

# Transformation of Activated Hopping into Free Diffusion Dynamics in the Glass-Forming Liquids

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**Abstract.** A method for measuring transformation of the activated hopping over potential barriers dynamics into free diffusion one in the glass-forming liquid has been found. In the glass-forming liquids the rearrangement of a local molecular structure is a cooperative process and the number of rearranging molecular species during the time of relaxation is defined as the size of the cooperatively rearranging region. At the glass-transition temperature every molecular species in the cooperatively rearranging region overcomes its own potential barrier and the number of the configurations per a basic molecular species is approximately equal to one, so the dynamics is assumed to be entirely activated. The increase of the number of configurations per a basic molecular species with increasing the temperature is applied as a measure for the transformation of the activated dynamics. Strong correlation of the level of transformation and the fragility of the liquid is observed.

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## 1 Introduction

The molecular dynamics in liquids has still remained as one of the challenges in the physics of the condensed matter [1, 2]. Recent progress in this field has been stimulated by the mode-coupling theory (MCT) [3]. The “idealized” MCT predicts a crossover in the dynamics at temperature  $T_c$  above the convention glass-transition temperature  $T_g$ . It has been demonstrated that at high temperature  $T > T_c$ , the theory describes the dynamics in several liquids nearly on quantitative level; however, in most cases this is observed only on a qualitative level [3–6]. The “idealized” MCT has been obtained for liquids composed of spherical particles in the state of free diffusion. However, MCT fails to describe the dynamics at temperatures below  $T_c$  [1, 4, 6, 7]. A common interpretation of  $T_c$  is that it signals a crossover to strongly activated hopping over potential barrier dynamics.

In the deeply supercooled range below  $T_c$  the most widely-used theory is the Adam-Gibbs one [8]. As a matter of fact, the macroscopic equation,  $\tau(T) = \tau_0 \exp [C/TS_c(T)]$ , which has the advantage to relate the relaxation time  $\tau(T)$  with the thermodynamic configuration entropy  $S_c(T)$  through a constant  $C$  and the vibration time  $\tau_0$  is a subject of interest in the experimental [9–12] as well as theoretical [13–16] works. In recent years Adam-Gibbs theory has been extended at the molecular level [17–21]. A molecular interpretation of the apparent activation energy and volume [19], the fragility classification system [18, 20] and the constant  $C$  in the macroscopic equation has been given [21]. In the Adam-Gibbs theory, as well as in the extended theory, the rearrangement of the molecular species is regarded as activated hopping over the potential barrier dynamics.

To summarize, the above  $T_c$  in the range of the validity of MCT free diffusion is needed, while below this temperature activated hopping dynamics is observed. Hence, the questions arise: in which way the activated dynamics is transformed into the free diffusion one, why MCT is nearly quantitatively applicable to several liquids, known as fragile and only qualitatively to other?

Here, we have suggested for the first time a method for measuring the transformation of the activated hopping dynamics into a free diffusion one. The dependence of this transformation on fragility of the liquids is investigated.

## 2 Theoretical Remarks

### 2.1 Relation between the Adam-Gibbs Theory and the Extended Theory

Adam and Gibbs regard molecular rearrangement in glass-forming liquids as a cooperative process. The number of the molecular species which is rearranged cooperatively has been defined as the size of the cooperatively rearranging region (CRR). The molecular equation for the temperature dependence of the relaxation time  $\tau(T)$  is

$$\tau(T) = \tau_0 \exp (zu/kT), \quad (1)$$

where  $z$  is the size of the CRR,  $T$  is the temperature,  $k$  is the Boltzmann constant,  $\tau_0$  is the vibration time and  $u$  is the potential barrier per a molecular species in the cooperative rearrangement. Some differences in the Adam-Gibbs theory and the extended theory do exist. In the Adam-Gibbs theory  $u = \Delta\mu$  is the difference between the chemical potential of the liquid and the crystal (or glass), but it is “essentially the height of the potential energy barrier per monomer unit” [8]. In the extended theory  $u$  is the average potential barrier per a basic molecular species in the CRR. In the Adam-Gibbs theory  $z = z^*$  is a critically small region with two configurations  $w = 2$ , namely, one before rearrangement and the other during the rearrangement; or, the rearrangement is simultaneous and CRR is a

