Translated from *Uspekhi Khimii*, 47, 332 - 356 (1978) U.D.C. 547.911

State of the Theory of Iso-free Volume and Glass Formation in Amorphous Polymers

Yu.S.Lipatov

Methods of determining the free volume fraction of polymers at the glass formation temperature and the concept according to which all polymers have a universal free volume fraction at the glass point are considered critically. The concept of iso-free volume in glass formation can be regarded only as a rough approximation and the free volume fraction is a function of several variables including the flexibility of the polymeric chain and the nature of the molecular packing. The development of the theory of glass formation by amorphous polymers on the basis of the free volume concept is considered and it is shown that a free volume distribution function has to be introduced for the correct description of the process. Conclusions are drawn concerning the inapplicability of the iso-free volume concept for describing glass formation processes in amorphous polymers. The possibilities of a more adequate description of glass formation are discussed. 69 references.

CONTENTS

I. The free volume concept and its connection with glass formation by amorphous polymers 186
II. Methods of calculating the free volume fraction at the glass formation temperature 187
III. Thermodynamic and molecular examination of the free volume concept 188
IV. State of the iso-free volume during glass formation 191
V. Variation of the free volume fraction at the glass formation temperature with the molecular parameters of linear polymers 193
VI. The concept of free volume distribution 194

I. THE FREE VOLUME CONCEPT AND ITS CONNECTION WITH GLASS FORMATION BY AMORPHOUS POLYMERS

Many of the properties of high- and low-molecular-weight substances (viscosity, thermal, mechanical, relaxation, etc.) and processes in them (diffusion, permeability, sorbtion) are connected with the molecular mobility and structure of these compounds, determined by the degree of ordering of the molecules. The structure and properties of such substances can be described from the thermodynamic viewpoint through configuration free energy[1] and enthalpy[2]. However, phenomenologically one of the most convenient ideas is excess or free volume. According to Covacs[3], free volume is a characteristic of the disorder of the structure and determines the rate of molecular rearrangements. This characteristic is closely connected with the configuration mobility of a liquid and its thermodynamic parameters and could be classified among the fundamental characteristics of the liquid state if the existing theory could give a precise definition of the concept of free volume and methods for its determination.

Actually, the most important properties of liquids, and above all viscosity and capability of glass formation, show they contain a free volume, which can be represented as holes or vacancies of approximately molecular dimensions, rated to the irregular packing of the molecules. Although, according to Ferry[4], the free volume per 1 g substance, v_f, is very difficult to determine, it is a useful semiquantitative concept. In particular, the greater part of the thermal expansion coefficient of liquids is due to an increase in the free volume, whereas its lesser part is linked with the anharmonicity of the relation between potential energy and the interatomic or molecular distances.

The concept of free volume is based on the Doolittle empirical equation[5], which connects viscosity with specific free volume:

$$\ln \eta = a + b/f, \qquad (1)$$

where a and b are constants,

$$f = (v - v_0)/v, \qquad (2)$$

v and v_0 are the actual and occupied volumes of the liquid at temperature T:

$$v - v_0 = v_f.$$

By occupied volume is meant the proper total volume of the molecules.

The concept of free volume proved very useful and was employed for the theoretical description of many processes in liquids, including processes in polymers. A theory of the diffusion of low-molecular substances in polymers[6,7], a theory of thermal conductivity[8], a theory of solutions and solubility of polymers[9], etc. were developed on the basis of the free volume concept. However, the free volume concept was used most extensively in the theory of viscoelastic properties of polymers, developed by Williams, Landell, and Ferry, and stated in detail in Ferry's monograph[4]. According to this theory, the change in the viscosity of a liquid with temperature in the range from T_g to T can be described with the aid of a normalisation coefficient

$$a_T = \eta_T/\eta_{T_g}.$$

By using Doolittle's equation (1) connecting the viscosity and the free volume, we can obtain:

$$\lg a_T = \frac{-(B/2{,}303 f_g)(T - T_g)}{f_g/\alpha_f + T - T_g}, \qquad (3)$$

where f_g is the free volume fraction at T_g, B a constant, and α_f is regarded as a coefficient for the increase in free volume (see below). The values of f_g found experimentally according to this equation are the same (0.025 ± 0.003) for most polymers.

Bueche[10] further developed the theory of viscoelastic properties based on the free volume concept, by starting from the assumption that some element of the structure can be displaced when the fraction of local relative free

volume f exceeds some critical value f_c. The frequency ν of the corresponding molecular process can be expressed by the equation

$$\nu = \nu_g \exp[-Nf_c(1/f - 1/f_g)],$$

where ν_g is the frequency at T_g. When (as will be considered below)

$$f = f_g + \alpha_f(T - T_g), \quad (4)$$

then

$$\ln(\nu/\nu_g) = \frac{Nf_c/f_g(T - T_g)}{T - T_g + f_g/f}.$$

This equation is identical in form with Eqn. (3).

Simha and Boyer[11] were the first to use the free volume concept in considering processes of glass formation in amorphous polymers. By analogy with Eqn. (2) they assumed that the free volume fraction at the glass formation temperature is

$$f_g = (v_g - v_{0g})/v_g = 1 - v_{0g}/v_g, \quad (5)$$

where v_g and v_{0g} are the actual volume and the volume occupied by the molecules, at T_g. On assuming that the specific free volume is a linear function of temperature then clearly condition (4) will be observed, at which

$$\alpha_f = (\partial f/\partial T)_p \simeq 1/v[(\partial v/\partial T) - (\partial v_0/\partial T)]_p. \quad (6)$$

Eqn. (5) can also be written in the form

$$f_g = [v_g - v_{0l}(1 + \alpha_g T_g)]/v_g \simeq [v_g - v_{0l}(1 + \alpha_g T_g)]/v_{0l},$$

where v_{0l} is the occupied volume in the initial state, $T = 0$, α_g the coefficient of expansion of the vitrified liquid below T_g. In this definition, f_g is found from the difference between the actual volume and the volume which the liquid would have at the glass formation temperature were the volume of the liquid v_{0l} to increase with the expansion coefficient α_g characteristic of the vitreous state. Then the actual volume at the glass point is

$$v_g = v_{0l}(1 + \alpha_g T_g),$$

and the free volume fraction equals

$$f_g = [v_{0l}(1 + \alpha_l T_g) - v_{0l}(1 + \alpha_g T_g)]/v_{0l}.$$

From this relation we have[11]

$$(\alpha_l - \alpha_g) T_g = f_g = K_1. \quad (7)$$

In 1950 Fox and Flory[12] introduced the concept according to which the glass formation temperature corresponds to the state of iso-free volume. This concept has been developed[13,14], is used widely, and with slight modification provides a basis for various theories of glass formation[11,15,16]. The constant value found by Simha and Boyer[11] for K_1 for various polymers served as confirmation of the definition of iso-free volume as the volume corresponding to the glass formation temperature.

If it is also assumed that at T_g the partial free volume is constant for all polymers, then having determined this volume as

$$K_2 = (v - v_{0l})/v,$$

it can be shown that

$$K_2 = \alpha_l T_g.$$

Actually, K_2 can be written as:

$$K_2 = \frac{v_{0l}(1 + \alpha_l T) - v_{0'}}{v_{0l}(1 + \alpha_l T)} = \frac{\alpha_l T}{1 + \alpha_l T} \simeq \alpha_l T.$$

Eqn. (6) also suggests that the ratio of the linearly extrapolated volumes v_{0g} and v_{0l} at $T = 0$, K is almost independent of the nature of the polymer. Then

$$v_{0g}/v_g = (1 + \alpha_l T_g)/(1 + \alpha_g T_g) = 1 + (\alpha_l - \alpha_g) T_g - \alpha_g(\alpha_l - \alpha_g) T^2 \simeq 1 + K_1.$$

It was found that $K_1 = 0.113$ and $K_2 = 0.164$ for most of the polymers. Hence the expressions for K_1 and K_2 characterise corresponding states in the free volume terms.

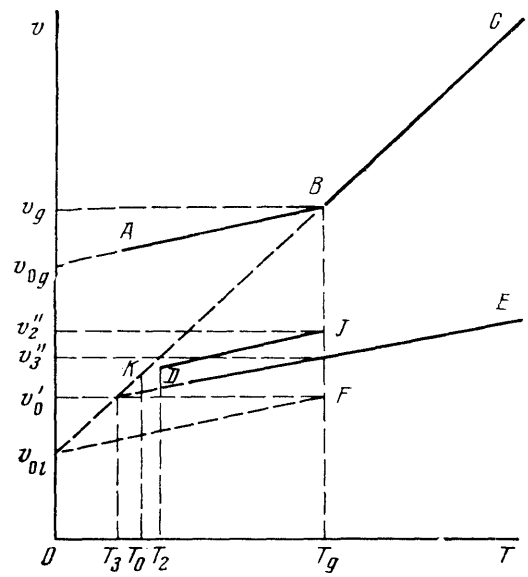


Figure 1. Scheme for the calculation of free volume characteristics in various theories.

II. METHODS OF CALCULATING THE FREE VOLUME FRACTION AT THE GLASS FORMATION TEMPERATURE

In the definitions considered above the free volume fraction depends on which volume was taken as the initial value for the state, that is, on the method of calculation. Even in this very fact some vagueness is introduced into the physical significance of free volume. In this connection, we will consider various computational methods of determining the initial volume, since on this depends the calculated fraction of the free volume at T_g.

