On Measuring the Characteristic Length of the Cooperative Molecular Dynamics in the Glass-Forming Liquids

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Abstract. An analysis of the methods for measuring the characteristic length of the cooperative molecular dynamics in glass-forming liquids is submitted. The equations and methods for measuring the size of the cooperatively rearranging regions in post Adam-Gibbs theories are compared, and it is proved that they give one and the same number, but with different interpretation for the relaxed molecular units. The interpretation that the rearranging units defined by Wunderlich are smallest structural units, named beads, is supported by the predicted “universal” value for the cooperatively rearranging range at the glass-transition temperature, as well as from a precise modeling for the relaxations by the generalized entropy theory. It has been found that the characteristic length estimated by random first order transition theory, as well as by the “four-point” dynamic susceptibility method, measured as the number of the bead’s diameters coincide with the length of the cooperatively rearranging region in Adam-Gibbs theory extended at the molecular level.

1. Introduction

The structure relaxation time of supercooled liquids exhibits fast non-Arrhenius temperature dependence which is yet assumed as an unexplained feature of glass-formation [1-6]. Despite its unsolved origin, this temperature dependence is expected to be related to a cooperative effect. A theory of such cooperatively rearranging has been put forward by Adam and Gibbs (AG) [7]. AG defined a size of cooperatively rearranging region (CRR) as the number of molecules, rearranging into another configuration by surmounting simultaneously the individual potential barriers independent of its environment. AG assumed that a critical lower limited size of such regions, with two configurations, and entropy $s^*_c = k \ln 2$, where $k$ is Boltzmann’s constant governs the relaxation properties of the liquids. By this assumption AG obtained a celebrated relation between the dynamics, presented by relaxation time $\tau(T)$ and thermodynamics, presented by configuration entropy $\Delta S = S_l - S_c$ where $S_l$ is entropy of the liquid and the $S_c$ is entropy of crystal or glass

$$\tau(T) = A_G e^{\frac{C}{\Delta S}}$$

where $T$ is the temperature and $C$ and $A_G$ are constants. This macroscopical equation has been supported by many experimental results, making AG theory one of the widely accepted and mentioned in all review articles [1-6,8-11,13-15].

AG have not written explicitly an equation for the size of the cooperatively rearranging region (CRR) and have not estimated the number of the molecules in such a range. Therefore, the molecular level of the theory has not been clarified and, due to this fact, several post AG theories [2-4,10,13-15] are devoted to developing the molecular level of the theory.
Measuring the size of the cooperatively rearranging region

2.1 Measuring the size of the cooperatively rearranging region by molecular entropy theory

In an extension by the author [13,14], the molecular level AG theory, which will be cited with the abbreviation as Molecular Entropy (ME) theory for the most probable size of the CRR \( j_s \), was obtained

\[
j_s(T) = \frac{T}{T-T_0}
\]

where \( T_0 \) is the temperature from the empirical Vogel-Fulcher Tamman (VFT) formula,

\[
\tau(T) = A \exp \left( \frac{B}{T-T_0} \right)
\]

where \( A \) and \( B \) and \( T_0 \) are empirical constant.

In ME theory two additional expressions equivalents to equation (2) have been obtained \( j_s(T) = \Delta C_p(T)/\Delta S(T) \) in the case of a linear temperature dependence of the configuration heat capacity \( \Delta C_p(T) \) [14] and in the case of a hyperbolic dependence \( j_s(T) = T_g \Delta C_p(T_g)/T_g \Delta S(T) \) where \( T_g \) is gla transition temperature and \( T_K \) is Kausmman temperature, which in AG theory is accepted equal to VFT temperature \( T_0 \) [19].

