ΔE and ΔZ are also the parameters of the BSCNF model, and each gives the fluctuation of the bond energy and the coordination number of structural units, respectively. Recently, it was shown [37] that under the condition given by Eq. (3), the BSCNF model reduces analytically to the VFT law. This finding gives a theoretical rationale to the empirical VFT expression. It also gives a reason of why the definition of Eq. (2) can be a measure of cooperativity, due to the fact that the relation between the non-Arrhenius structural relaxation and the cooperativity has not been fully understood. In the present work, the above notion is extended to derive the expression of the cooperativity $N_B^*(T)$. Furthermore, by comparing the expression $N_B^*(T)$ with the empirical function that reproduces N_x [24,39], we discuss the origin of cooperativity onset, which appears at temperature higher than T_g . Finally, in the same section, remarks on the difference between N_B^* and N_x at high temperature is given. The relation between the BSCNF model and the AG model is also briefly mentioned.

In Section 3, our attention turns to the high-temperature relaxation property of fragile liquids. At temperature much higher than T_g , the degree of the cooperativity is believed to be smaller. Here, a question related to the present subject arises: 'At what temperature does the molecular cooperativity actually begin?' As a matter of fact, some peculiarities have been detected in the liquid state at high temperatures, such as the violation of the Stokes–Einstein relation [40,41], the splitting into the α and β process in the crossover region [40,42]. Often, these are observed at a temperature $T_B (\approx 1.2T_g - 1.3T_g)$ which is thought to indicate the onset of cooperativity [8]. The theoretical description of the crossover temperatures is one of the major concerns. In considering a possible link of these phenomena with the cooperativity, study on the relation between the cooperativity onset and the high-temperature relaxation properties of a liquid is of particular interests. In this section, we attempt to describe the onset temperature of the cooperativity N_B , by applying the BSCNF model to the reorientational

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