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The apparent activation energy and relaxation volume from the point of view of Adam–Gibbs theory

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Abstract

The temperature and pressure dependence of the glass-transition process is discussed on the basis of the molecular Adam–Gibbs equation for the relaxation time. An equation for measuring the temperature and pressure dependence of the Adam–Gibbs size of the cooperative rearranging region is suggested. The apparent activation energy and the apparent relaxation volume by this equation are presented as the product of the activation energy and the activation volume per basic molecular kinetic unit respectively with the size of the cooperative unit to the second power. In this way, for the first time, an equation for measuring the activation volume of a basic molecular kinetic unit involved in the cooperative molecular dynamics is obtained. The isobaric and the isothermal activation volume of a basic molecular species (BMS) measured by this equation correlate with the molar volume of the liquid. From the experimental results it follows that the size of the cooperatively rearranging region at isothermal conditions increases with pressure until at the glass-transition pressures it reaches an apparent limit. On the basis of the activation volume measured per BMS, a method for evaluating their volume in liquids and their number in molecules or in repeated units in polymers is suggested. By this method, for the first time, from a relaxation experiment, the basic kinetic units in several molecular glass-forming liquids are found to be close to the fragments of the monomer segments or molecules known in thermodynamics as Wunderlich’s beads.

1. Introduction

One of the most successful theories of the glass-transition process was suggested by Adam and Gibbs [1]. At the macroscopic level this theory is supported by experiment in all cases when the configuration entropy has been measured [2–6]. At the molecular level the temperature dependence of the relaxation time τ is given by

$$\tau = \tau_0 \exp\left(\frac{zU}{RT}\right) \quad (1)$$

where U is a potential barrier per monomer segment hindering the cooperative rearrangement, τ_0 is a frequency factor, R is the gas constant, T is the temperature and z is the size of the cooperative rearranging region (CRR). Adam and Gibbs define the size of CRR as the number of monomer segments, which are rearranging cooperatively.

In the absence of a cooperative rearrangement, $z = 1$, equation (1) is reduced to the Arrhenius equation. The Arrhenius activation energy is defined by

$$U = R \left(\frac{d \ln \tau}{d(1/T)} \right)_p \quad (2)$$

In this case U is identified with the potential barrier formed by the interaction of the molecule with its neighbours [7, 8].

In glass-forming liquids the temperature dependence of the relaxation time is described by the Vogel–Taman–Fulcher (VTF) equation

$$\tau(T) = A \exp \left[\frac{B}{T - T_\infty} \right] \quad (3)$$

where A , B and T_∞ are material parameters. The VTF equation gives

$$R \left(\frac{d \ln \tau}{d(1/T)} \right)_p = RB \left(\frac{T}{T - T_\infty} \right)^2 = U_{app} \quad (4)$$

As follows from equation (4), the apparent activation energy U_{app} is strongly temperature dependent and close to the glass-transition temperature T_g exceeds by a large margin the molecular heat of vaporization of the material [8–11]. This fact is the main argument for the glass-transition process to be regarded as cooperative [9–11].

From the pressure dependence of the relaxation time the relaxation volume V^* is defined by

$$V^* = RT \left(\frac{d \ln \tau}{dp} \right)_T \quad (5)$$

where p is pressure.

It is interesting to note that the definition of V^* is common for the Arrhenius approach [12–19], transition state theory [12, 20, 21] and the approach based on the terminology of equilibrium thermodynamics [23–26]. Several controversial molecular interpretations of V^* exist. Hirai and Eyring [20, 21] assumed that V^* is the molar volume of a hole in the quasi-lattice (or hole) model of liquids. McDuffie and Kelly [27] also used this interpretation. Bueche [28], having in mind a distribution of hole sizes, interprets V^* as a critical hole size, or a volume just large enough that the hole can accommodate the volume of a molecule. In many cases V^* is interpreted on the basis of the transition state theory as the difference in the molar volume of activated and inactivated molecules [12, 17, 29–33]. In some cases V^* is identified with the volume of the molecule or monomer segments involved in relaxation or flow processes [22, 23, 25, 34, 35]. In other cases V^* is not interpreted but only compared with other measurements [14–16, 24, 36–38]. As the molecular approach to V^* is of questionable validity, sometimes it is called the apparent relaxation volume [19, 22, 63], or it is assumed that V^* has only a phenomenological significance [39, 44, 47]. In the investigations during the last few years, some new equations for $\tau(p)$ as well as for $\eta(p)$ on the basis of the free-volume conception have been given, but new ideas for the molecular interpretation of V^* were not suggested [38, 40–47]. Attention will be drawn here to the fact that information has been obtained which suggests a focus on activated dynamics rather than on free volume [48]. When V^* is measured at temperature close to T_g the obtained values are several times larger than the

volume of the molecule or the monomer segment, which fact is interpreted as evidence for the cooperativity of the process [16, 23, 33, 35].