Fig. 1 shows schematically the variation of specific volume with temperature. Here the line AEC represents the curve of the change in actual volume of an amorphous polymer during passage through T_g. The segment AB (with slope α_g) corresponds to the vitreous stage, segment BC (with slope α_l) to the highly elastic state. The straight line DE parallel to AB corresponds to a change in volume in the crystalline state if it is assumed (as is usual[11,17]) that the coefficients of thermal expansion in the vitreous (α_g) and crystalline (α_c) states are equal. On extrapolating the segment BC to 0 K, the value of v_{0l} is obtained, and extrapolating AB gives the value of v_{0g}. Hence the free volume fraction according to Simha and Boyer is determined (the segment $BF = \Delta\alpha \cdot T_g$, is the occupied volume v_0').

According to Williams–Landell–Ferry, the occupied volume is taken to be the quantity v_f^* obtainable by extrapolation of the volume of the liquid corresponding to some temperature T_2, determinable from the viscometric results[15,18] parallel to AB up to T_g (the segment BJ). According to Tobolsky's determination[19], the occupied volume v_3^*, corresponds to the volume of the specimen in the crystalline state at T_g. According to Miller[20], the free volume is determined from the relation to the temperature T_0 entering into the Fogel equation for the temperature dependence of viscosity. Point K represents a hypothetical volume larger than for the crystalline state, but less than for the glass at the same temperature. Consequently, the free volume here is somewhat greater than that determined according to Williams–Landell–Ferry.

According to Miller,

$$v_f = v - v_0 = 0 \quad \text{at} \quad T = T_0.$$

Then at any other temperature

$$v_f = \Delta\alpha\,(T - T_0), \tag{8}$$

where

$$\Delta\alpha = \alpha_l - \alpha_g.$$

Correspondingly at T_g

$$v_f = \Delta\alpha\,(T_g - T_0). \tag{9}$$

According to the Simha–Boyer theory,

$$\Delta\alpha \cdot T_g = K_1$$

By equating the $\Delta\alpha$ in expressions (8) and (9) we can obtain the following relation:

$$K_1/(v_f)_{T_g} = T_g/(T_g - T_0).$$

Covacs[3] gives yet another definition of the free volume fraction. Since the extrapolatable volume of the supercooled liquid reaches the volume of the crystalline state v_c at some temperature $T_c > 0$ K this critical temperature can be compared with $T_{g,\infty}$ the limiting temperature of glass formation at infinitely slow cooling, assuming that in the crystalline state the free volume is zero. Then the quantity f_g defined according to Doolittle can be compared with the $f_{g,c}$ characterising the excess free volume of a glass compared with the crystal:

$$f_{g,c} = (v_g - v_c)/v_g.$$

The comparison of f_g and f_c for amorphous polymers is naturally difficult since the volume v_c can be found experimentally only when the polymer is capable of crystallising. In this approach it is assumed that $\alpha_c \simeq \alpha_g$; thus for polystyrene usually $f_{g,c} = 2f_g$. It is usually assumed that the free volume fraction varies with the temperature in accordance with relation (4), where the coefficient of expansion is determined by Eqn. (6). According to Ferry[4], when the macroscopic coefficient of expansion α_l at temperatures higher than T_g reflects the appearance of free volume, then $\alpha_f = \alpha_l - \alpha_g = \Delta\alpha$ should apply. Actually, the $\Delta\alpha$ found experimentally correspond well with the values of α_j calculated from the Williams–Landell–Ferry theory. In addition, we wish to emphasise that the actual value of $\Delta\alpha = \alpha_f = \alpha_l - \alpha_g$ is not the coefficient of expansion of the free volume as such, but the temperature coefficient of the free volume fraction. Elementary calculation shows that the actual increase in volume above T_g cannot be equal to $v_g\alpha_f(T - T_g)$, if v_g is determined by starting from the actual specific volume at T_c and the known f_g.

As is evident from what has been stated, irrespective of the method of estimating the occupied volume adopted in the various theories the free volume fraction is always determined by Eqn. (5) and consequently the values of f_g calculated by the various methods do not agree with one another. This emphasises that this is not an absolute quantity and shows the need to regard it only as a convenient parameter for describing the properties of a liquid. Even in 1963, Boyer[17] noted that the free volume at T_g is constant only under certain conditions and varies with the molecular mass, the degree of cross-linking, and other characteristics of the polymer.

III. THERMODYNAMIC AND MOLECULAR EXAMINATION OF THE FREE VOLUME CONCEPT

Hirai and Eyring[21] found that the quantity $\Delta\alpha \cdot T_g$ depends on ϵ_h, the energy of hole formation:

$$\Delta\alpha \cdot T_g = (\varepsilon_h/RT_g)\exp[-(\varepsilon_h/RT)].$$

By taking $f_g = 0.02$, they theoretically calculated the value $\Delta\alpha \cdot T_g = 0.08$. According to their views:

$$\varepsilon_h/RT_g \simeq -\ln f_g.$$

Since ϵ_h is proportional to the cohesion energy density E, it can be shown that

$$T_g = [\Delta H' + ME]/(-R\ln f_g),$$

where

$$\Delta H' = \Delta H_f - \Delta H_h,$$

ΔH_f is the heat of fusion, ΔH_h is that part of the heat of fusion associated with the "fusion" of the holes, and M is a constant.

The free volume concept as applied to processes of glass formation was developed further in Miller's work[20,22]. The basis of Miller's ideas was that if any excess function

$$\Delta X\,(\text{liquid}) - X\,(\text{crystal})$$

is extrapolated to zero at some temperature exceeding 0 K;[22] these temperatures correspond to the excess volume equalling zero. Miller showed that the excess entropy and excess volume are reduced to zero at the same temperature, corresponding to the temperature T_0 in the Fogel equation. According to Miller, the coefficient A in the Fogel equation:

$$\lg\eta = \lg A + B(T - T_0)$$

is connected with the weighed mean number of the bonds in the macromolecule z_w by the ratio:

$$\lg A = \lg K + 3.4\lg z_w.$$

From these two equations, at T_g:

$$\lg\eta_g = \lg K + 3.4\lg z_w + B(T_g - T_0).$$

The parameters for the vinyl polymers give the relation $B/(T_g - T_0) \simeq 15$. From the standpoint of ideas about free volume:

$$\lg\eta \propto b/(v_f)_{T_g}.$$

From this it can be shown that:

$$(v_f)_{T_g}/b = (T_g - T_0)/2, \quad 3b \simeq 0.029.$$

This corresponds to the value given by the Williams–Landell–Ferry theory. Hence in principle the idea of iso-free volume follows directly from the viscosimetric

measurements. The difference in the definition of the free volume according to Miller from the Simha–Boyer definition is that

$$(v_f)_{T_g} = \Delta\alpha\,(T_g - T_0) \approx 0.11 - \Delta\alpha T_0,$$

and the last term is not constant for different vinyl monomers. Hence

$$0.11/(v_f)_{T_g} = T_g/(T_g - T_0).$$

Miller[23] suggested that the right-hand side of this equation equals the number of monomeric units at T_g in the "cooperative unit", z_g^*. Then

$$z_g^*(v_f)_{T_g} = 0.11.$$

This condition is another criterion of the glass–liquid change. According to this determination the greater the free volume fraction left for segmental motion movement, the less the "cooperative unit" which is required for this movement to maintain the state of isomobility at T_g. An analogous concept was proposed by Bueche[24], who considered the variation in the free volume and greatest free volume f_c, necessary for the movement of a group of n units.

From what has been stated above, Miller assumes[25] that there is a relation

$$z_g^* S_c = A,$$

where S_c is the configuration entropy. Miller was the first to present the problem of whether the concept of free volume reflects the configuration entropy changes which are taken into account by the parameter z_g^*, the cooperative unit for segmental motion.

It is generally accepted that the viscous flow of polymeric liquids is connected with the rotation of the segments of chains, that is, with conformation entropy. From this point of view Miller assumes that the Simha–Boyer equation is incorrect, since according to it the relative free volume is zero at 0 K, and not at $T = T_0$; under this condition K_1 should be constant. Hence we here again encounter the fact that the constancy or non-constancy of the free volume fraction at T_g depends on how this fraction is expressed. Subsequently, from a consideration of the viscosity of melts at various temperatures and pressures Miller[26] concluded that the mobility of polymeric liquids depends to a much greater extent on the thermal factor than on the volume and that any versions of the free volume theory connecting the viscosity with the relative free volume fraction are inapplicable in real examples.

In all the examples considered above the concept of free volume is based on the position that free volume plays the main part in the properties of a liquid. Meanwhile Miller[27] notes correctly that the whole theory of liquids presumes that the intermolecular potential energy $U(r)$ is an important factor, which determines molecular friction. At the same time the free volume fraction f is connected solely with the intermolecular distance; all the equations which include f are incomplete owing to the absence of an energy term from them. According to Miller[27], for a hypothetical liquid at 0 K the kinetic energy is zero and the volume v_0 is determined exclusively by the potential energy of interaction U_0. The value of U_0 should be closely connected with the vaporisation energy ϵ_0 at 0 K. Hence the parameters ϵ_0, v_0, and the "zero" cohesion energy density, $(\epsilon_0/v_0)_0$, provide a basis for determining the free volume, $v_f = v - v_0$.

