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Cooperative molecular dynamics and a random walk model

H. ZAPOLSKY[a], A. SAITER[b], H. SOLUNOV[c*]
[a]Laboratory GPM, UMR CNRS 6634, [b] laboratory LECAP, PBM UMR 6522 Faculté des Sciences, Université de Rouen, Site du Madrillet76801, Saint Etienne du Rouvray, Cedex, France
[c]University of Plovdiv "P Hilendarsky", Plovdiv 4000 Bulgaria

The liquid-glass transition in three families of polymers has been described within the framework of the random walk model and the extended Adam-Gibbs theory. The predictions and conclusions of these theories have been compared.

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1. Introduction

The glass transition is one of the unresolved problems of Condensed Matter Physics [1]. One of the key theories of the glass transition is the Adam-Gibbs Theory (AGT) [2-4]. According to this, the glass transition can be described by the introduction of a cooperative rearrangement region (CRR). The size of the CRR is defined as the number of molecules or the monomeric segments in polymers which are rearranging simultaneously. Recently, this theory has been extended at its molecular level [5-8] An equation for measuring the size of the CRR has been suggested and the basic molecular units have been identified as fragments of the molecules, known in thermodynamics as "beads". On this basis, a molecular interpretation of the fragility of the liquids, the apparent activation energy and the apparent activation volume have been obtained

Another approach called the Random Walk Model (RWM), proposed by Arkhipov et al. [9-11], describes the glass transition as a structural unit jump within a multi-dimensional energy landscape. The RWM predicts that the transition from a non-cooperative relaxation process to a cooperative one occurs at a critical temperature T_c. From the Vogel-Tamann-Fulcher equation

$$\tau = A\, exp\left[B/\left(T - T_\infty\right)\right] \tag{1}$$

where A, B and T_∞ are material constants, and RWM, it is possible to define the quantity $\Delta T = T_c - T_\infty$, which characterizes the cooperative range. It was shown [11-12] that this quantity correlates with the fragility index m, firstly introducing by Angell [13] in order to quantify the deviation of the temperature dependence of the viscosity (relaxation time) from the Arrhenius law near the glass transition.

The aim of this article is to compare the predictions and conclusions of the RWM and the extended AGT, for three families of polymers.

2. Theoretical remarks

The random walk model assumes that at high temperature $\left(T > T_c\right)$, the energy landscape fluctuates at a frequency that is large enough to allow a unit to jump to an adjacent site in the configuration space, without further activation. For $T < T_c$, the unit jump involves thermal activation over the associated energy barrier. For this temperature range, the relaxation time for fragile systems can be written as

$$\begin{gathered}\tau = \tau_0 \left[\frac{\pi}{2(\alpha - 1)}\right]^{1/2} \alpha^{(2\alpha-3)/2(\alpha-1)} \times \\ \left[\Gamma(1/\alpha)\right]^{-1} \left(T_0/T\right)^{(2-\alpha)/2(\alpha-1)} \times \\ exp\left[(\alpha - 1)\left(T_0/\alpha T\right)^{\alpha(\alpha-1)}\right],\end{gathered} \tag{2}$$

where Γ is the gamma function, α is the stretched exponent $1 \prec \alpha \prec \infty$ in the extended Gaussian distribution function, ($\alpha = 2$ yields the Gaussian distribution), $kT_0 = E_0$ is the width of the density of states of the structural units and τ_0 characterises the contribution of structural unit jumps via the fluid state towards the relaxation state.

The temperature dependence of the relaxation time $\tau(T)$ in the extended AGT is given by

$$\tau(T) = \tau_0\, exp\left[z(T)U/RT\right] \tag{3}$$

where $z(T)$ is the size of the CRR, U is the potential barrier height per basic kinetic unit in the CRR and τ_0 is the vibrational relaxation time.

By comparison of Eqs. (1) and (3), we obtain

$$z = \left[T/\left(T - T_\infty\right)\right], \tag{4}$$

and

$$U = RB \tag{5}$$

The fragility index in the extended AGT is given by

$$m = C_1 z(T_g) \tag{6}$$

where $C_1 \approx 16$ is the constant in the Williams-Landel-Fery equation [5]

3. Results and discussion

Three series of polymers have been investigated. The first family consisted of three samples of poly (2,2 dialkylpropane-1,3-diyl) carboxylbisphenyl-4,4 dicarbonyl] abbreviated as DP1.1, DP1.2 and DP1.3, where the numbers indicate the number of carbon atoms in the side chain, attached to the tertiary carbon of the propyl spacer. The second sample family consists of three samples of poly-methyl (α-n-alkyl) acrylate, abbreviated as C3, C5, C8, where the numbers indicate the number of carbon atoms in the lateral chain. The last sample family contains the Unsaturated Polyester Resins denoted as UPR25, UPR30, UPR35 and UPU40. The samples were obtained by changing the styrene concentration from 25% to 40% W/W [10]. Details on the synthesis and the methods for measuring the relaxation parameters for the investigated series are given in [10 -12]. In Fig. 1, the exponent α, calculated from the RWM, is plotted as a function of the size of the CRR at T_g

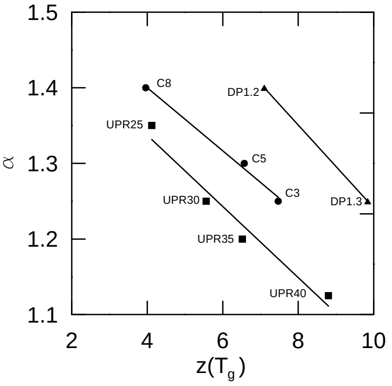


Fig. 1. The extended exponent α from the RWM, versus the size of the CRR at T_g from AGT.