Recently the Adam–Gibbs theory was extended at its molecular level [49–53]. It was assumed that the basic molecule species (BMSs) in glass-forming liquids are not molecules or monomer segments but fragments of them, called by Wunderlich ‘beads’ [54]. Wunderlich defined ‘beads’ on the basis of the quasi-lattice (or hole) theory of liquids [20, 21] as ‘the smallest molecular units whose movement may change the hole equilibrium’. Wunderlich observed that the heat capacity jump at the glass transition temperature, $\Delta c_p(T_g) = c_{pl}(T_g) - c_{ps}(T_g)$, where c_{pl} and c_{ps} are respectively the heat capacity of the liquid and the crystal or the glass, varies within narrow limits around an average value if it is calculated per mole of bead and defines ‘the rule of constant $\Delta c_p(T_g)$ per bead’. Later Chang *et al* [55] found a similar rule for the configuration entropy. It was found that the Adam–Gibbs size of the cooperatively rearranging region may be expressed as $z(T_g) = \Delta c_p(T_g)/S_c(T_g)$ [50]. On the basis of the ‘universal’ values for $\Delta c_p(T_g) = 11.3$ J/mol bead K and $S_c(T_g) = 2.9$ J/mol bead K it was predicted that the ‘universal’ value of $z(T_g) = 3.9$ beads. As the values of $z(T_g)$ in low molecular weight liquids, polymers and inorganic glasses have been obtained to be of the order of magnitude of the ‘universal’ value, it was accepted that the beads are the basic molecular kinetic units in glass-forming liquids [50]. The beads are usually regarded as the basic molecular units when the thermodynamic phenomena are discussed [54–59], but attention should be drawn to the fact that the possibility of their being the basic molecular units in kinetic phenomena has also been assumed [55, 60–63].

In the case of saturated carbon backbone polymers with small side-chain groups the number of beads, n , in the chain repeating unit can be defined as the number of main-chain carbon atoms [54–59], but in general the empirical rules for counting the beads in small organic and inorganic molecules are unfortunately rather ambiguous [55–63]. Hence it is of principal interest for the basic kinetic units to be identified on the basis of measuring their physical properties instead of using semi-empirical rules.

The aim of this paper is to discuss U_{app} and V^* from the point of view of the Adam–Gibbs theory. Equations expressing U_{app} and V^* by means of z are suggested. The equation obtained for V^* gives the possibility for the activation volume of a BMS to be measured. By measuring this activation volume a method for identification of the BMS in glass-forming liquids is described. The pressure dependence of z as a component of both U_{app} and V^* is also illustrated by the experimental results.

2. Theoretical treatments

From the point of view of the Adam–Gibbs theory the activation energy that governs relaxation is the activation energy of the cooperative unit zU , which, as follows from equation (1), can be measured by

$$zU = RT \ln \left(\frac{\tau(T)}{\tau_0} \right). \quad (6)$$

If $\tau(T)$ in this equation is replaced by the VTF equation and assuming $A = \tau_0$ we obtain

$$zU = RB \frac{T}{T - T_\infty} \quad (7)$$

from which it follows that

$$U = RB \quad (8)$$

and

$$z(T) = \frac{T}{T - T_\infty}. \quad (9)$$

Equation (8) is used by a variety of authors [13, 64, 65, 73], and the VTF parameter B is interpreted as an activation parameter by many scientists. The right-hand side of equation (9) is found in a variety of articles [66, 67, 78] as well as in the case when U_{app} , equation (4), is discussed, but it is not recognized as a separate physical quantity. Miller [64, 65] regards this equation as the size of the CRR but interprets it as the number of monomer segments according to the definition by Adam and Gibbs. Several authors [32, 33, 68] use Miller's interpretation. Equation (9) has been obtained by the present author but with the interpretation that it gives the number of Wunderlich 'beads' [49, 50]. This interpretation seems to be supported by the work of Xia and Wolynes [69], who found a correlation between the strength parameter and the heat capacity jump per mole of beads at T_g . In general we regard the beads as occupied lattice sites in the quasi-lattice model of liquids [49]. Very recently equation (9) has also been obtained by Johari [70].

