Probabilistic interpretation of liquid fragility

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A B S T R A C T

After a brief critical review of available interpretations of liquid fragility, our probabilistic approach is introduced and validated by comparing reported fragility data with the material parameters extracted from reported structural relaxation times, namely, the thermodynamic cooperativity N_c^T and the enthalpy E_m and entropy S_m of activated molecular migration available for 26 glassformers. Quantitatively, the relevance of N_c^T together with S_m and E_m as a measure of liquid fragility is verified in principle, and hence our probabilistic interpretation of liquid fragility is supported.

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1. Introduction

At temperatures above the melting point, T_m, the structural relaxation time, τ, or viscosity of liquids generally shows Arrhenius temperature dependence [1–8]. With temperature decreasing to below T_m, the structural relaxation time of most glass-forming liquids deviates quite significantly from the normal Arrhenius behavior and shows super-Arrhenius temperature dependence [9,10].

Phenomenologically, the departure from the Arrhenius law can be conveniently measured by using the fragility parameter [11–13], m, defined as the slope of $\log(\tau)$ against T_g/T at $T_g/T = 1$ in the Oldekop–Laughlin–Uhlmann–Angell (OLUA) plot [14–18]:

$$m = \frac{d\log(\tau)}{d\left(T_g/T\right)}\bigg|_{T=T_g}, \tag{1}$$

where T is temperature in K and T_g the glass transition temperature. The larger m is, or the more fragile a liquid is, the more significant is the departure. For most glass-forming liquids, a single fragility parameter at T_g is sufficient to describe equilibrium dynamics across the full range of temperatures [19]. However, it is noted that some glass-forming liquids, e.g., water and metallic liquids, show anomalous dynamics, namely, fragile-to-strong transition, and in this case two liquid fragility indices are needed to describe the dynamics [19]. In the present work, only the fragility parameter at T_g is considered. For systems showing a fragile-to-strong transition, interested readers may refer to Ref. [19] and references therein.

No detectable structural changes in liquids can be found to accompany the deviation from the normal Arrhenius law [10] and, for decades, the causes of the super-Arrhenius behavior and hence the physics behind liquid fragility have been under intensive debates [9,10,18]. Regarding the structure of liquids, it was generally believed that "the structure of dense liquids is predominantly determined by the steep repulsive forces between molecules and longer-ranged attractive interactions merely establish a cohesive background that affects the thermodynamics, but neither the structure nor the dynamics". [20,21] This view may seem to be updated according to Berthier and Tarjus [20,21] who showed through molecular dynamics simulation that the attractive interactions, although did not significantly affect the static pair correlations, did strongly influence the dynamic behaviors e.g. structural relaxation of viscous liquids. Nevertheless, a clear understanding of liquid fragility in terms of molecular interactions is still to be worked out.

In this paper, in Section 2, available interpretations of liquid fragility, namely, thermodynamic approaches, cooperatively rearranging regions, many-body relaxations and elastic models will be briefly and critically reviewed, to show that a clear and, particularly, microscopic understanding of fragility is still missing. In addition, the probabilistic nature of the Adam–Gibbs approach will be discussed in Section 2. After this, in Section 3, our probabilistic approach developed over the years will be introduced and be employed to search for possible molecular origins of liquid fragility. In Section 4, the present results will be discussed in comparison with historical efforts.

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2. A brief critical review of available interpretations of liquid fragility

2.1. Thermodynamic approaches

Intuitively the free volume model [22] and the entropy model [23] are laudable; however, the resulting Vogel–Fulcher–Tammann (VFT) type equation was found to always fail in a wide temperature range [15,24,25]. Despite this, empirical correlations were found between liquid fragility and the thermodynamic parameters of liquids and glasses [26,27], with the work of Adam and Gibbs (AG) [23] as the possible underlying theoretical basis. (For a comprehensive review on the relation between thermodynamic properties and fragility, please refer to Ref. [18], Section 2.2.3.5).

One of the problems for the entropy version of the AG model is that in the model there is lack of an accurate expression of the temperature dependence of the configuration entropy S_c. Recently, this problem was solved in the Mauro–Yue–Ellison–Gupta–Allan (MYEGA) model [28] by introducing an exponential temperature dependence of S_c. In addition, the VFT type divergence at a nonzero temperature was successfully avoided. In Ref. [28], the MYEGA model was shown to provide better fits to measured viscosity data compared to previous three-parameter models. However, in Ref. [29], when the same model was employed to calculate liquid fragility by using S_c, an otherwise derived VFT type expression was preferred. It seems that, for a clear understanding of the origin of liquid fragility by using the MYEGA model, the microscopic details of structural relaxation considered, i.e. bond constraints breaking, were to some extent complex [29] on the one hand, and on the other hand, other known important factors e.g. cooperativity may need to be added. Nonetheless, the proposed exponential temperature dependence of S_c was very interesting which will be further discussed in Section 4.3.