There has been shown to be an empirical relation connecting the compressibility coefficient of the liquid β with the free volume fraction:

$$-\beta \simeq kf^2(1-f).$$

Here $\beta = 1/v(\mathrm{d}v/\mathrm{d}p)_T$ at $p = 1$ atm. It was suggested that

$$-f^2(1-f) \approx 5\beta\,(\epsilon/v)_0,$$

or

$$-f^2 \approx 5\beta\epsilon_0/v.$$

In this consideration, energetic and volume factors are introduced into the equations which describe the compressibility of the liquid, and from the standpoint of molecular theory these factors essentially determine the properties of liquids.

On the other hand, in a series of papers after that of Hirai and Eyring[21] ideas have been developed concerning the energies of formation of unit free volume or of 1 mole of holes. The latest of these views was developed by Kanig[28], who simultaneously introduced a refinement into the concept and definition of the free volume. By starting from the position of Frenkel',[29] Kanig divides the free volume into two parts, one of which is determined solely by the thermal vibrations of the atoms in the lattice of a real crystal or liquid, and the other consists of the vacancies or holes proper in the liquid, which make possible an exchange of particles with the sites, that is, ensure the very existence of the liquid state. For this example, new definitions of the free volume fractions are introduced:

$$\varphi_{f_1} = \frac{N_1 v_{f_1}}{N_1 v_{f_1} + N_2 v_{f_2}},$$

$$\varphi_{f_2} = \frac{N_2 v_{f_2}}{N_1 v_{f_1} + N_2 v_{f_2}},$$

where N_1 and N_2 are the numbers of holes and molecules in the system, v_{f_2} is the volume determined by the thermal vibrations, and v_{f_1} the volume determined by the holes. These expressions involve the ratio of the proper volume of the vacancies and the "volume of the vibrations" to the total free volume, as distinct from the usual definition, which includes the ratio of the free volume to the total volume:

$$f_g = \varphi_1^* = \frac{v_1^*}{v_1^* + v_2^*},$$

where v_1^* is the partial volume of the holes, and v_2^* the partial volume of the molecules at T_g, including the volume due to the thermal vibrations. In the first instance, by starting from the total dilatometric curve it can be shown that (Fig. 2) the segment BE represents the quantity

$$N_2 v_{f_2} = T_g \mathrm{d}v_g/\mathrm{d}T,$$

and the segment EL the volume of the vacancies

$$N_1 v_{f_1} = T_g \mathrm{d}v_l/\mathrm{d}T - T_g \mathrm{d}v_g/dT.$$

Hence the free volume is defined as the segment BL:

$$N_1 v_{f_1} + N_2 v_{f_2} = T_g\,\mathrm{d}\,v_l/\mathrm{d}\,T.$$

From many experimental results Kanig deduced that the free volume fraction at T_g usually determined is not constant and that for characteristics of the state of iso-free volume it is more desirable to use the quantities φ_{f_1} and φ_{f_2}, referred to the glass formation temperature, $\varphi_{f_1}^*$ and $\varphi_{f_2}^*$. Then from Fig. 2,

$$\varphi_{f_1}^* = \frac{v_{0g} - v_{0l}}{v_g - v_l},$$

$$\varphi_{f_2}^* = \frac{v_g - v_{0g}}{v_g - v_{0l}}.$$

Actually, it appeared that the quantities $\varphi_{f_1}^* \simeq 0.64$ and $\varphi_{f_2}^* \simeq 0.36$ are less different for different polymers than is the quantity usually determined. The fractions $\varphi_{f_1}^*$ and $\varphi_{f_2}^*$ are, according to Kanig, constants independent of the nature of the substance and which characterise the corresponding states at the glass formation temperature. The relations given show that at the glass formation temperature there should be a constant ratio between the volume of the vacancies and the volume determined by the thermal vibrations, at which translational motion of the molecules becomes possible. In particular, these quantities enter into the equation describing T_g as a function of the degree of polymerisation.

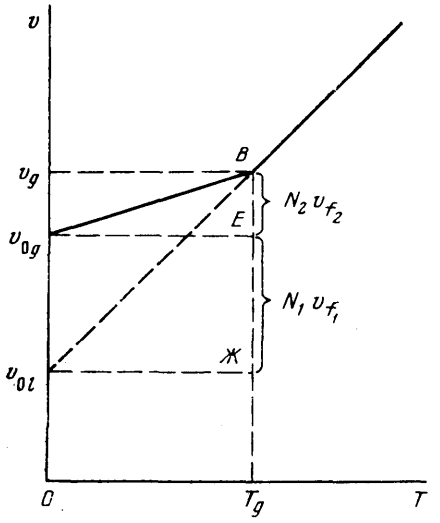


Figure 2. Scheme for the calculation of free volume characteristics after Kanig.

Kanig[30] has introduced allowance for the temperature dependence of the quantity $\varphi_{f_1}^*$, determined from the results for the free volume fraction defined by him above, Below T_g, as the temperature is reduced $\varphi_{f_1}^*$ increases owing to the decrease in the volume due to the vibrations when there is "freezing" of the volume of the vacancies. Above T_g, there is an increase in $\varphi_{f_1}^*$, due to the increase in the volume of the vacancies being faster than the increase in the volume due to the vibrations. At $T = T_g$ the quantity $\varphi_{f_1}^*$ is a minimum. From the condition for an extremum $d\varphi/dT = 0$ it can be found that $\varphi_{f_1}^* = (\alpha_l - \alpha_g)/\alpha_l$. This actually gives the same value for $\varphi_{f_1}^*$, also without allowance for the temperature coefficient. However, Kanig introduces a refinement, according to which for the corresponding states at T_g there are extremal values $\varphi_{f_1}^*$ and $\varphi_{f_2}^*$, which are constants irrespective of the nature of the substance.

Experimental verification of the relations obtained by Kanig and given by him[31] showed that the traditional definition of the free volume fraction according to Fox and Flory or according to Williams, Landell, and Ferry can lead to the best agreement with experiment when allowance is made for the geometric parameter α. Kanig[31] began from the fact that the partial free volume $\varphi_1^* = f_g$ at the temperature of glass formation, as stated above, can be regarded only to a rough approximation as a constant, the mean value of which corresponds to the universal value obtained by the Williams–Lindell-Ferry theory. The real picture is that polymers with more flexible chains exhibit lower values of φ_1^* than polymers with rigid chains. Consequently, Kanig considers it necessary to introduce a parameter a for a characteristic of the corresponding states. The basis for such introduction is the thermodynamic consideration of a polymer melt as a mixture of chain molecules *2* with holes *1* assuming that the melt is saturated with holes at any temperature. By the introduction into the consideration of the energies of interaction in pairs W_{11} (hole–hole), W_{21} (polymer–hole), and W_{22} (polymer–polymer) the partial thermodynamic characteristics of the dilution of the melt with holes can be calculated. The following parameters enter into these expressions: O_1 the contact surfaces of a mole of holes, and O_2 the contact surfaces of a mole of repeating units of the polymer. For the displacement of n_2 moles (links) of the polymeric chains and n_1 moles of holes it can be shown that

$$1/\varphi_{f_1} \simeq \frac{n_2 O_2}{n_1 O_2} \simeq \frac{O_2/v_2}{O_2/v_1}\,\frac{n_2 v_2}{n_1 v_1} \simeq \frac{1}{a}\cdot\frac{1}{\varphi_1},$$

if it is assumed that

$$n_1 v_1 \ll n_2 v_2$$

and

$$\varphi_1 = \frac{n_1 v_1}{n_1 v_1 + n_2 v_2},\quad \varphi_2 = 1 - \varphi_1,$$

where v_1 and v_2 are the molar volumes of the holes and links, and $a = (O_1/v_1)/(O_2/v_2)$. Here a has the physical significance of a parameter determining the size and form of the macromolecules. Kanig assumes that this parameter is more real for the description of the molecule than the coordination number usually employed. From this he deduces an expression for the glass formation temperature:

$$T_g = -\frac{(1 - a\varphi_1^*)\,H_{0l}^*}{R(\ln \varphi_1^* + \varphi_2^*)} = -\frac{\Delta H_1^*}{R(\ln \varphi_1^* + \varphi_2^*)},$$

or

$$T_g = K(\varphi_1^*)\,\Delta H_1^*,$$

where

$$H_{0i} = O_1 \cdot \Delta W_{12},\ \Delta W_{12} = -{}^1/_2(W_{22} + W_{11});$$

the asterisk shows that all the values relate to T_g. Hence the glass formation temperature is related to the free volume and the energy of formation of the holes, and consequently depends on the intermolecular energy ΔW_{12} and the geometric factor a. Starting from the method of consideration used, Kanig found[31], that

$$T_g \Delta\alpha^* = K(\varphi_1^*, a) = \frac{\varphi_1^*}{2a_1\varphi_1^* + (\varphi_2^*)^2/(\ln \varphi_1^* + \varphi_2^*)},$$

where $\Delta\alpha^*$ is the difference between the expansion coefficients above and below T_g. Clearly, this equation would correspond to the Simha–Boyer empirical equation were the quantity K to be constant, that is, in accordance

with the iso-free volume theory, were constant and the value of the parameter a would be the same for all polymers.