The activation energy of the CRR is closely related to the glass transition temperature as follows from equation (6), $z(T_g)U/RT_g = \ln \tau(T_g)/\tau_0$. It was shown that $\log \tau(T_g)/\tau_0 = C_1$, where C_1 is the constant in the Williams–Landel–Ferry equation [50]. As C_1 is a 'universal' constant with the value ≈ 16 [8, 71], it follows that the Adam–Gibbs factor at T_g is also a 'universal' $z(T_g)U/RT_g \approx 37$ and a linear dependence between $z(T_g)U$ and T_g is observed [50, 52].

From equations (4), (8) and (9) we obtain

$$U_{app} = Uz^2(T). \quad (10)$$

Equation (10) gives the explicit relation between U_{app} and the size of the CRR. To summarize, in the cooperative molecular dynamics three activation energies are used, namely activation energy per BMS U , activation energy of the cooperative unit zU and apparent activation energy z^2U .

The VTF equation (3) is often applied when the pressure dependence of the relaxation times is investigated but in this case B and T_∞ appear pressure dependent [15, 16, 31, 38, 42, 68, 72, 73]. As T_∞ is pressure dependent, as follows from equation (9), z will be also pressure dependent.

Taking z and U in the Adam–Gibbs equation (1) as pressure dependent and using this equation and equations (5), (8) and (9) we obtain

$$V^* = v_{ba}(T, p)z^2(T, p) \quad (11)$$

where

$$v_{ba} = \left\{ \frac{dU}{dp}[T - T_\infty(p)] + \frac{dT_\infty}{dp}U(p) \right\} T^{-1}, \quad (12)$$

where v_{ba} has the dimension of volume per BMS. In comparing equations (10) and (11) a close correlation is observed, as both U_{app} and V^* depend on the size of the CRR to the second power and a quantity per basic kinetic molecular unit. On the other hand, from equations (10) and (11) it follows that the interpretation of U_{app} and V^* , respectively, as the activation energy and activation volume of the cooperative unit [10, 11, 16, 22, 23, 33, 35, 68] is misleading, since both depend on z to the second power.

The volume given by equation (12) on the basis of the transition rate theory should be interpreted as the difference in volumes of activated and inactivated states of a BMS or as an

Table 1. VTF parameters of polyisoprenes. NR—natural rubber, PI—polyisoprenes.

Substance	Mode	T_g (K)	$\log A$ (s)	B (K)	T_∞ (K)	Reference
NR	α	201	−15, 81	2067	151	[73]
PI 1200	α	191	−13, 9	1529	153	[19]
PI 10600	α	204	−14	1543	164	[22]
PI 1200	n		−10, 84	1487	149	[19]
PI 10600	n		−9	1462	162	[22]

activation volume. Hence, the volume of a BMS in the liquid is the sum of an inactivated hard-core volume v_{bu} and an activation one v_{ba}

$$v_b = v_{bu} + v_{ba}. \quad (13)$$

v_b can be expected to be close to the volume of a BMS measured by ordinary dilatometric experiments. It should be mentioned that the molar volume of a molecule or monomer segment v_m is the sum of the volumes of the BMSs or $v_m = nv_b$, where n is the number of ‘beads’ [54].