rigid unit. Hence, in the Adam-Gibbs theory  $\tau$  has the meaning of a waiting time for a heat fluctuation to excite  $z^*$  molecular units simultaneously for rearrangement. In the extended theory each molecular species overcomes its molecular barrier statistically independently and  $w \cong z(T_g)$  or the relaxation time has the meaning of time of rearrangement, or time of the reaction, and  $z$  is a unit with internal rearrangement (a liquid unit). In the extended theory comparing Eq. (1) with the empirical Vogel-Tammann-Fulcher (VTF) equation

$$\tau(T) = A \exp[B/(T - T_\infty)], \quad (2)$$

we obtain

$$z = T/(T - T_\infty), \quad (3)$$

$$u = kB \quad (4)$$

and

$$\tau_0 = A. \quad (5)$$

Two thermodynamic equations equivalent to Eq. (3) have been obtained [18, 20] and from these equations the basic molecular species in the CRR has been identified as fragments of molecules known in thermodynamics as “beads” [22]. It will be pointed out that the beads practically coincide with the “functional chemical groups” on the basis of which the physical and chemical properties of the liquids [23] and the polymers [24] are estimated and predicted outside the available experimental results, this being very important for engineering practice. The number of configurations in the CRR is measured from [18, 21]

$$w = \exp [S_c(T)z(T)/nR], \quad (6)$$

where the configuration entropy  $S_c$  is per a mol of molecules;  $n$  is the number of the beads in the molecule or in the monomeric segment and  $R$  is the gas constant. As Adam and Gibbs assume  $w_z = 2$ , *i.e.* the product  $S_c(T)z(T)$  should be temperature independent, but it is also temperature independent at every other value of  $w$ . For example, a macroscopic estimation of this value with the hyperbolic approximation for configuration heat capacity  $\Delta c_p(T) = \Delta c_p(T_g)T_g/T$  is  $S_c(T)z(T) = \Delta c_p(T_g)T_g/T_\infty$  [21]. The measured number of the configurations in the CRRs for the alcohols, the isomeric n-paraffin hydrocarbons, the polymers [18], the inorganic glasses [20] and the molecular liquids [21] is  $w \cong z(T_g)$ .

## 2.2 Method for Measuring the Transformation of the Activated Hopping Dynamics

To measure the transformation of activated dynamics we shall use the number of the configurations per basic molecular species in the CRR [18]

$$v = w/z(T). \quad (7)$$

As  $z$  measures the number of the activated hopping over potential barrier processes, see Eq. (1), and  $z(T_g) \cong w$ , it follows that the processes at  $T_g$  are activated and  $v(T_g) \cong 1$  as has been observed. As  $w$  is a constant and  $z$  decreases, with the increase of temperature the  $v(T)$  will increase and the new configurations introduced will be assumed as non-activated.

It will be noted that  $w$  is measured with some degree of uncertainty. Adam and Gibbs assumed that the vibration entropy of the liquid is equal to the entropy of the crystal. In current literature the difference between entropy of the liquid and the crystals is called excess entropy. The vibration entropy of the liquids is not well known, and its estimation, and correspondingly, the net configuration entropy, is a problem open for discussion [12–16, 25, 26]. On the other hand, the number of the beads in some molecules is not well known [19], and the reference there in. To avoid these uncertainties we shall use the ratio [27]

$$g(T) = v(T)/v(T_g) = z(T_g)/z(T) \quad (8)$$

as in this way  $w$  is eliminated and, naturally, so are the uncertainties related with it. We shall call the ratio, given by Eq. (8), the coefficient of transformation of the activated dynamics. Precisely speaking  $g(T)$  measures the level of the transformed dynamics above the reference point  $T_g$ .