Kanig's approach has the advantage in comparison with the others that there is a relation between φ_1^* and a with those parameters determined experimentally, such as $\Delta\alpha$ and ΔC_p (change in heat capacity on going from glass to liquid) and also with ϵ_g the molar energy of cohesion at T_g. This allows φ_1^* and a to be calculated from the experimental results. The mean values thus determined with allowance for the concept of iso-free volume are:

$$\bar{\varphi}_1^* = 0.0235 \pm 0.0050$$

(mean error ± 21%) and

$$\bar{a} = 3.15 \pm 0.35$$

(mean error ± 11%). On the one hand, the correspondence found for the universal value in the Williams–Landell–Ferry theory indicates that the free volume is that volume determined by the holes; on the other hand, from what has been stated it seems that the Simha–Boyer constant is a complex function of φ_1^* and a. The obtaining of an experimental relation between

$$\frac{\varphi_1^*}{2a\varphi_1^* + \varphi_2^{*2}/(\ln\varphi_1^* + \varphi_2^*)} \cdot \frac{1}{T_g}$$

shows a significant departure from linearity. φ_1^* not being constant shows that the iso-free volume concept is not strictly true.

IV. STATE OF THE ISO-FREE VOLUME DURING GLASS FORMATION

The idea that the free volume fraction, determined experimentally using various equations, at the glass formation temperature depends on the type of molecular movements was first expressed in 1967 [32,33] in connection with results on the relaxation of volume for various polymeric systems. Calculations made on the basis of curves for finding equilibrium volume[32,33] allowed the relaxation time to be determined for different temperatures and then the free volume fraction at T_g was determined by the equation of the Williams–Landell–Ferry theory from the calculated quantities a_T and the $\Delta\alpha$ found.

On accepting the validity of the main position of the theory concerning the universal dependence of the coefficient of reduction a_T on the difference $T - T_g$, f_g can be determined from the results for $\Delta\alpha$ and the theoretical values of a_T calculated from the universal values of the coefficients C_1^g and C_2^g of the Williams–Landell–Ferry theory. The value found in this calculation corresponds to the universal one. However, when experimental values of a_T, and not theoretical ones, are used, the calculated free volume fraction, by remaining constant, will be significantly higher than the universal value and be $f_g = 0.08–0.09$. In considering this fact it is necessary to take into account that the value of f_g in the Williams–Landell–Ferry theory comes from results on dynamic mechanical properties, when relaxation processes are connected with the appearance of segmental mobility. In this instance the value of f_g for many polymers is close to universal, since it corresponds to the size of the holes necessary for the migrations of small structural units which determine the relaxation properties under these experimental conditions. However, it was found[33,34] that in polymers there are isophase transformations connected with the mobility of the structural units larger than statistical segments up to the processes which determine the mobility of the supermolecular formations. It is quite evident that the motion of the large structural elements requires a large hole dimension or a large free volume. It must therefore be assumed that in investigating various relaxation mechanisms the free volume fraction needed for the migrations of structural units of various dimensions can be determined. This also follows from other results[32,33] corresponding to the relaxation process with long periods, that is, with kinetic units of large dimensions. It is also quite evident that at the same density of molecular packing (volume of intermolecular vacancies) the actual free volume necessary for effecting one motion or another will be determined by the nature of these movements.

Actually, depending upon the type of molecular motion and the size of the corresponding movement of the kinetic unit the mobility can appear only at a definite value of the free volume, which therefore will depend on the type of the molecular motions. When the free volume is sufficient for the motion of relatively small structural units, for example, of segments, but insufficient for the motion of larger segments of the chains or of the chains as independent kinetic units, then the well-known non-correspondence between the values of T_g determined by different methods occurs. The same conclusion was reached by Sanchez[35], who found theoretically that the mean size of the holes increases with T_g. He assumes that this is connected with the higher T_g for polymers having more rigid chains. The packing of the rigid chains cannot be so compact as that of flexible chains, as a result of which the mean size of the holes increases. For example, for low-molecular-weight compounds the free volume fraction at T_g is less than for polymers, which is regarded as the result of the greater mobility of small molecules, for the realisation of which a smaller free volume is required. According to Mandelkern and coworkers[36], the Simha–Boyer rule should not be observed at all, since the $\Delta\alpha$ for various systems in which T_g can differ significantly lie within narrow limits, $(2.5–4.0) \times 10^{-1}\ K^{-1}$. However, Simha and Boyer[37] consider such a conclusion erroneous owing to the incorrect treatment of the experimental results.

The limitations of the picture predicted within the framework of the Simha–Boyer theory lead to a search for new ways of improving it. It was carried out by Simha and Weil[38] who allowed for the temperature dependence of the coefficients α_l and α_g, which led to the need for extrapolating the volumes for the liquids to temperature below T_g with the aid of non-linear functions connecting volume and temperature. Such a consideration is based mainly on the fact that in a series of polymers with increasing side-chain length there is a systematic decrease in $\Delta\alpha \cdot T_g$, which suggests that there should be a considerable decrease in f_g in such systems.

According to Simha and Weil[38] there is a need to reconsider the postulate of free volume at T_g. On taking into account the temperature dependence of α_l and α_g, Simha and Weil[38] gave the following alternative expression for the free volume fraction:

$$(v_f)_{T_g} = 1 - \exp\left[-\int_0^{T_g}(\alpha_l - \alpha_g)\,dT\right] \equiv (v_{0g} - v_{0l})/v_{0g}, \qquad (10)$$

where v_{0l} and v_{0g} are the experimental and absolute zero volumes of the liquid and glass corresponding to the non-linear functions of the temperature dependence of both the expansion coefficients. Hence v_f is independent of temperature in the range $0 \leq T \leq T_g$, since the second identity is observed in this range of temperatures. Hence v_f can

be regarded as a characteristic of the packing density of the glass at absolute zero. The first equality can be formally extended to the range $T > T_g$ by extending the upper limit of integration, which requires extrapolation of the vitreous state into the liquid region.

On the other hand, the occupied volume is simply v_{0l}, and hence

$$(v_f)_{T_g} = 1 - \exp\left[-\int_0^{T_g} \alpha_l dT\right] \equiv (v - v_{0l})/v. \qquad (11)$$

Eqns. (10) and (11) give the most general expression for the Simha–Boyer rule. Simha and Weil[38] showed that since $\alpha \leq 8 \times 10^{-4}$ K^{-1} and $T_g < 5 \times 10^2$ K, for most of the polymers the exponents can be replaced by a series yielding

$$(v_f)_{T_g} \approx \int_0^{T_g} (\alpha_l - \alpha_g)\, dT \left[1 - {}^1/_2 \int_0^{T_g} (\alpha_l - \alpha_g)\, dT\right]$$

and

$$(v_f)_{T_g} \approx \int_0^{T_g} \alpha_l dT \left[1 - {}^1/_2 \int_0^{T_g} \alpha_l dT\right].$$

From the first equation, by neglecting the quadratic terms, we find that

$$(\alpha_l - \alpha_g) T_g \approx (v_f)_{T_g} + [\alpha_l n/(n+1) - \alpha_g m/(m+1)]\, T_g,$$

where α_l and α_g should be taken at T_g; n and m are constants. Hence the constancy of the left-hand part of the last equation does not signify that the free volume is constant, but quite the contrary. Since Eqns. (10) and (11) involve integration of the function $\alpha_l(T)$ over the range $0 \leq T \leq T_g$, not realisable experimentally, Simha and Weil give a method for the necessary extrapolation using reduced functions of temperature and pressure. Application of Eqn. (11) to the experimental results showed that there is a systematic decrease in the product $(\alpha_l - \alpha_g)T_g$ as the length of the linear side-chains of the polymers in the methacrylate series is increased. The experimental results also showed that the value of $(v_{0g} - v_{0l})/v_{0g}$ is not constant at T_g, whereas the ratio $(v - v_{0l})/v$ at T_g is comparatively stable. It was found that the main part of the discrepancies between the f_g for the individual systems at T_g is connected with the contribution of the vitreous rate to the free volume.

The change in the value of f_g for the various polymers can be significantly less when allowance is made for the non-linear temperature dependence of the specific volume of the polymer in the liquid and vitreous states. The decrease in f_g as the temperature is reduced also follows from Moacanin and Simha[39], who considered the entropy of mixing of holes and segments with allowance for the temperature dependence of the hole concentration needed for the minimisation of the free energy. The temperature T_2 at which the system is in equilibrium and the product $\Delta\alpha \cdot T_2$ in the Gibbs–DiMarzio theory[40] are functions only of the free volume v_g. The constancy of the product $\Delta\alpha \cdot T_2$ at $T = T_2$ corresponds to the constancy of $\Delta\alpha \cdot T_g$, if the temperature T_2 is proportional to T_g.

The results described above suggest that the concept of iso-free volume at T_g cannot be considered as proved and it is disproved by new experimental results. Consequently several papers[27,30] suggest that at T_g the liquid and polymer are not in a state of iso-free volume but in a state of iso-viscosity (the iso-viscous state).