3. Application of theory to experiments

The application of equation (12) to experimental data needs fitting for the pressure dependence of VTF parameters by analytical relations. As the pressure experiments are time consuming and the experimentally available frequency range is normally limited, the pressure dependence of relaxation times is usually investigated at one or several temperatures and for $B(p)$ and for $T_\infty(p)$ a linear dependence is assumed; hence, at present, a few experimental investigations may be used for measuring v_{ba} . Furthermore, we shall discuss mainly the dielectric experimental results of Dalal and Phillips [73] for *cis*-polyisoprene (natural rubber (NR)), since Dalal and Phillips obtained analytical expressions for $U(p)$, $T_\infty(p)$ and $T_g(p)$. Moreover, the VTF parameters at atmospheric pressure for this material correlated very well with the same parameters of other investigators [74–77] for polyisoprene. This is an advantage, as it is known that VTF parameters depend on the temperature range of investigation [13, 78–82] and are meaningful from the point of view of the Adams–Gibbs theory when $\tau(T)$ is measured close to T_g [5, 6]. A further advantage is that their results can be compared with the recently published dielectric investigation for fractions of *cis*-polyisoprene with different molecular weights [19, 22]. In this way, some information on the influence of the degree of polymerization on relaxation quantities, including the activation relaxation volume per BMS, can be obtained. The last reason is that in *cis*-polyisoprenes an additional one to the primary α relaxation, the so-called n-mode process, is observed. The n-mode relaxation is correlated with the viscosity [76, 82] and, hence, additional information may be gained. The VTF parameters at atmospheric pressure for the polyisoprene materials are given in table 1. The numbers added to the abbreviations of polyisoprenes indicate the number-average molecular weights [19, 22].

Dalal and Phillips [73] obtained the following equations: $U(p) = 17.26 + 1.57 \times 10^{-2}P - 9.9 \times 10^{-6}P^2$, where U is in kJ/mol and P in MPa, and $T_\infty(p) = 150.5 + 13.19 \times 10^{-2}P - 3.91 \times 10^{-5}P^2$, where T is in K and P in MPa. The behaviour of T_∞ is in agreement with the theoretical prediction [83].

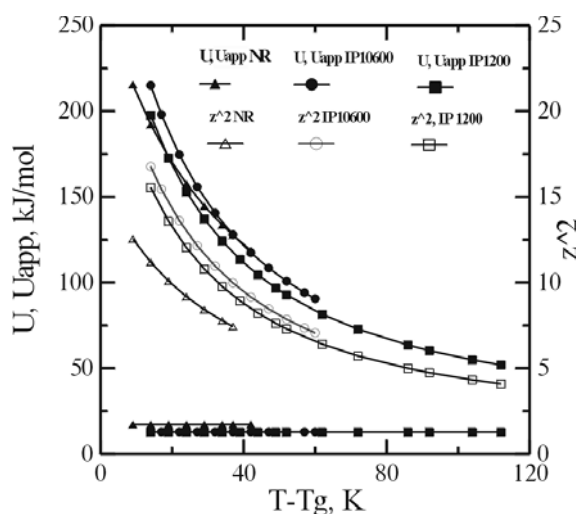


Figure 1. The temperature dependence of U_{app} is compared with the temperature dependence of the size of the cooperative unit z to the second power for NR and polyisoprenes. The activation energy per BMS, U , is also plotted. Notation is given in the figure and the results are for atmospheric pressure.

3.1. Isobaric analysis

In figure 1 the activation energies per BMS U , z^2 and the apparent activation energies U_{app} of NR and polyisoprenes as functions of the temperature difference $T-T_g$ are plotted. The results are for atmospheric pressure and the glass-transition temperatures are for the corresponding polymers. The activation energies per BMS of the dielectric α relaxation in polyisoprenes practically coincide and are smaller than that of NR while the CRRs for polyisoprenes are a little larger than that of NR. In all three polymers a close correlation between z^2 and U_{app} is observed, in accordance with equation (10).

In figure 2 the temperature dependence of the apparent relaxation volumes for NR and polyisoprenes is plotted. The apparent relaxation volume of NR is extrapolated by the Dalal–Phillips equation for $T_\infty(p)$ and $B(p)$ to the temperature range where the apparent relaxation volumes of polyisoprenes are measured. As may be seen from figure 2, the apparent relaxation volumes scaled to the temperature difference from the respective T_g are similar to these obtained for α relaxation and n-mode by Floudas *et al* [19] for the fractions of polyisoprenes. In figure 2 the molecular volume per monomer unit is also given [84]. As may be seen from figure 2, close to T_g the apparent relaxation volume is much higher than the molecular volume, but it decreases proportionally to z^2 in accordance with equation (11), and about 80 °C above the corresponding T_g it becomes smaller than the monomer volume. In figure 2 the apparent relaxation volumes for the n-mode of polyisoprenes are also plotted. The V^* for the n-mode in polyisoprenes are a little smaller than that for α relaxation.

