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SIGNIFICANCE OF THE INTRAMOLECULAR DEGREES OF FREEDOM ON THE GLASS-FORMING PROCESS

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The Adam-Gibbs theory of the glass-transition is extended at its molecular level. An expression for the number of configurations in the cooperatively rearranging region, which makes the macroscopic and molecular Adam-Gibbs equations compatible, is obtained. The number of configurations in the cooperatively rearranging region depends on the method for estimating the contribution of the vibration entropy to the entropy of the liquid. Two ways of extracting the vibration component from the entropy of the liquid have been used. In the first, the configuration entropy is regarded as the difference between those of the liquid and the crystal, and the second as the difference between the entropies of the liquid and the glass. In both cases the obtained number of configurations is larger than $w_z=2$, as accepted by Adam and Gibbs. The measured number of configurations was found to increase with the size of the cooperatively rearranging regions or the kinetic fragility of the liquids. This indicates that the cooperatively rearranging region is a flexible, with internal rearranging, dynamical cluster. As the basic kinetic units in the Adam-Gibbs cooperatively rearranging region have been identified as fragments of molecules known in thermodynamics as “beads,” it is concluded that the intramolecular degrees of freedom are substantial for avoiding the crystallization, during the cooling and forming of the glass.

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1. Introduction

Slow dynamics in the supercooled range of the glass-forming materials is of great importance, and has recently been the subject of intense study [1,2]. The “Idealised” Mode Coupling Theory [3] provides an approximate self-consistent description of the dynamics above the crossover temperature T_c in moderately supercooled liquids. The T_c is typically a factor of 1.1-1.4 above the glass-transition temperature T_g. A common interpretation of T_c is that it signals a crossover to strongly activated dynamics. There are many different theoretical approaches to the dynamics of glass-forming liquids, the validities of which remain controversial. The most widely used Adam-Gibbs (AG) theory has an advantage relating the kinetic with the thermodynamic properties of the liquids [4]. The AG macroscopic equation for the dielectric relaxation time τ is

$$\tau(T) = \tau_o \exp\left[C/TS_C(T)\right] \tag{1}$$

where T is temperature, S_c is configuration entropy, τ_0 is vibration time and C is a constant. Recently AG theory has been extended at its molecular level. An expression for measuring the size of the cooperatively rearranging region (CRR) z, defined as the number of the particles, which are rearranging cooperatively, has been suggested [5-7]. Various evidence that the basic molecular units

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in the cooperative rearrangement are not molecules but fragments of them, known in thermodynamic as ‘beads” has been obtained [5-7]. The measured number of configurations of the CRR in polymers [5] and optical glasses [7] has been found to be of the order of the beads in the same range. This is in contrast to the AG assumption that their number is two, independent of the substances. The aim of this paper is to measure the number of conformations in low molecular weight liquids using different approximations for S_c and in this way to obtain additional information for the nature of the dynamics and the basic kinetic units in glass-forming liquids. The compatibility of the macroscopic and the molecular AG equations of τ (T) is discussed, and the meaning of T_c, from the point of view of the extended molecular theory, is examined.

2. Theoretical treatments

Adam and Gibbs molecular equation is

$$\tau(T) = \tau_O \exp(zU/RT) \tag{2}$$

where z is the size of the CRR, U is mainly the potential energy barrier per mole, in basic molecular units, and R is the gas constant. AG did not suggest an equation for z, and avoided this by using the Boltzman relation for the configuration entropy of the CRR

$$s_z = k \ln w_z , \tag{3}$$

where k is the Boltzman constant and w_z is the number of configurations in the CRR. In this relation, they accepted w_z=2, one configuration before the rearrangement and the second one during the rearrangement. The parameter s_z may also be presented as

$$s_z = \frac{S_c}{N} z , \tag{4}$$

where S_c is the configuration entropy and N is Avogadro's number. From (3) and (4), we obtain

$$z = \frac{R \ln 2}{S_C} . \tag{5}$$

The configuration entropy was defined as [4]

$$S_C = \int_{T_\infty}^{T} \left(c_{pl} - c_{ps} \right) d \ln T , \tag{6}$$

where c_{pl} and c_{ps} are correspondingly the heat capacities of the liquid and the crystal or glass, and T_∞ is the Kauzmann temperature at which S_c becomes zero. AG accepted that this temperature is the same as in the Vogel-Tammann- Fulcher (VTF) empirical equation

$$\tau(T) = A \exp B/(T - T_\infty) \tag{7}$$

From Equations (2) and (5) we obtained Eq. (1) where

$$C = U \ln 2 \tag{8}$$

By comparing Eqs.(2) and.(7) in [5,6] it was found that

$$z = T/(T - T_\infty). \tag{9}$$

Various evidence has been obtained [5-7] that Eq. (9) measures the number of thermodynamic ”beads” [8,9] in the CRR, and not the number of molecules or monomer segments as defined by AG. Hence, a correct estimation of s_z may be obtained from

$$s_Z = \frac{S_C}{Nn} z, \tag{10}$$

where S_c is per mole and n is the number of the beads in the molecule or the monomer segment. In this case, S_c/Nn has the same dimension as z. From Eqs.(2),(3) and (10), we obtain Eq.(1) with