In connection with this a modification of the Simha–Boyer rule was proposed, which can be expressed in the form[41]:

$$\frac{{}^1/_2\,[(dv/dT)_l + (dv/dT)_g]\, T_g}{v_g} = K_3.$$

The constant K_3 depends upon the type of bond in the main chain of the polymer and is constant for each class of polymer. Ellerstein[41] assumes that the physical interpretation of this equation can be combined with the concept of iso-free volume. However, in practice the introduction of this correction implies, as we assume, a departure from the concept of iso-free volume. There are other arguments against the ideas of iso-free volume. Thus, Kastner[42] observed that the dielectric losses decrease during isothermal decrease in volume, which shows that relaxation time depends on the free volume. However, the reduction factor calculated assuming that the relaxation time is determined solely by the free volume differs significantly from that found experimentally.

Serious objections against the concept of iso-free volume have been expressed[43] on the basis of published results[44]. It was shown that β-relaxation in poly(methyl methacrylate) and poly(hydroxypropylene glycol) under constant pressure and constant volume conditions proceed analogously. This is difficult to reconcile with the concept assuming that the changes in viscosity and mean relaxation time are due mainly to a change in free volume. To keep this concept in force it is necessary to postulate the existence of a large negative expansion coefficient for the occupied volume.

A departure from the Simha–Boyer equation for linear polymers with increase in the length of the side-radical was observed by Simha[45]. Mandelkern and coworkers[36] used many published results and their own experiments to try to find the limits of applicability of the Simha–Boyer equation. $\Delta\alpha \cdot T_g$ and $\Delta\beta \cdot T_g$ were plotted against T_g, where

$$1/v\,[\partial v/\partial T)_l - (\partial v/\partial T)_g] \equiv \Delta\alpha$$

and

$$[(\partial v/\partial T)_l - (\partial v/\partial T)_g] \equiv \Delta\beta.$$

It was found that $\Delta\alpha \cdot T_g$ and $\Delta\beta \cdot T_g$ are not constant and consequently the Simha–Boyer equation is of restricted application. The results obtained show that $\Delta\alpha \cdot T_g$ increases with T_g therefore it is incorrect to use concepts including the product $\Delta\alpha \cdot T_g$ as a universal constant in theoretical investigations of glass formation. Mandelkern and coworkers[36] emphasise that this conclusion does not touch the free volume theory itself or its role in glass formation phenomena.

Practical arguments in support of the concept of iso-free volume and attempts at the direct determination of f_g from experimental results have not been given. Thus whereas Curro[46] found $f_g = 0.0261$ for poly(methyl methacrylate) on the basis of a determination of free volume from results on the difference in the specific volume of a polymer and its partial volume in solution, Buniyat-Zade and Ismailov's studies[47] of the temperature dependence of specific volume gave $f_g = 0.025$ for linear polyethylene, whereas for branch-chain or with graft acrylonitrile chains the f_g considerably exceeds the universal value, reaching 0.127. In considering the state equation of the polymers and the characteristics of the vitreous state, Curro[46] found that the agreement between the experimental results

and the product $\Delta\alpha \cdot T_g$ is only semiquantitative. It was also shown[48] that the relation between T_g and pressure, which is predicted by the iso-free volume concept, is not observed by many polymers which also casts doubt upon it. Letunovskii and Zelenev[49] calculated the free volume fraction by starting from the relation they proposed:

$$T_\infty = T_g - f_g/(\alpha_l - \alpha_g),$$

where T_∞ is the temperature at which the viscosity tends to infinity. Assuming that there is a better basis for this equation, since it does not contain the arbitrary quantity B of the Williams–Landell–Ferry equation, Letunovskii and Zelenev[49] found $f_g = 0.0048$ for poly(methyl methacrylate) which is significantly lower than the universal value. The lower free volume fraction at T_g for n-alkanes and polyethylene than for vinyl polymers has been found[1,50].

A very interesting approach to the theoretical prediction of the limiting value of $\Delta\alpha \cdot T_g$ has been published[35]. Free volume theory has been used to consider the thermodynamics of the mixing of molecules with holes. As a result Sanchez[35] concluded that

$$T\alpha_h = \frac{E_h/RT}{\exp(1 - 1/r + E_h/RT) - 1}, \qquad (12)$$

where α_h is the fraction of thermal expansion associated with the change in the concentration of the holes (expansion of the free volume), E_h the hole formation energy,

$$r = M/\rho v_h N_A,$$

N_A is Avogadro's number, M the molecular mass, ρ the density of a hole-free liquid at absolute zero, and v_h the hole volume. The $1/r$ term is very small for polymer systems and then $T\alpha_h$ is a function only of E_h/RT. The quantity α_h is identified with the experimentally determinable change in the coefficient of thermal expansion at T_g, that is:

$$T_g\alpha_h = T_g \cdot \Delta\alpha.$$

The graph constructed from Eqn. (12) shows that the predicted value of $\Delta\alpha \cdot T_g$ passes through a maximum at a value of 0.159, which corresponds to $E_h/RT = 0.841$. Almost all the values of $\Delta\alpha \cdot T_g$ given in the literature lie below this theoretical limit. The hypothetical value of $\Delta\alpha \cdot T_g$ varies relatively little with hole formation energy. For E_h/RT between 0.5 and 2.0 we have $0.105 < \Delta\alpha \cdot T_g < 0.159$.

It has been shown[35] that changes in the difference between the expansion coefficients at T_g can be predicted from the constant of the Williams–Landell–Ferry equation ($T_\infty = T_g - C_2$). Then

$$\Delta\alpha = 2(T_\infty/T_g)[\exp(1 + 2T_\infty/T_g) - 1]^{-1}.$$

Here it is assumed that $T_\infty = T_2$, where T_2 is the temperature of a second-order transformation, according to the Gibbs–DiMarzio theory[40]. The free volume is then determined as:

$$v_f = (v - v_\infty)/v_0,$$

where v_∞ is the macroscopic volume of the liquid at the temperature T_∞ and v_0 is the volume of the molecules.

Theory predicts that at the T_0 appearing in the Fogel equation the iso-free volume state should occur. However, consideration of the calculated values of f_g shows that this does not take place. Other examples of departures from the behaviour predictable within the framework of the iso-free volume concept have been described[51,52]. We have already noted Kanig's conclusion about the variation of f_g with the flexibility of the polymeric chain[31] and our conclusion about dependence upon the packing density[32,33]. In this connection it is desirable to consider the problem of whether there really exists a definite relation between the free volume fraction at the glass formation temperature and the molecular parameters of the polymeric chain.

V. VARIATION OF THE FREE VOLUME FRACTION AT THE GLASS FORMATION TEMPERATURE WITH THE MOLECULAR PARAMETERS OF LINEAR POLYMERS

As noted above, the constancy of f_g for various polymers differing in their chemical structure is only a rough approximation. From several qualitative arguments and results on glass formation in a series of polyurethanes it was suggested[53] that the experimentally observable change in free volume for different polymers can be connected with their molecular parameters, above all with the flexibility of the chain. It is now desirable to prove this in detail by finding the relation between the free volume and the nature of the molecular packing.

For this purpose it is convenient to use the definition of the free volume fraction given by Litt and Tobolsky[19], that is, to state, in accordance with Fig. 1, that the occupied volume is v_3''. From an analysis of results on the molecular parameters of a series of polymers there is a definite tendency towards an increase in the ratio v_3''/v_g as the size of the side-groups of the polymeric chain is increased. The ratio of the volumes of the polymer in crystalline v_c and amorphous v_a states is connected with the characteristic parameter of the chain a/σ, where a is the thickness of the chain determined by the dimensions of the elementary cell and σ a steric factor or the flexibility parameter of the isolated polymeric chain, which usually can be estimated from measurements of the characteristic viscosity in the ideal solvent[54]. A relation was found between v_c/v_a and a/σ.[55,56] It was found that there is a definite tendency for v_3''/v_g to increase with a/σ.

It can be proved that the ratio v_3''/v_g equals the ratio of the packing factors of the polymer in the amorphous and crystalline states K_a/K_c at T_g, since by definition

$$K_a = N_A v_i/v_a \text{ and } K_c = N_A v_i/v_c;$$

here v_i is the van der Waals' volume of the repeating unit of the chain, and N_A Avogadro's number. We note that the calculated values of $(K_c)_g$ correlate with the characteristic parameter of the chain a/σ, and the ratio between them can be expressed as follows:

$$(K_c)_g = 0.9(1 - 0.058\, a/\sigma). \qquad (13)$$

Hence we can state that the free volume fraction at the glass transformation temperature, as determined according to Eqn. (2) will be less when the packing of the chains in the bulk of the polymer becomes looser. This conclusion agrees with the analogous quantitative conclusion reached earlier[35,34].