In figure 3 the activation relaxation volumes per BMS v_{ba} of the three liquids are compared with the volume per mole of monomer units. As can be seen from figure 3, v_{ba} is approximately five times smaller than the monomer volume. For all the substances the v_{ba} values scaled to the corresponding T_g are very close. As VTF temperatures for the n-modes are lower than those for α relaxation, the sizes of the CRRs for the n-mode at a given temperature are a little smaller than those for the α relaxation. As a result, the absolute difference in v_{ba} of the α relaxation and the n-mode is smaller than in the corresponding apparent relaxation volumes.

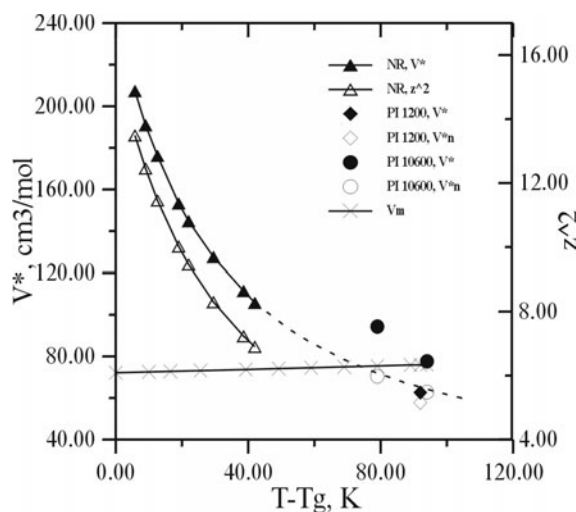


Figure 2. The temperature dependence of the apparent relaxation volume V^* of NR and polyisoprenes is compared with the size of the CRR to the second power, z^2 , of NR. The dashed curve is an extrapolation of the apparent relaxation volume of NR by the equations in the text to the temperature range of investigation of polyisoprenes. For polyisoprenes the apparent relaxation volumes for the α segmental V^* and for the n-mode (V_n^*) are plotted. The temperature dependence of the monomer volume v_m of NR is also given. The results are for ambient pressure.

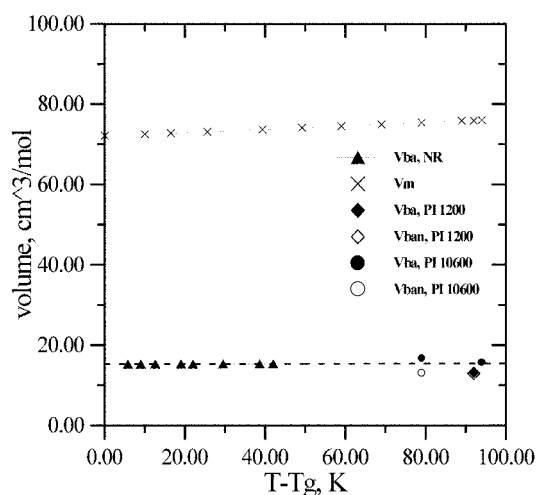


Figure 3. The activation relaxation volume per BMS v_{ba} , and the monomer volume v_m of NR as a function of the temperature difference from T_g . For polyisoprenes 1200 and 10600 the activation relaxation volumes per BMS for the α segmental v_{ba} and for the n-mode v_{ban} as functions of the temperature distance from the respective T_g are plotted. The results are for atmospheric pressure.

This is the reason that for PI 1200 volumes v_{ba} and v_{van} are very close and in figure 3 their points coincide. While V^* decreases rapidly with increasing temperature, v_{ba} increases with increasing temperature in coordination with the molar volume (figure 3).

From the results in figure 3 we may estimate the number of BMSs in the monomer segment. As the activation relaxation volume v_{ba} is measured, an estimation of the hard-core volume v_{bu} of the BMS needs to be assumed to apply equation (13). One possibility is to accept the

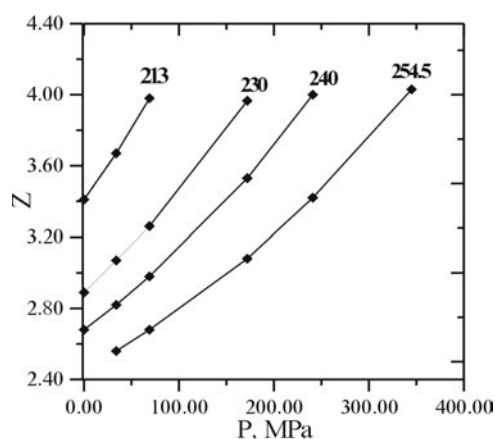


Figure 4. The isothermal size of the cooperative unit z of NR as a function of pressure at the temperature marked on the curves.