In the RWM, the parameter α governs the fragility of the liquids [9,10]. In the extended AGT, the size of the CRR at T_g (see Eq. (6)) is the molecular base of fragility. In Fig. 1, a pronounced correlation between the quantities governing the fragility in both theories is observed.

The direct verification of the relation between the fragility index and the size of the CRR, Eq. (6), is also supported by experiment [12].

In Fig. 2, ΔT is plotted as a function of the size of the CRR at T_g.

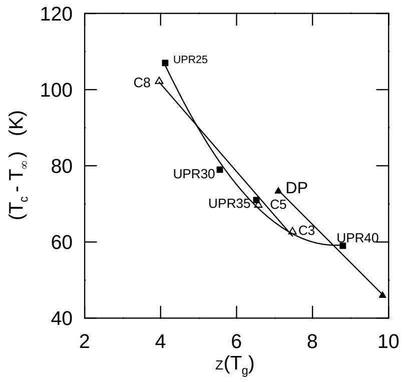
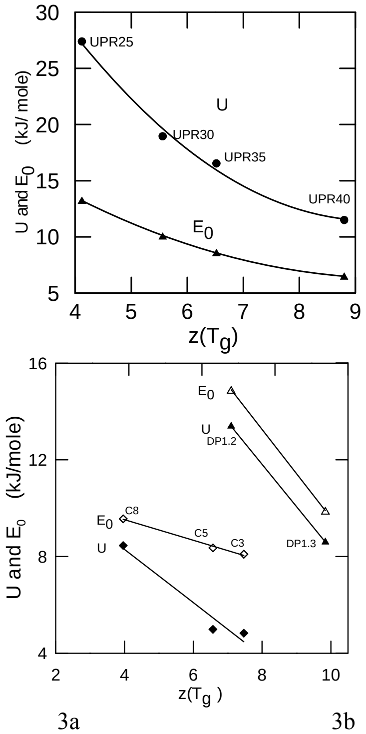


Fig. 2. Temperature range of the activated dynamics in the RWM, as a function of the size of the CRR.

The critical temperature T_c of the RWM is an analogue of the dynamic phase transition temperature of the MCT T_{cd} [9]. Adam-Gibbs theory is applicable in the range $T_{cd} - T_g$ [4], where Eqs (3) and (4) operate and the correlation demonstrated in Fig.2 is expectable.

In the extended AGT, the potential barrier U per individual molecular rearrangement is an average over the barriers into the CRR. In the RWM, the average barrier height is proportional to the square of the characteristic energy E_0. Furthermore, a correlation between these two values may be expected. As may be seen in Figs.3a and b, this correlation is well observed.



3a 3b

Fig. 3a and b. The average activation energy per basic kinetic unit in the CRR, U, and the width of the density of the metastable states E_0, as a function of $z(T_g)$ for three families of polymer.

The basic molecular units in the CRR have been identified as the thermodynamic beads [5, 6]. This permits us to measure the volume and diameter of the CRR (characteristic length of the glass transition). In the cases of the three series of polymers investigated, the rules for estimating the beads in the molecules or the monomeric segments [14, 15], may be applied with the best accuracy to the poly-methyl (α -n-alkyl) acrylate The beads in C3 may be identified as: $-CH_2-$, $-C=O$, $-COCH_3$, $-CH_2CH_2-$ and $-CH_2CH_3$, so that the monomeric segment of the C3 is constituted from 5 beads. The volume of this segment at T_g is 92 cm^3/mol, as estimated from the rules in [16]. Also, as $z(T_g) = 7.5$ beads, or 1.5 monomer units, the volume of a mole of CRRs is $V_z = 138\,\text{cm}^3$ and the characteristic length is $\xi_\alpha = (V_z)^{1/3} = 0.54$ nm. The characteristic length for the other polymers is in the same range of 0.5 - 1nm [17]. The characteristic lengths observed are in agreement with investigation of supercooled liquids, confined in nanopores [18].

The characteristic length of the cooperative molecular dynamics is an important quantity in the investigation of the compatibility of polymers in industrial applications such as nanostructred thin film coatings, as well as understanding the kinetics of glass-forming liquids confined in nanopores [18,19]. It will not be surprising if the measured level of activated and non-activated (free-diffusion) rearrangements into the CRRs [20] may be used as “switch on” and “switch off“ elements in nanotechnology.

4. Conclusions

Three families of polymer, two with increasing lengths of the side chains and the third with an increasing length of the bonding chains of the macromolecules, have been investigated by the Random Walk Model and the extended Adam-Gibbs theory. A close correlation between the parameters of the extended Adam-Gibbs thermodynamic theory and the statistical microscopic approach of the random walk model has been observed. The correlations observed support their common basis and the theoretical predictions of both approaches.

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*Corresponding author:solunov@pu.acad.bg