In analyses of the heat capacity jump at glass-transition temperature \( \Delta C_p(T_g) \) Wunderlich [16] observed that if molecules were regarded as constructed by structure units named beads, then the value of \( \Delta C_p(T_g) = 11.3 \text{ J/mol bead K} \) appears as “universal”. Wunderlich defined the smallest structural units as -CH\(_2\)-, -CH\(_3\), -OH, or -O- as beads. Accepting the beads conception Bestul and, Chang [17] defined the “universal” rule for the configuration entropy \( \Delta S(T_g) = 2.9 \text{ J/mol bead K} \). Replacing both values in \( j_s(T_g) \) in the case of the linear temperature dependence of \( \Delta C_p(T) \) one obtains \( j_s(T_g) = 3.9 \text{ beads} \) and in the hyperbolic dependence, accepting \( T_g/T_K = 1.24 \), as an average value from investigated liquids [7], for \( j_s(T_g) \) one obtains 4.8 beads. Hence, the “universal” value for the CRR at \( T_g \) is obtained around 4-5 beads. The measured values [10,13,14] are around this “universal” value and supported the hypotheses that the beads are rearranging units [14].

2.2 Measuring the size of the cooperatively rearranging region by the maximal value of the configuration entropy.

Another method for measuring the size of the CRR has been suggested by Takahara et al [8], using AG definition for the entropy \( s^c_z \) of the critical low limited size of the CRR \( z^* \)

\[
s^c_z = \frac{\Delta S}{N_A} z^*
\]

where \( N_A \) is Avogadro number. From equation (4) it follows that \( N_A s^c_z \) is a constant since AG accepted \( s^c_z = k ln 2 \). Hence if this constant can be estimated by using the measured \( \Delta S(T) \) the \( z^*(T) = N_A s^c_z / \Delta S(T) \). Takahara et al observed that \( \Delta S(T) \) as a function of \( T \) comes to a saturated, maximal value.
at temperatures far above the fusion temperature $T_f$ and accepted the extrapolated value, when $T \to \infty$ to be $N_\alpha s^*_c$. For 3-brompentane this constant was estimated between 80-100 J/molK, and the upper value is listed in Table 1. In a later study [9] it has been assumed that $\Delta S(T) = N_\alpha s^*_c - K/T^2$, where $K$ is a constant and by fitting the last 50 $K$ of $\Delta S(T)$ the $N_\alpha s^*_c$ was estimated. Within the uncertainty cited by them the upper values of $N_\alpha s^*_c$ for o-terphenyl and 1-butene are also given in Table 1. In ME theory equation (4) is replaced by a rule of the individual constant number of configurations (RICNC) [18]

$$N_\alpha s_{cj} = j_s(T)\Delta S(T) = nRlnw_{js}$$

where $n$ is the number of the beads in the molecule $R$ is the gas constant and $w_{js}$ is an individual number of configurations in the most probable CRR of ever liquid. The values of $j_s$, calculated from equation (2) at the glass-transition temperature $T_g$ and at the fusion temperature $T_f$ multiplied by corresponding configuration entropies [11] are listed also in Table 1.

It will be mentioned that Richert and Angell [11], comparing VTF equation with the macroscopic AG equation (1) found that the $\Delta S(T)$ will obey

$$\Delta S = S_\infty \left(1 - \frac{T_K}{T}\right).$$

As $T_K = T_0$ by using equations (2) and (6) one obtains

$$j_s(T)\Delta S(T) = S_\infty.$$

The values of the $S_\infty$ [11] are also given in the table. Hence independent of the mining introduced in constant $= j_s(T)\Delta S(T)$ it is obvious that if this constant is estimated to be one and the same for given liquid the measured values of $j_s(T)$ will coincide.

| Liquids          | $S_\infty^a$ (J/molK) | $j_s(T_g)\Delta S(T_g)$ (J/molK) | $j_s(T_f)\Delta S(T_f)$ (J/molK) | $N_\alpha s^*_c$ (J/molK) |
|------------------|------------------------|---------------------------------|---------------------------------|---------------------------|
| o-terphenyl      | 137                    | 137.2                           | 137.3                           | 131                       |
| Salol            | 138.4                  | 138.4                           | 138.4                           | - - -                     |
| 2MTHF$^c$        | 97.5                   | 97.4                            | 97.6                            | - - -                     |
| n-propanol       | 72.2                   | 70.0                            | 70.4                            | - - -                     |
| 3-brompentane    | 99.0                   | 100.8                           | 100.8                           | 100                       |
| 1-butene         | - - -                  | 68.1                            | 96.5                            | 70                        |