concept of Hirai and Eyring and of Bueche that the relaxation volume is equal to the volume of one hole, but it will be emphasized that v_{ba} is taken in our case, instead of the apparent relaxation volume, which they used. On the other hand, Bueche obviously assumed that the volume of a hole is equal to the volume of a BMS. The same postulate is also used in several other variants of the quasi-lattice theory of liquids [85, 86]. According to this concept, the volume of the BMS will be twice the measured activation relaxation volume, or $v_b = 2v_{ba}$. The average v_{ba} in the investigated temperature range of NR in figure 3 is $15.26 \text{ cm}^3/\text{mol BMS}$ and within the same temperature range the volume of the monomer unit is $v_m = 72.93 \text{ cm}^3/\text{mol}$; with these values we obtain $n = 2.4$ BMS in a monomer unit. For the α -relaxation of PI 1200 and PI 10600 with the corresponding $v_{ba} = 13.12$ and $16.67 \text{ cm}^3/\text{mol BMS}$ at respective temperatures we obtain $n = 2.9$ and 2.3 . For the n-mode for both polyisoprenes $n = 2.93$ BMSs in a monomer segment is obtained. The numbers obtained are close to the empirically defined number of beads in NR [54], $n = 3$. Another possibility exists, namely to choose the van der Waals volume as a hard-core volume of the BMS [51]. The van der Waals volume of a monomer segment of polyisoprenes is $47.6 \text{ cm}^3/\text{mol}$ [87]. If we take the number of beads to be three we obtain $v_{bu} = 15.29 \text{ cm}^3/\text{mol beads}$; this volume practically coincides with the activation relaxation volume per BMS in figure 3, and negligible differences in n on this basis from previous estimations are obtained.

3.2. Isothermal analysis

In figure 4 the pressure dependences of the size of CRRs of the marked temperatures are plotted. As can be seen from the figure, $z(p)_T$ increases with the pressure and at the level of glass-transition pressures it reaches a limit independent of temperature.

Dalal and Phillips [73] found that the glass-transition temperature $T_g(p)$ of NR increases with the pressure according to the equation $T_g(p) = 201 + 1,642 \times 10^{-1} P + 2,3 \times 10^{-5} P^2$. In figure 5 the activation energy per BMS, U , the activation energy of the cooperative unit, zU , and the apparent activation energy, z^2U , are plotted as functions of $T_g(p)$. As U increases with pressure from 17.26 kJ/mol BMS at atmospheric pressure to 21.5 kJ/mol BMS at 345 MPa and the $z[T_g(p)]$ are practically the same, the activation energy of the cooperative unit and the apparent activation energies increased with the pressure proportionally to U . Note that

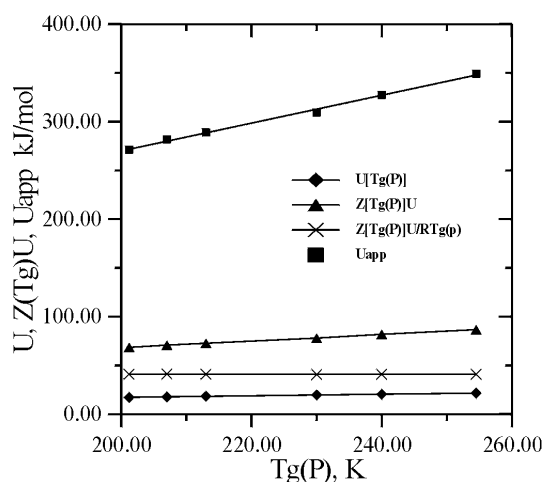


Figure 5. The activation energy per BMS, U , the activation energy of the cooperative unit, zU , and the apparent activation energy, U_{app} , of NR as functions of $T_g(p)$. The ‘universal’ Adam–Gibbs factor is also given.