2.2. Cooperative rearranging regions

Of course, as Ngai pointed out in Section 2.2.3.5 of Ref. [18], influences of thermodynamic factors on the structural relaxation of liquids, although significant, may not be exclusive. Actually, in essence, the Adam–Gibbs approach [23] is not on thermodynamics but on cooperative motions of structural relaxation units. The idea of cooperatively rearranging region (CRR) is quite intriguing and stimulated a branch of researches alone this line (see Ref. [30] and references therein, for a review please refer to Section 2.2.2 of Ref. [18]).

Studies on the size of the CRR or the number, N_c, of structural relaxation units in the CRR produced roughly two groups of data. On the one hand, by using measured heat capacities, Yamamuro et al. [30,31] reported $N_c(T_g)$ values of less than 10, which was in agreement with the calculations of Johari [32]. On the other hand, Donth et al. [33,34] estimated that $N_c(T_g)$ would be around several tens to several hundreds, coinciding with the data derived from multi-point dynamical susceptibilities [35,36].

In Fig. 33-1b of Ref. [18], when Ngai was comparing the $N_c(T_g)$ data reported in Ref. [36] with measured fragilities, no obvious correlation was found, even when restricted to glassformers in the same class. The lack of correlation with liquid fragility (and especially with non-exponentiality as was shown in Fig. 33-1a of Ref. [18]) seriously undermines the relevance of the N_c data reported in Refs. [35 and 36] as a measure of the length scale of cooperative dynamics [18].

It is noticed that, until now, only the *size* of the CRR was studied, with little agreement, so that the *effect* of cooperativity on structural relaxation and hence the correlation between N_c and m could not be quantified.

2.3. Many-body relaxations

To measure the effect of cooperativity on structural relaxation, Ngai et al. proposed to use the stretching parameter β appearing in the Kohlrausch stretched exponential correlation function for structural relaxation (see Ref. [37] and Section 2.2.1 of Ref. [18]). They suggested that the deviation from exponential relaxation indicates many-body relaxation, and β or the derived coupling parameter [38–43], $n = 1 - \beta$, should give a measure of the many-body relaxation. Many general properties of the structural relaxation were found to be governed by the parameter n [18,37].

However, "many-body relaxation is currently an unsolved problem" [37] and "none of the theories ever proposed … can calculate the stretching parameter for any real liquid" [42]. At present, except for the empirical stretching parameter, β, little is known for the microscopic details of many-body relaxation, hence the prominent role of many-body relaxation, in the center of various convincing connections revealed, is not understood. Consequently, the effect of correlated motions on structural relaxation and the connection between cooperativity and fragility remain quite elusive [12,44–47].

2.4. Elastic models

Dyre et al. [10,48] proposed a shoving model, in which "a flow event takes place if a region volume briefly expands sufficiently due to a thermal fluctuation" and "the activation energy is dominated by the work done to shove aside the surroundings", which, "in the simplest case (that of spherical symmetry, the surroundings are subjected to a pure shear deformation) is proportional to the instantaneous shear modulus G_∞ [49]." Accordingly, "the logarithm of the viscosity depends linearly on $G_\infty(T)/T$." [48]

"Unfortunately, measuring the high-frequency plateau shear modulus of the equilibrium metastable supercooled liquid is difficult and few data are available even today." [49]. As such, experimental verifications of the shoving model could only be made in limited temperature ranges near T_g.[50–55] In a wide temperature range, computer simulation results showed that the shoving model did not hold exactly. [56,57] And experimental testing results in oxide glassformers suggested that "the dynamics of the glass transition were governed by additional factors beyond the evolution of the shear modulus" [58,59].

Anyway, in the shoving model [48], the fragility parameter should be determined by the temperature dependence of G_∞, which however is quite unclear so far [60–68], both theoretically and experimentally. Then, before the temperature dependence of G_∞ is understood microscopically, it seems difficult to interpret liquid fragility quantitatively in terms of the shoving model.

2.5. Diverging vs. non-diverging approaches

On the basis of Ref. [25], it has been probed that there are strong empirical arguments that the VFT description lacks a direct experimental basis and thus theories not predicting a dynamic divergence should be focused on (at least, on the basis of this reference) e.g. the Avramov–Milchev (AM) model [69], the MYEGA model [28], the frustration-limited domain (FLD) theory [70,71] and the parabolic law model [72].

However, on the other hand, it has also been argued that critical-like diverging descriptions, e.g. the dynamical scaling model (DSM) [73,74], can describe better the relaxation time as a function of temperature for glass-forming systems. Within this framework, critical equations establish that $\tau \sim (T - T_c)^{-\phi}$, where ϕ is the critical exponent and T_c the critical temperature usually below T_g. Such critical dependence was already known for spin-glass-like systems and was later applied to glasses through the dynamical scaling model [75]. In Ref. [76], a comparison of some of the non-diverging models and the diverging DSM model was given, applied for different kinds of systems.