$a$ $S_\infty$ from Ref. [11],
$b$ $N_\alpha s^*_c$ from References [8,9]
$^c$ 2-Methyltetrahydrophuran

As it can be seen from the table the values of the constants are in good agreement. Hence, measured $j_s(T)$ by equation (2) and the ones estimated by Takahara’s method are practically equivalent, if the constant $K$ is correctly estimated. However, the interpretation is different as Takahara et al following AG equations interpreted $j_s(T)$ as the number of the molecules, and in Ref. [9] the $s^*_c$ has been also interpreted per molecule. In AG $s^*_c$ is the configurational entropy of the CRR with smallest number of
configurations equal to two, while in the [8,9] it should be the configurational entropy of the CRR with the largest number of configurations. Both statements can coincide only in the case when the minimal and the maximal values are one and the same or in the case of validity of the $w_{js} = constant$, as it is assumed in ME theory [13].

In Generalized Entropy Theory (GET) a similar method for the estimation of the size of the CRR as the one of Takahara et al is used [4]. In GET a configuration entropy density is defined as $s_c = \Delta S/N_l$, where $\Delta S$ is the configuration entropy of the system with $N_l$ number of lattice sites. The size of the CRR is measured by $z^* = s^*_c/s_c(T)$, where $s^*_c$ is the high-temperature limit of $s_c(T)$. In modeling the properties of polymers by GET [4] the estimated size of the CRR at $T_g$ is 4.46 for a polymer with flexible backbone and flexible side groups and 5.53 for the ones with flexible backbone and rigid side branches. These values are in the range of the ones measured by equation (2) [14]. The size of the CRR in this theory [4] should be measured in the ‘‘united atom groups’’, usually known as functional chemical groups, which in Ref. [4] coincide with the empirical beads [16,17]. Hence, the model of liquids and the values and the interpretation of $z^*$ in GET are practically the same as in ME theory[13,14].

2.3. Confirmation of the formula for the measuring the size of the cooperatively rearranging region by the measuring the activation energies.

The molecular equation for the most probable relaxation time in ME theory is

$$\tau(T) = \tau_0 exp\left(\frac{\Delta\mu}{kT}\right)$$

(8)

where $\tau_0$ is the vibration time, $k$ is Boltzmann constant and $u$ is the average value from the individual potential barriers of the rearranging beads during the relaxation time. The equation (10) is an extension of the original AG molecular equation since the critical small size of the CRR, $z^*$ is replaced by $j_s(T)$ and the meaning is changed. Two configurations, accepted by AG, agree with statement that the relaxation units overcome their individual potential barriers essentially simultaneously. In this way, the relaxation time has the meaning of a waiting time a fluctuation of enthalpy to rearrange in bloc the molecules included in the CRR. In ME theory meaning of $\tau(T)$ is the living time of the CRR [14]. In ME theory comparing equation (8) with VTF equation (3) for the $j_s(T)$, the equation (2) has been obtained and

$$u = kB.$$  

(9)

As the equations for $j_s(T)$ and $u$ are obtained simultaneously, if the estimated value of $u$ coincides with the experimentally measured one then an additional support for the correctness of equation (2) will be obtained. The estimated values for $u$ are in the range of the measured values for the rotations around R1-C-CR2 bonds, where R1 and R2 are different chemical groups [20]. An additional evidence for the correctness of the measured values of the $u$ by ME theory are estimated by GET, where the proper values for the activation energy in polymers were obtained to be $\Delta\mu/k_B = 2000 - 2600 K (16.6-21.6) \text{kJ/mol}$ [4]. The values in this range have been measured for polymers by equation (9) [14].