the Adam–Gibbs factor at T_g , $z(T_g)U/RT_g$, which is a ‘universal’ constant for glass-forming liquids at atmospheric pressure, appears, according to the investigation of Dalal and Phillips, to be pressure independent. The fragility of the liquids is related to the scaling to the glass transition temperature [88, 89]. Thus, from the molecular point of view [50], the fragility index $m = C_1 z(T_g)$, where C_1 is the constant in the Williams–Landel–Ferry equation. Since $z[T_g(p)]$ and $C_1(p) = 17.8$ [73] are independent of pressure, it follows that in polyisoprene fragility is pressure independent within the investigated pressure range. Such independence of fragility within the experimental errors is observed in other van der Waals liquids, namely dibutyl-phthalate [42], orthoterphenyl [43] and epoxy resins [46]. The relaxation behaviour of hydrogen-bonded liquids is more complicated and will be discussed elsewhere.

In figure 6 the isothermal activation relaxation volume per BMS v_{ba} is plotted as a function of pressure at temperature 243 K, where the largest number of experimental points in the investigated frequency and pressure range are available. In figure 6 the dependence of the molecular volume v_m at 243 K is also given [84] for comparison. As can be seen from figure 6, a correlation between the activation relaxation volume per BMS and the molar volume is observed. The results from the figure can be used for estimation of the number of BMSs in a monomer unit. Assuming $v_b = 2v_{ba}$ at temperature 243 K, we obtain $n = 2.5$ at an average pressure of 86 MPa. This number is in agreement with the results estimated at atmospheric pressure.

In figure 7 the activation relaxation volumes per BMS v_{ba} , the activation relaxation volume per cooperative unit zv_{ba} and the apparent relaxation volume z^2v_{ba} are plotted against the glass-transition temperatures enhanced by pressure. Comparing figures 5 and 7, it may be observed that the activation energies increased and the relaxation volumes decreased with increasing glass-transition temperature $T_g(p)$.

As equations (12) and (13) give the possibility for the BMS to be identified, it is useful that they should be applied to other molecular substances. From the literature experimental results available the tabulated values for the relaxation times of poly(methyl acrylate) (PMA) [34], poly(ethyl acrylate) (PEA) [32] and *o*-terphenyl (OTP) [26] were found to be suitable. The VTF parameters T_∞ and B were fitted by the second-order polynomial $a + bP + cP^2$ following

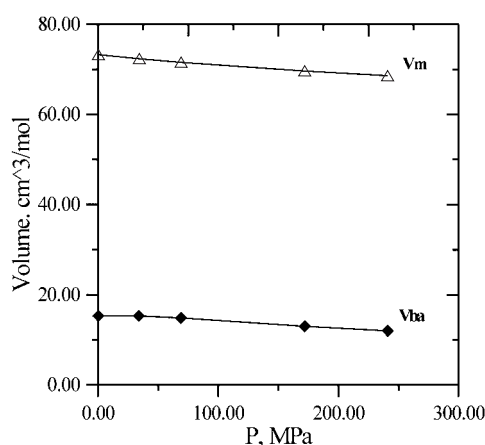


Figure 6. The isothermal activation relaxation volume of the BMS v_{ba} and the monomer volume v_m of NR as functions of pressure at 243 K.

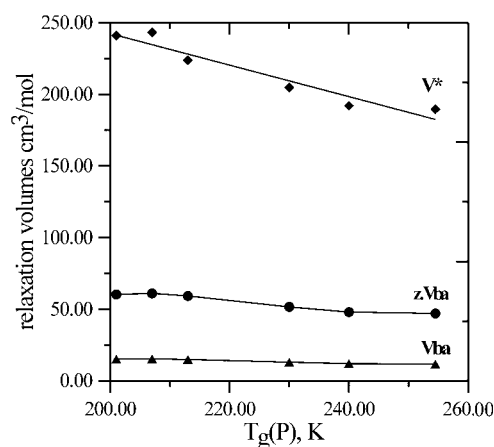


Figure 7. The activation relaxation volume per BMS v_{ba} , the activation relaxation volume of the CRR $z v_{ba}$ and the apparent relaxation volume V^* of NR plotted against $T_g(p)$.