Presumably this conclusion is general for all polymers in the amorphous state. However, Eqn. (13) cannot be applied directly to polymers which do not crystallise, since then v_3'' or a is unknown. In trying to extend to

these polymers the ideas expressed above we can propose another definition of f_g, analogous to the Simha–Boyer expression:

$$f_g = (\alpha_l - \alpha_g)(T_g - T''),$$

where T'' is a comparison temperature connected with the occupied volumes v_0'', v_3'', and v_2'', as is shown in Fig. 1. For example, $T'' = 0$ K corresponds to the Simha–Boyer theory, $T'' = T_3$ to the Little–Tobol'skii theory, and $T'' = T_2$ corresponds to the Williams–Landell–Ferry definition. We obtained[53] the following empirical equation, connecting T_g with the chain rigidity parameter σ:

$$T_g = A(\sigma - b), \qquad (13a)$$

in which A and b are constants. This equation can be compared with the Simha–Boyer equation (7). If now it is assumed that A is proportional to K_1, Eqn. (7), and $\Delta\alpha$ is proportional to $(\sigma - b)^{-1}$ and then Eqns. (7) and (13a) are solved for T_g, we obtain:

$$\Delta\alpha, K^{-1} = 4.2 \cdot 10^{-4}(\sigma - 1)^{-1}. \qquad (14)$$

As was shown above, our results[53] are a basis for this assumption. Consequently, if the assumed proportionality between the parameters of the equations is real, the constant K_1 in Eqn. (13) does not have to be the same for all the polymers.

Clearly $\Delta\alpha$ is actually not constant but increases with the flexibility of the chain (that is, with decrease in σ). Hence if the Simha–Boyer equation and our Eqn. (13) are valid, the relation between $\Delta\alpha$ and $\Delta\alpha\sigma$ should be straight lines with slope unity. And actually $\Delta\alpha$ has a tendency to increase as σ is reduced, although this behaviour also cannot be described quantitatively by Eqn. (14). The departure of the experimental points from the theoretical line becomes especially significant when $\Delta\alpha$ is reduced.

It is noted that the best agreement between the experimental values of $\Delta\alpha$ and the theoretical relation is observed for those polymers which obey the Simha–Boyer rule. This again emphasises that f_g is not constant. A more complete representation of the relation between $\Delta\alpha$ and σ is given by the relation between $\lg\Delta\alpha$ and $\Delta\alpha\sigma$, for which considerably better agreement is observed between the experimental points and the theoretical straight line even for those polymers which do not obey the Simha–Boyer rule.

It seems possible to give a qualitative explanation of the observed relation between $\Delta\alpha$ and the rigidity parameter σ. By definition, α_g depends on the anharmonicity of the thermal vibrations of the individual molecules or of the groups they contain and hence the physical nature of α_g is approximately the same for polymers and low-molecular weight liquids. On the other hand, the nature of α_l is not the same. The value of α_l for liquids is reduced as the forces of intermolecular interaction are increased, whereas T_g increases[16], and therefore it is natural to expect an approximately constant product $\Delta\alpha \cdot T_g$, that is, the Simha–Boyer rule is satisfied.

For polymers the quantity α_l does not depend solely on the intermolecular interaction, which affects the mean distance between the centres of gravity of the molecular groups of the chain, but also on the ability of the macromolecules to undergo conformational transformations, which are closely connected with the flexibility of the chain. Then for polymers we can write approximately

$$\Delta\alpha = (\alpha_l)_p - \alpha_g = (\alpha_l - \alpha_c)_m + \Delta\alpha_{conf},$$

where the indices m and p refer to the polymer and monomer, $\Delta\alpha_{conf}$ is the additional contribution to $(\alpha_l)_p$ due to the change in the number of conformations of the chains in the melt[56]. Hence it seems that the numerical value of the coefficient $\Delta\alpha$ for the polymers will depend significantly on the size of the "polymer" contribution $\Delta\alpha_{conf}$, which apparently will be different for polymers with chains of different flexibility.

The conclusion that the free volume fraction at T_g is not a universal constant for linear polymers of different molecular structure can be confirmed qualitatively by the following arguments[57]. We assume that at temperature much lower than T_g the polymeric chains are in a state with minimal energy of the intermolecular interactions, that is, the fraction of the bonds with high energy equals zero[40]. On the other hand, the equilibrium of the fraction of bent chains at $T > T_g$ obey Boltzmann statistics. Then the fraction of bent chains at T_g can be determined from the well-known relation:

$$\varphi_g = [\exp(-\epsilon/kT_g)]/[1 + \exp(-\epsilon/kT_g)]. \qquad (15)$$

From Eqn. (15), the fraction φ_g decreases with increase in ϵ/kT. On taking into account the fact that an increment of volume for a single bent bond will be greater than for a straight bond, this indicates that the fraction of the free volume f_g at T_g which can be identified with the quantity φ_g of Eqn. (15) will actually decrease as the packing density of the polymers in the crystalline state is reduced. Treatment of the experimental results on the variation of the glass formation temperature with the flexibility of the polymeric chain[57] showed that by starting from general equation (13) an expression can be obtained for linear polymers relating T_g with the free volume in the following manner:

$$T_g = T_g(\text{LPE}) + [\sigma - \sigma(\text{LPE})] \cdot Y(f_g),$$

where σ(LPE) refers to linear polyethylene, and $Y(f_g)$ is a function which can be determined from the experimental results.

Hence the results considered show the need for reconsidering the concept of glass formation temperatures as corresponding to the state of iso-free volume. It is remarkable that f_g decreases as a/σ is increased. These changes are brought about mainly by variations in the packing coefficients in the crystalline state, whereas the packing coefficients in the amorphous state $(K_a)_g$ remain almost constant. It seems reasonable to assume that this quantity $(K_a)_g$ should be chosen as a measure of the free volume at glass formation temperature. In other words, the determination of the occupied volume as a characteristic volume or van der Waals' volume of a repeating unit of a chain with a low (approximating to zero) thermal expansion coefficient is the most suitable. Such an approach does not conflict with the possible definition of free volume discussed by Bondi[58].

VI. THE CONCEPT OF FREE VOLUME DISTRIBUTION

From the standpoint of the ideas introduced that the free volume fraction at T_g is not constant even for the same type of molecular movements in different polymers and for different types should be different, a consideration of the distribution of the free volume in a system is of interest.

The concept of free volume distribution was developed by Turnbull and Cohen[16]. It is based on the assumption that molecular movements, like transport phenomena, take place only when the vacancies or holes in a body have dimensions greater than some critical value v^*. This critical volume arises as a result of the redistribution of free volume in the system. It is assumed that such a redistribution of free volume takes place without consumption of energy. The concept of excess volume is therefore introduced:

$$\bar{v} - v_0 = \overline{\Delta v}$$

(where $\bar{v}$ is the specific volume and v_0 the volume of the molecules) and the free volume is v_f, such that

$$\overline{\Delta v} = v_f + \Delta v_c,$$

where Δv_c is the volume determined by the thermal vibrations.

It was suggested[16] that only part of the excess volume v_f can be redistributed without consumption of energy. This takes place above the critical temperature T_2. In this instance the thermal expansion of the amorphous phase at low temperatures is due solely to the anharmonicity of the thermal vibrations of the molecules. Hence $v_f \simeq 0$ at the $T < T_2$ and $\Delta\bar{v} \simeq \Delta v_c$. It is also suggested that in this instance an increase in entropy due to the change in volume is also very small. As the temperature is raised and a certain value of Δv is reached the main contribution starts to be the expansion of the "free" for redistribution volume,

$$v_f = \alpha \bar{v}_m (T - T_2),$$

where α is the mean expansion coefficient, and $\bar{v}_m$ the mean volume of the molecules in the temperature range from T_2 to T_g.

The free energy of the amorphous phase should be a minimum when the free volume is distributed in a random manner. Since a random distribution of the volume occurs only in the amorphous, and not the crystalline, phase, under the condition $\Delta\bar{v} > \Delta\bar{v}_g$ the amorphous phase should be more stable than the crystalline, owing to the positive configuration entropy, determined by the definite distribution of the free volume. Therefore, according to Turnbull and Cohen[16], the glass formation temperature of the amorphous phase is defined as the temperature at which the excess volume reaches the value $\Delta\bar{v}_g$, above which a free volume exists.

The probability that the free volume at a given temperature exceeds some value v^* is, according to Fujita[6], given by the relation

$$P(v^*) = \exp[-Bv^*/\langle v\rangle],$$

where $\langle v\rangle$ is the mean free volume of one molecule, that is, the total free volume divided by the number of molecules; B is a numerical factor close to unity. Another definition can also be introduced—the mean free volume per unit volume, that is, the mean free volume fraction f. On putting $Bv^* = C$, then

$$P(C) = \exp(-C/f).$$

These ideas were used to describe diffusion in polymers of low-molecular-weight substances[59]. The mobility of the molecules m_d in the medium will depend on the probability that the molecule will appear in a neighbouring hole is large enough to ensure its displacement. We will use C_d to denote the value of C corresponding to the least hole size necessary for such a displacement. Then

$$m_d = A_d \exp(-C_d/f),$$

where A_d is a factor depending upon the size and form of the solvent molecules.

Litt[60] developed ideas about the least possible diameter b^* of a hole associated with a macromolecule for effecting molecular or segmental motion. According to him, only a hole with a diameter not less than b^* can affect the viscosity. Hence a modified Doolittle equation can be obtained:

$$\ln(\eta/\eta_0) = \pi^{1/2}/[A(T^*/T)^{1/2}(1 + T^*/T)^{-1}\exp(T^*/T)],$$

where

$$A = {}^1/_3\,\pi b^{*}n,$$

n is the number of molecules per 1 cm^3, $T^* = 4\pi b^{*2}\epsilon/\kappa$, ϵ is the surface tension, κ the Boltzmann constant, and T^* the characteristic temperature. The A varies from 0.75 for flexible to 1.4 for rigid polymers. The constant $T_g/T^* = 0.360 \pm 0.1$ was observed for many systems. It is suggested that such a modification of the free volume theory improves its physical reliability. Thus, whereas according to the Williams–Landell–Ferry equation $f \simeq 0$ at $T_g = 50°C$, and then $\ln\eta \to \infty$, in the example under consideration f/f decreases monotonically at $T < T_g$ reaching zero only at 0 K.