The correctness of the equation (2) indirectly seems to be confirmed from the expression for the free activation energy of RFOT theory [2], given by

$$F^{++} = k_B T K \frac{T}{T - T_K}$$

(10)

where $k_B = k$ and $D$ is the constant in VFT formula presented as $\tau(T) = \tau_0 exp\left(\frac{DTK}{T - T_K}\right)$. Having in mind $DT_K = B = u/k$ the equation (10) became

$$F^{++} = u\left(\frac{T}{T - T_K}\right)$$

(11)
and by the equation (2) we obtain

$$ F^{++} = u j_s(T) $$

(12)

or accepting $j_s(T)$ given by equation (2) the activation energy of RFOT theory appears to be equal to that of ME theory and thus $r(T)$ will be the same.

The separate measuring of $j_s(T)$ and $u$ in ME theory makes it possible the activation energies per bead $u$, the cooperative activation energy $j_s(T)u$ and the apparent activation energy $j_s^T(T)u$ to be correctly interpreted. Then it follows that the glass transition temperatures $T_g$ and the crossover temperatures of Mode Coupling theory $T_c$, to be identified at the energetic scale [19,20,21]. In analogy to the energies, the relaxation volumes have been interpreted and for first time the relaxation volume of a bead has been measured [21]. The correct interpretation of $j_s(T)$ gives the possibility of measuring the number of configurations in the CRR [18] and the processes at $T_g$, $T_c$ as well as the fusion temperatures to be guessed in the entropic mode [22]. The methods for measuring the number of the beads in the molecules also have been found [22].

2.4 The size of the cooperatively rearranging region and the characteristic length of the cooperative molecular dynamics.

In several theories the size of the CRR is not measured but a “characteristic length” is measured [1-3, 12, 15] which is an indirect measure of this size. In the case of AG theory, the length of the size of CRR form a cooperative or characteristic length. The “universal” cooperative length in ME theory in this term will be 4-5 bead diameters and this predication is supported by the measured values in the range 3-9 bead diameters [20].

In RFOT theory the characteristic length at the $T_g$ have been estimated $\xi / r_0 = 4.5$ where $\xi$ is the length of the critical configuration droplet size and $r_0$ is the mean lattice space [2]. In this theory a hard sphere model of the liquids is used, and as the beads are regarded as relaxing units, thus the interpretation of $r_0$ should be the diameter of a bead. So, in this estimation of RFOT theory the characteristic length corresponds to the length of “universal” number of beads in the size of the CRR of ME theory.

In the “four-point” susceptibility method a “dynamic heterogeneity length” [5,12] while in Dons’ method a “cooperativity length” [15] are measured. Both these methods are based on the fluctuation-dissipation theorem. In both methods the dynamic heterogeneity is related to the distribution of the relaxation times. The “dynamic heterogeneity length” measured by the “four-point” susceptibility method in the order of 4.6-5.2 bead diameters [12] and it is in the range of that, measured by ME theory [14,20]. These methods are not directly related with the AG theory, but by using the configurational heath capacity in the interpretation of the experimental results [12, 23, 24] a common point with AG theory is observed. In both these methods through the fluctuation dissipation theorem a “correlation volume” is introduced. The number of molecules $N_{corr.A}$ [24, 26] or $N_a$ [25] measured in the “correlation volume” in the order of 75 and more molecules are debatable as such “correlation volumes” are rejected by experiments [23]. Both Don’t’s method and the “four-point” susceptibility method measured only one parameter a “characteristic length” and not some energy of activation. A lack of correlation between fragility $m$ and $N_{corr.A}$ has been found by experiments [24], while a close correlation between fragility and the size of the CRRS is observed [14,20].

3. Conclusions

The mathematical expression for measuring and interpretation of the size of cooperatively rearranging region presented only in the Molecular Entropy theory (extended at molecular level Adam-Gibbs theory), is supported by the subsequent methods for the measuring or the estimation this region as well as by measuring characteristic length by post-Adam-Gibbs theories. Indirectly this formula is supported by measuring the activation energies of the relaxation processes and the suggested kinetic and
thermodynamic methods for measuring the “fragility” of the glass-forming liquids. The large number of physical properties of the glass-forming liquids explained on energetical, volumetric and entopic scales on the basis of this formula seem to push the most probable size of the cooperatively rearranging region at a favorable position for long-term searching of a cooperative scale governing the glass-formation.

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