the procedure of Dalal and Phillips for polyisoprene. The parameters a , b and c as well as $\log A$ for these substances are listed in table 2. The activation volume per BMS for these substances at atmospheric pressure increases with the temperature, as observed for polyisoprenes (figure 3). The investigated temperature range and the values of v_{ba} in these ranges are given in table 3. In table 3 the average values of the monomer volumes of PMA and PEA [87] and the molecular volume of OTP are included as well [90]. The numbers of BMSs in a monomer segment in PMA and PEA and in a molecule of OTP estimated by means of v_{ba} and assuming $v_b = 2v_{ba}$ are given in the last column of table 3. For PMA and PEM the numbers of BMSs obtained are 3.7 and 4.6, values very close to the estimated number of beads, corresponding to four and five [57, 59]. For OTP the estimated number of BMSs is 6.5. OTP is constituted from three phenyl groups, each connected by a single bond to the molecule. From investigations by Wunderlich and Jones [56] a similar construction is observed in polystyrene. The number of beads estimated on the basis of the rule of the constant $\Delta c_p(T_g)$ per mole of beads in polystyrene

Table 2. Results obtained for the VTF parameters as a function of pressure fitted by the polynomial $a + bp + cp^2$.

Substance	T_∞ (K)			B (K)			log A (s)
	a	b	c	a	b	c	
PMA	221	1.27×10^{-1}	-3.59×10^{-5}	1872	1.573	-3.47×10^{-4}	-13.52
PEA	210.7	5.7×10^{-2}	3.05×10^{-4}	1445	3.517	-1.05×10^{-2}	-12.47
OTF	201.8	1.32×10^{-1}	1.01×10^{-3}	1699.5	5.025	-3.46×10^{-1}	-15.55

Table 3. Molar volumes and the number of BMSs in the monomer segments of PMA and PEA as well as in the molecule of OTP.

Substance	ΔT (K)	V (cm ³)	v_{ba} (cm ³)	n
PMA	280–307	73.1	9.96	3.7
PEA	265–290	87.9	9.47	4.6
OTP	257–272	207.8	15.92	6.5

by Wunderlich and Jones is $n = 3$, or the phenyl group is estimated as one bead. On this basis Chang and Bestul [3] estimated the number of beads in OTP, $n = 3$. Becker [57] on the basis of several semi-empirical equations estimated the number of beads in polystyrene, $n = 4$, or the phenyl group is estimated as two beads. It is interesting that in polystyrene restricted rotation and rotation vibrations of the phenyl group have been assumed [7]. On the other hand Privalko [58] assigned $n = 3$ to the phenyl group and correspondingly $n = 9$ to OTP. The number of beads obtained on the basis of the measured v_{ba} in OTP, $n = 6.5$, is close to the $n = 2$ estimated by Becker for the phenyl group connected with a single bond to the molecule.

The results obtained for the number of BMSs in the monomer segment or molecule of the investigated molecular liquids are close to the estimated number of 'beads' for this substance. Hence, the method described for measuring the number of BMSs in molecular liquids is promising, as so far only semi-empirical methods for this estimation are known.

4. Conclusion

The equation for the temperature dependence of the size of the Adam–Gibbs cooperatively rearranging region has been extended to describe the effect of pressure as well. By this equation the apparent activation energy U_{app} and the apparent relaxation volume V^* are presented as products of two components. The first one is, respectively, the activation energy and the activation relaxation volume per BMS, while the second one in both cases is the size of the cooperative unit to the second power. By this representation an equation for the activation relaxation volume per BMS in the cooperative molecular dynamic of any supercooled liquid is obtained. The isobaric and isothermal activation relaxation volumes per basic molecular kinetic unit measured by this equation increase in correspondence with the temperature and decrease with pressure in co-ordination with the volume of the liquid. The estimated activation relaxation volumes per BMS in polyisoprenes are very similar, with a negligible difference in the degree of polymerization.

The volume of a BMS is assumed to be the sum of the measured activation relaxation volume and a hard-core one. Using the hypothesis that the two volumes are equal, the number of basic molecular kinetic units in a monomer segment or in a molecule of several molecular liquids has been estimated, and the number obtained has been found to be close to the number of empirically postulated Wunderlich beads. The obtained results also support the suggested

molecular interpretation of the apparent relaxation volume V^* .

The size of the CRR of NR in isothermal measurements has been observed to increase with pressure, reaching a top temperature-independent limit at the glass-transition pressure. As a result the fragility index, which is closely related to the size of the cooperatively rearranging region, is also pressure independent within the pressure range investigated by Dalal and Phillips.

The 'universal' value of the Adam–Gibbs factor at T_g has been observed to be pressure independent.

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