The need to divide free volume into its constituent components was also stated by Razumovskaya and Bartenev[61]. It was noted that the free volume fraction according to Williams–Landell–Ferry is less than its estimate from other results, for example, from compressibility. According to Razumovskaya and Bartenev's results[61], for several polymers the free volume fraction at the glass formation temperature reaches 10–15%, whether it is calculated from compressibility results or from assumptions concerning the additivity of volume for different atomic groups. Mason[62] explains this difference by certain "holes" having lost their characteristic mobility, termed "frozen". Reference is made here not to a quantitative retardation of the hole migration process, but to the complete exclusion of some of the holes from the process. Hence a distinction must be made between the geometric free volume (~10–15% of the entire volume), which corresponds to the Simha–Boyer definition, and the physical free volume, determined by the relaxation time (3%).

The physical free volume v_f is defined as $v_f = v_d n^*$, where v_d is the volume of excited holes, n^* the number of excited holes. The fraction of excited holes at the glass formation temperature will then be $n^*/n = f^*/f_{eff} \simeq 0.1$, where n is the total number of holes in the system, f^* the fraction of physical free volume, and f_{eff} the fraction of geometric free volume. Glass formation is regarded from this standpoint as "freezing" of the characteristic frequencies, which is accompanied by a decrease in the free volume and mobility of the holes. In this it is suggested that molecular rearrangements are brought about by the movement of holes corresponding to definite kinetic units with a characteristic frequency of the thermal vibrations. Such a position corresponds to the ideas we have developed that the motion of parts of different size or different groups of atoms requires a different free volume.

Actually, results on the isothermal contraction for several polymers[3] treated on the basis of the free volume theory show that the quantitative kinetics are not described

by a simplified model of the polymer with a single mean relaxation time. Many investigations showed that instead of one relaxation process, relaxation spectra and a distribution of relaxation times must be considered. Kastner[59] attempted to connect this distribution with the free volume distribution. In this connection, Covacs concluded[3] that in considering only the mean parameters of macroscopic specimens (complex modulus, volume, heat content, etc.) the free volume concept should be linked with the change in the molecular mobility and with different types of molecular movements. These processes include a wide distribution of delay times, which can be associated with the local distribution of holes.

Mason[62] developed ideas about the distribution of free volume to explain the diffuseness of the change from the vitreous state to the liquid by assuming the localisation of part of the free volume, which distinguishes the polymeric substance from the true liquid state, where the free volume is not localised. In connection with rubber vulcanisers Mason assumes that in the non-cross-linked state there can still be an arbitrary distribution of the free volume v_f connected with the free volume v_f' of each monomeric unit. Taking the universal value of 0.025 for f_g in this, he assumes that the mean volume per monomeric unit is expressed as

$$\bar{v}' = M_v/nN_A,$$

where M is the molecular mass of the rubber, n the number of monomeric units in the molecule, and v the specific volume. The monomeric specific free volume f' will be defined as

$$f' = v_f'/\bar{v}' = (nN_A/M_v)v_f'.$$

The geometry of the packing can be characterised by distribution functions $P(f')$ which represent the density of the monomeric units with the specific free volume[62].

The effective T_g for a monomeric unit is determined by the condition $f' = f_g$. Hence the number of monomeric units in 1 g rubber at temperature T_g equals

$$n_g = \int_0^{f_g} P\,df'$$

in the vitreous state and

$$n_l = \int_{f_g}^{\infty} P\,df'$$

in the liquid state; under normalisation conditions

$$\int_0^{\infty} P\,df' = N_A n/M.$$

Hence the distribution coefficient is

$$\alpha = \left(\int_0^{f_g} P\,df' \cdot \alpha_g + \int_{f_g}^{\infty} P\,df' \cdot \alpha_l\right) \Big/ \int_0^{\infty} P\,df'$$

and

$$\alpha - \alpha_g = \frac{M(\alpha_l - \alpha_g)}{N_A n} \int_{f_g}^{\infty} P\,df'.$$

In the last equation it is assumed that at an arbitrary temperature T there are units present in both the vitreous and in the liquid state, as determined by the distribution coefficient. The coefficient α is regarded here as the sum of the expansion coefficients of each region with allowance for the numerical fraction of the units.

The value of the integral, representing the number of monomeric units found in the liquid state decreases from $N_A n/M$ at a temperature above T_g (where $\alpha = \alpha_l$) to zero below T_g (where $\alpha = \alpha_g$). When all the monomeric units have the same specific free volume f', then the change into the liquid state will take place at a single temperature. The "blurring" of the change for some interval of T is connected with the distribution of f' and the temperature interval in which α decreases from α_l to α_g gives a measure of the width of this distribution. Hence assuming a normal distribution of f' at a temperature above T_g the mean value of f' will equal the macroscopic f, and the distribution will be:

$$P = P(f) = \frac{1}{\sigma\sqrt{2}} \exp\{-[(f' - f)^2/2\sigma^2]\},$$

where σ is the dispersion. Hence with allowance for the normalisation conditions, we have:

$$\alpha - \alpha_g = \frac{M(\alpha_l - \alpha_g)}{N_A n} \frac{1}{\sigma\sqrt{2}} \int_{f_g}^{\infty} \exp[-(f' - f)^2/2\sigma^2]\,df'.$$

Close to T_g the value of σ can be taken as constant, and then the temperature enters into the function being integrated only through f. Bearing in mind the equations obtained, Mason[62] succeeded in calculating the distribution of the free volumes for monomeric units $P(v_f')$ with vulcanisers which are characterised by a different cross-linking density.

Ideas about the free volume distribution provide a significant contribution to understanding the mechanism of the glass formation processes in polymers and in the development of free volume theory. The need for taking into account the free volume distribution in the system was also shown in passing by Kanig[31] and Sanchez[35]. However, ten years elapsed before a new treatment of the problem of free volume distribution based on the ideas of the distribution of holes according to size appeared. Kilian[63] analysed glass formation from the viewpoint of thermodynamics as the displacement of the polymeric chains with holes of homogeneous dimension, the mixture being regarded as a saturated solution of linear chains, containing y_p repeating units. However, since the vacancies or holes exhibit a distribution in sizes, a quasistatistical glass formation temperature is considered at which glass formation takes place according to a cooperative mechanism. From this we calculated the partial molar enthalpy of mixing with allowance for the zero interaction of the holes with one another and of the holes with the polymer. It is assumed that the formation of holes in the medium always requires the same excess enthalpy. On this basis Manabe and Takayanagi[64] obtained the following equation for T_g:

$$\frac{1}{T_g} = \frac{R}{A_p^h \varphi_p} \cdot \frac{1}{y_p} + \frac{A_p^s}{A_p^h} + \frac{R}{A_p^h y_{Li} \varphi_p^2} \left\{ \frac{y - \varphi_p}{\bar{y}_i} y_{Li} - \ln \varphi_{Li} - 1 \right\},$$

$(i = 1, \ldots, N)$,

where A_p^h is the specific entropy of formation of any holes, A_p^s the excess entropy of formation of the holes, $\varphi_p = y_m n_m / \Sigma y_i n_i$, y_{Li} is the hole size, $\bar{y}_i$ the mean particle size in the mixture, φ_{Li} the fraction of holes of size i. From this equation, it follows that for a polymeric system in which there is a distribution of holes according to sizes,

the volume fraction of holes φ_{Li} should be different and depend on y_{Li}. From the thermodynamic point of view, for each fraction of holes there is a quantity y_{Li}, which should satisfy the condition of thermodynamic equilibrium.

Comparison of the last equation with published results relating T_g with the chain length y_p showed[63] that if the normalisation condition is taken to be

$$\Sigma \varphi_{Li} = 1 - \varphi_p,$$

then

$$\varphi_{Li} = \left[\frac{(1-\varphi_p)e}{(1-\varphi_p)e+1}\right]^{y_{Li}} \cdot \frac{1}{e}$$

is a distribution function for the holes according to size. When the iso-free volume condition $\varphi_L(T_{g\infty}) = \text{const}$ is obeyed, the distribution function φ_{Li} is also invariant with respect to the system.

Calculations of the entropy of formation of the holes showed that it is negative, that is, there cannot be a statistically disordered homogeneous distribution of holes. However, Kilian[63] considers as problematical the distribution of holes according to the condition $1 \leqslant y_{Li} = \infty$ without a connection with the molecular structure. The distribution function is monotonic for a saturated mixture and the volume fraction of holes of large dimension rapidly decreases as y_{Li} is increased. It is assumed that the ideas about distribution correspond best to the statistical nature of the molecular configurations in the liquid phase. According to Frenkel', the free volume in a liquid in principle is not connected with the sizes of the molecules but is comparable with the atomic dimensions[29]. It must be taken into account that the holes should be distributed irregularly, at least in a polymer to ensure that a variety of types of molecular movement is possible.