$$C = nU \ln w_z \tag{11}$$

which is also a constant, as n and w_z are constants for a given liquid. Hence, Eq. (1) is compatible with the molecular Eq. (2), independently of the nature of the basic kinetic units. However, a correct estimate of the number of configurations in CRR will be obtained from the relation

$$w_Z = \exp \frac{S_C(T_g)z(T_g)}{nR} , \tag{12}$$

as by missing n an unrealistically large number for w_z is measured . Eq. (12) is obtained from Eqs. (3) and (10). From Eq. (12) it follows that w_z will be a constant when the product $S_c(T)z(T)$ is temperature independent, as in the AG approximation (Eq. (5)). $S_c(T)z(T)$ is temperature independent when the configuration heat capacity has a hyperbolic dependence [9,10] $\Delta c_p = c_{pl} - c_{ps} = \Delta c_p(T_g)T_g/T$. In this case, from Eq.(6) we obtain

$$S_C(T)z(T) = \frac{\Delta c_p(T_g)T_g}{T_\infty} \tag{13}$$

Inserting $S_c(T)z(T)$ from Eq. (13) in Eq. (12), w_z may be measured by a great variety of data for T_g, T_∞ and $\Delta c(T_g)$.

3. Discussion of the experimental results

Experimental results for three low molecular weight liquids, investigated very carefully from the point of view of the AG theory [10], will be used for the verification of the above equations. Two of these liquids are at both ends of the Fragility Classification System, O-terphenyl (OTP) is a very fragile liquid with a fragility index m= 89, n-Propanol (n-Pr) is a strong liquid with m= 42 and 3-Brompentane has an intermediate fragility m=64 .The fragility index values are strictly proportional to $z(T_g)$ [5], and for OTP,3-BP and n-Pr $z(T_g)$ they are 5.6, 4.3 and 3.6 respectively. All three liquids have been investigated in both crystal and glassy form, which allows the vibration contribution to the entropy of the liquid to be estimated in two ways. The number of beads in the molecules of these liquids is known [6,9]. In Fig. (1) the number of configurations in the CRR w_z and the number of the configurations per bead, $w_b = w_z / z(T_g)$, in the same range at T_g are plotted as a function of the fragility index m.

From Fig (1), it may be realised that the reduction of the vibration component in the Sc slightly reduces the values of the configurations. The obtained values of w_z are considerably larger than 2. It is interesting that the values of the configurations per bead is $w_b \approx 2$. This supports the statement that CRR is not a rigid system, as accepted by AG assuming w_z =2. In our interpretation, CRR is a liquid unit with its own internal rearrangement [5-7]. Regarding beads as basic molecular units, the intra-molecular degrees of freedom are accepted to participate in the cooperative molecular dynamics. Hence, it may be concluded that the intramolecular degrees of freedom are a substantial factor in avoiding crystallization. This is important in forming optical fibers without

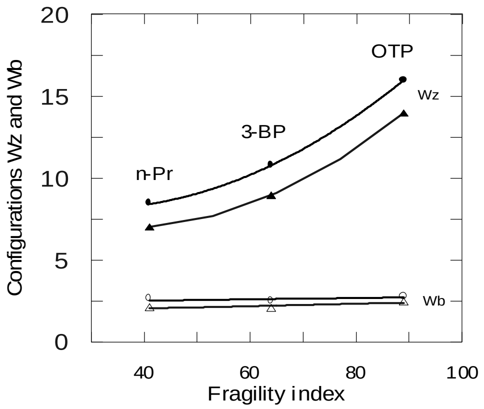

Fig.1. The number of the configurations in the cooperatively rearranging regions w_z, and per a basic molecular unit w_b in the same ranges at T_g, as a function of the fragility index. The curves illustrate the reductions of the number of configurations by reduction of the vibration component in the configuration entropy, since it is regarded as a difference of the: 1) entropies of the liquid and the crystal, upper curves (circles); 2) entropies of the liquid and the glass, lower curves (triangles).

introducing unacceptable light scattering loss [11]. Attention will be drawn to the fact that while w_z is a specific constant in the (T_c-T_g) range, w_b increases as z decreases with the temperature, Eq. (9). At T_c, the sizes of the CRR for OTP, 3-BP and n-PR are correspondingly 3.3, 2.5 and 2. Hence the number of $w_b(T_c)$ is about 1.7 times larger than at T_g, or about 40% of the rearranging molecular units still participate in activating hopping transport.

4. Conclusions

The Adam-Gibbs macroscopic equation for the relaxation time is compatible with that for molecules with intra-molecular degrees of freedom.

The number of configurations in the CRR can be correctly estimated if the basic molecular units are identified. In the Adam-Gibbs cooperatively rearranging region, these are identified as fragments of molecules or the intra-molecular degrees of freedom form a substantial part of the cooperative molecular dynamics.

The number of configurations in the cooperatively rearranging region, w_z, is temperature independent in the deeply supercooled (T_c-T_g) temperature range. This number is specific and increases with the size of the CRR of the kinetic fragility of the liquids.

The number of configurations per basic molecular unit in the cooperatively rearranging region, w_b, increases with increasing temperature. At the crossover temperature T_c, it is about 1.7 times larger than at T_g.

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