The most widely-used classification of the glass-forming liquids is the Angel's calcification by fragility [1, 12, 25]. The fragility index is defined by the equation  $m = [d \log \tau(T)/d(T_g/T)]_{T_g}$  and from the point of view of cooperative molecular dynamics,  $m$  is given by [18]

$$m = C_1 z(T_g), \quad (9)$$

where  $C_1$  is the constant in the Williams-Landel-Ferry equation  $\log [\tau(T)/\tau(T_g)] = -[C_1(T - T_g)/(C_2 - T - T_g)]$  [28] and  $C_1$  is a “universal” constant  $C \cong 16$  [28, 29, 18] coinciding with the minimum fragility [30]. From Eqs. (8), (9) and “universality” of  $C_1$  we obtain

$$g(T) = \frac{m}{C_1 z(T)} \approx \frac{m}{16z(T)}, \quad (10)$$

or the transformation coefficient is proportional to the fragility of the liquids.

### 3 Discussion of the Experimental Results

The VTF parameters  $T_g$  and  $T_c$  of the investigated substances are given in Table 1.

In Figure 1 the coefficient of transformation  $g(T)$  is plotted as a function of the reduced to glass transition temperature. Abbreviations of the substances are given in Table 1. In the blackest the size of the cooperatively rearranging regions at the glass-transitions temperatures are given. From Figure 1 it can be seen that

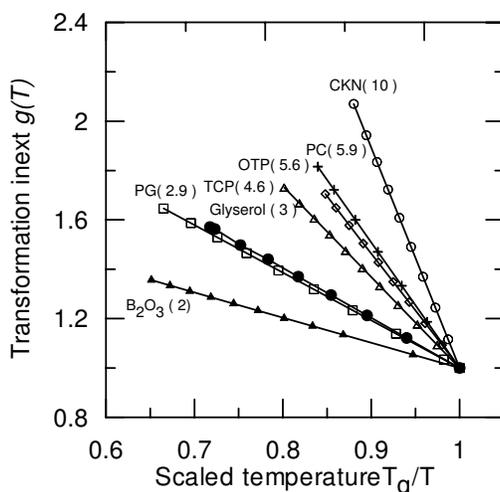


Figure 1. The coefficient of transformation  $g(T)$  plotted against the reduced to glass-transition temperature, for the abbreviations see Table 1. In the blacked the sizes of the cooperatively rearranging regions at the glass transition temperatures are given.

transformation of activated hopping over potential barrier dynamics is a continuous process in the deeply supercooled region. The lines in Figure 2 are straight lines, described by the equation  $g(T) = z(T_g) - z(T_g) T_\infty/T$ . The slope of these lines is  $[dg(T)/d(T_g/T)] = -z(T_g) T_\infty/T_g$  and it may be regarded as rate of transformation of activated hopping dynamics. As it shown in Figure 1 at every reduced temperature  $T/T_g$  the level of transformation increases with increasing the  $z(T_g)$  or the fragility of the liquids. The rate of transformation also increases with the fragility of the liquids.

Table 1. Properties of the glass-forming liquids.

Substances*	$T_c$ (K)	$T_g^\#$ (K)	$T_\infty$ (K)	$-\log A$ (sec)	$B$ (K)
CKN	379 <sup>a</sup>	333.6 <sup>c</sup>	300	13.5	1199
PC	187 <sup>b</sup>	157 <sup>e</sup>	131.2	14.2	958
OTP	290 <sup>b</sup>	246 <sup>b</sup>	202.4	13.73	1575
TCP	255.5 <sup>c</sup>	204.7 <sup>e</sup>	161	14.4	1649
Glycerol	262 <sup>c</sup>	188 <sup>e</sup>	126	15.1	2452
PG	251 <sup>b</sup>	167 <sup>e</sup>	110	14.4	2141
B <sub>2</sub> O <sub>3</sub>	800 <sup>d</sup>	521	263	13.5	9205

\* CKN – Ca<sub>0.4</sub>K<sub>0.6</sub>(NO<sub>3</sub>)<sub>1.4</sub>, PC – Propylene Carbonate, OTP – o-Terphenyl, TCP – m-Tricresyl phosphate, PG – Propylene Glycerol

# – The glass transition temperature is defined as temperature at which  $\tau(T_g) = 100$  sec.

a, b, c, d and e are correspondingly references: [5], [12], [31], [32] and [33].