The concept of free volume distribution was developed further by Manabe and Takayanagi[64-66], who applied it to the glass formation temperatures of mixtures of two polymers. Comparison of the theoretical ideas with experiment showed that a different distribution of the free volume is possible in mixtures. They found experimental proof that the glass formation temperature corresponds to the iso-free volume state. The same T_g can also correspond to different distribution functions owing to a difference in the structure of mixtures. Hence although the free volume is an important characteristic of the glass formation process, different distribution functions of T_g correspond to different distribution functions of free volume.

The inapplicability of the concept of iso-free volume to mixtures of polymers was also shown in studies[68,69] based on theoretical ideas about the distribution and localisation of the free volume in heterogeneous polymeric systems.

---o0o---

The results of the many investigations reviewed in the present paper suggest that the concept of glass formation as a state of iso-free volume cannot be regarded as justified, either theoretically or experimentally. This became especially clear after it was observed that even for the same polymer the free volume fraction could change depending upon the conditions of formation of its structure[68]. All this shows that although the concept of free volume is physically reasonable, its use to describe the properties of polymers involves considerable difficulties in some instances. This restriction is evident particularly clearly in considering glass formation as a process corresponding to the iso-free volume condition.

Therefore one of the main tasks in the field of free volume theory and the theory of glass formation is the development of new concepts and the production of new parameters of corresponding states. Thus, Miller[23] introduces the concept that glass formation corresponds to an iso-relaxation state, and at molecular masses below critical it corresponds already to the condition of an "iso-viscous" state. We assume that since the free volume concept itself characterises the state of ordering of the system (especially when we consider the free volume distribution function), then the thermodynamic description of the processes which take place during glass formation through configuration entropy and the breakdown of the kinetic description of this process is more hypothetical. According to Adam and Gibbs[1], glass formation takes place when the system reaches some minimum configuration entropy. Its value can be calculated from the relation:

$$\Delta S_c = \Delta C_p \ln (T_g/T_0),$$

where ΔC_p is the jump in heat capacity during glass formation. Such an approach shows, in particular, that the quantity ΔS_c can also reflect the effects connected with the existence and distribution of free volume. Hence ideas about glass formation as an isentropic transformation, in accordance with the Gibbs–DiMarzio theory, can be extremely promising.

REFERENCES

1. G. Adam and J. Gibbs, J. Chem. Phys., 43, 139 (1965).
2. M. Goldstein, J. Chem. Phys., 39, 3369 (1963).
3. A. Covacs, Rheol. Acta, 5, 262 (1966).
4. J. D. Ferry, "Viscoelastic Properties of Polymers" (Translated into Russian), Inostr. Lit., Moscow, 1963.
5. A. Doolittle, J. Appl. Phys., 22, 1471 (1951).
6. H. Fujita, Fortschr. Hochpolymer Forsch., 3, 1 (1961).
7. D. Machin and C. Rogers, Makromol. Chem., 155, 269 (1972).
8. J. Waghizadeh and K. Ueberretier, Koll. Z. Z. Polymere, 250, 98 (1972).
9. D. Patterson, Macromolecules, 2, 672 (1969).
10. F. Bueche, J. Chem. Phys., 21, 1850 (1953).
11. R. Simha and F. Boyer, J. Chem. Phys., 37, 1003 (1962).
12. T. Fox and P. Flory, J. Appl. Phys., 21, 581 (1950).
13. N. Hirai and H. Eyring, J. Polymer Sci., 37, 51 (1959).
14. B. Wunderlich, J. Phys. Chem., 64, 1052 (1960).
15. M. Williams, R. Landell, and J. Ferry, J. Amer. Chem. Soc., 77, 3701 (1955).
16. D. Turnbull and M. Cohen, J. Chem. Phys., 34, 120 (1961).
17. R. Boyer, Rubber Chem. Technol., 36, 1303 (1963).
18. A. Miller, J. Polymer Sci., [A2], 1095 (1964).
19. M. Litt and A. Tobolsky, J. Macromol. Sci.-Phys., B1, 433 (1967).
20. A. Miller, Macromolecules, 2, 355 (1969).
21. N. Hirai and H. Eyring, J. Appl. Phys., 29, 810 (1958).
22. A. Miller, Macromolecules, 5, 679 (1970).

23. A. Miller, J. Chem. Phys., 49, 1393 (1968).
24. F. Bueche, in "The Physics of Polymers" (Translated into Russian), Inostr. Lit., Moscow, 1960, p.70.
25. A. Miller, J. Polymer Sci., [A2], 6, 249 (1967).
26. A. Miller, Amer. Chem. Soc. Polymer Prepr., 15, 412 (1974).
27. A. Miller, J. Polymer Sci., [A2], 4, 415 (1966).
28. G. Kanig, Kolloid Z. Z. Polymere, 190, 1 (1963).
29. Ya. I. Frenkel', "Kineticheskaya Teoriya Zhidkostei" (Kinetic Theory of Liquids), Izd. Akad. Nauk SSSR, Moscow, 1949.
30. G. Kanig, Kolloid Z. Z. Polymere, 203, 161 (1965).
31. G. Kanig, Kolloid Z. Z. Polymere, 233, 829 (1969).
32. Yu. S. Lipatov, Vysokomol. Soed., 10B, 527 (1968).
33. Yu. S. Lipatov and T. E. Geller, Vysokomol. Soed., 9A, 223 (1967).
34. P. V. Kozlov, V. G. Timofeeva, and V. A. Kargin, Dokl. Akad. Nauk SSSR, 48, 886 (1963).
35. J. Sanchez, J. Appl. Phys., 45, 4204 (1974).
36. S. Sharma, L. Mandelkern, and F. Stehling, J. Polymer Sci., [B10], 345 (1972).
37. R. Boyer and R. Simha, J. Polymer Sci., [B11], 33 (1973).
38. R. Simha and C. Weil, J. Macromol. Sci.-Phys., B4(1), 215 (1970).
39. J. Moacanin and R. Simha, J. Chem. Phys., 45, 964 (1966).
40. J. Gibbs and E. DiMarzio, J. Chem. Phys., 28, 373 (1958).
41. S. Ellerstein, J. Polymer Sci., [B1], 311 (1963).
42. S. Kastner, J. Polymer Sci., [C16], 4131 (1968).
43. J. D. Hoffman, G. Williams, and E. Passaglia, in "Transitions and Relaxations in Polymers" (Edited by R. F. Boyer) (Translated into Russian), Izd. Mir, Moscow, 1968, p. 193.
44. G. Williams, Trans. Faraday Soc., 60, 1556 (1964).
45. R. Simha, J. Macromol. Sci., [B5], 331 (1971).
46. I. Curro, J. Macromol. Sci., [C11], 321 (1974).
47. A. Buniyat-Zade and T. Ismailov, Plastmassy, (4), 70 (1974).
48. S. Matsuoko and Y. Ishida, "Transitions and Relaxations in Polymers" (Edited by R. F. Boyer), Interscience, New York, 1966.
49. M. Letunovskii and Yu. A. Zelenev, Vysokomol. Soed., 15A, 1936 (1973).
50. A. Miller, J. Polymer Sci., [A2], 6, 249 (1968).
51. R. Beevers, J. Polymer Sci., [A2], 5257 (1967).
52. S. Krause, J. Polymer Sci., [A3], 3573 (1965).
53. V. P. Privalko and Yu. S. Lipatov, Vysokomol. Soed., 13A, 2733 (1971).
54. M. Kurata and W. Stockmayer, Fortschr. Hochpolymer Forsch., 3, 196 (1963).
55. Yu. Lipatov and V. Privalko, J. Macromol. Sci.-Phys., B7(3), 431 (1973).
56. Yu. S. Lipatov and V. P. Privalko, Vysokomol. Soed., 15A, 1517 (1973).
57. V. Privalko and Yu. Lipatov, J. Macromol. Sci.-Phys., B9(3), 551 (1974).
58. A. Bondi, J. Phys. Chem., 58, 929 (1954).
59. S. Kastner, Kolloid Z. Z. Polymere, 252, 143 (1974).
60. M. Litt, Amer. Chem. Soc. Polymer Prepr., 14, 109 (1973).
61. I. V. Razumovskaya and G. M. Bartenev, in "Stekloobraznoe Sostoyanie" (The Vitreous State), Izd. Nauka, Moscow–Leningrad, 1971, p. 34.
62. P. Mason, Polymer, 5, 625 (1964).
63. H. Kilian, Kolloid. Z. Z. Polymere, 252, 353 (1974).
64. S. Manabe and M. Takayanagi, J. Chem. Soc. Japan, Ind. Eng. Chem. Sect., 23, 57 (1967).
65. S. Manabe, K. Murukami, and M. Takayanagi, Memoirs Fac. Eng. Kyushu Univ., 28, 295 (1969).
66. S. Manabe and M. Takayanagi, Kogyo Kagaku Zasshi, 70, 525 (1967).
67. Yu. S. Lipatov and V. A. Vilenskii, Vysokomol. Soed., 17A, 2069 (1975).
68. Yu. Lipatov, V. Posovizky, and V. Babich, Europ. Polymer J., 13, 651 (1977).
69. Yu. Lipatov, Pure Appl. Chem., 43, 273 (1975).

Institute of the Chemistry of High-Molecular Compounds, Academy of Sciences of the Ukrainian SSR, Kiev