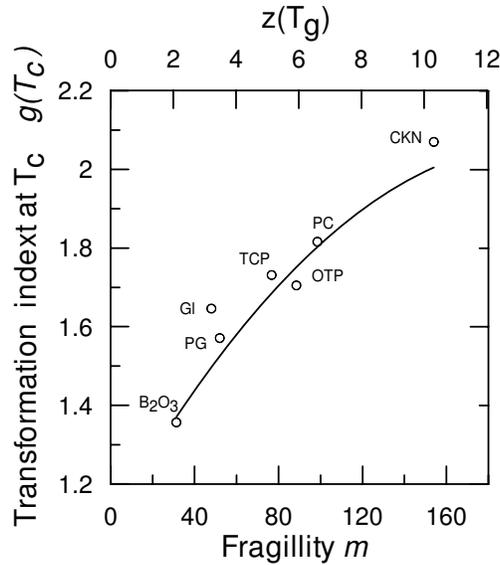


Figure 2. The level of transformation measured by the coefficient of transformation at the dynamical phase transition temperature  $g(T_c)$  as a function of fragility  $m$  and the size of the cooperatively rearranging region at the glass-transition temperature  $z(T_g)$ , the line is a approximation by the Eq. (10) in the text.

In Figure 2 the coefficient of transformation at  $T_c$  is plotted as a function of the fragility  $m$  and the size of the CRR at  $T_g$ . It can be seen that the level of the transformation at  $T_c$  strongly increases with the increase of fragility, or  $z(T_g)$ . The results obtained, give an explanation to the experimental finding that the levels of applicability of MCT increase with the increase of fragility [3, 6]. Indeed, CKN is the most fragile liquid investigated with the ratio of the free diffusion to activated dynamic at  $T_c$  1.1:1 and this substance is the nearest to the preconditions of the MCT. So it is not surprising that the main prediction of the theory has been supported by the experiments for this liquid at a higher level compared to other glass-forming liquids [6]. From Figure 2 can be seen that  $z(T_g)$  appears as a molecular characteristic for the applicability of MCT.

The free diffusion dynamics obtained, is not an activation process or  $u = 0$  and, it is expected to behave as a modified vibration process, and to be observed at the low-frequency side of the vibration relaxation time. For CKN  $\tau_0 = 3.16 \times 10^{-14}$  sec (see Table 1 where  $\log A = \log \tau_0$ ) and the corresponding frequency is 5.04 THz. This frequency is on the high-frequency shoulder of the Raman spectrum or on the boson peak, (see Figure 2 in the reference [5]), or collective vibration of the boson pick may be expected to participate in the forming of the vibration time in the cooperative dynamic [18]. At temperatures above  $T_g$

the boson peak transforms into an over-dumped state which seems to be the emergence of the free diffusion dynamics.

#### 4 Conclusions

The glass transition temperature is identified as onset of the transformation of activated hopping (solid-like) dynamics to the free diffusion (liquid-like) one during the warming of liquids. Continues increasing of the relative part of the free diffusion dynamics with the increasing temperature is measured by increasing the number of configuration per a basic molecular space into the cooperative rearranging region, or by an introduced transformation coefficient. A relation between the fragility indexes and the coefficient of transformation has been obtained. The level of transformation, or the free diffusion dynamics, at a given reduced temperature  $T_g/T$  increases with the increasing fragility of the liquid.

At the dynamic phase transition temperature, the level of transformation measured by the coefficient of transformation in the substances investigated varies between 1.36 and 2.1 from the strong to the fragile edges, or in the most fragile liquid at this temperature free diffusion dynamics dominated.

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