

ANHARMONIC OSCILLATIONS AND T_g , T_m TRANSITIONSBorivoj HLAVACEK^a, Viera KHUNOVA^b and Miroslav VECERA^a^a Department of Polymers,

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A working hypothesis has been developed to account for a change in character of thermal motion at glass transition. According to this hypothesis the pronounced onset of anharmonic vibrations is responsible for a stepwise increase in the thermal expansion coefficient α as well as in the similar temperature change in specific heat coefficient c_p . In this paper the both transitions (the first order transition at melting point and the second order transition at T_g) are investigated on the basis of the viewpoint connected with the change in characteristics of motion of the particles, so typical for an onset of a liquid state. At present, two different definitions for the coefficient of thermal expansion are used. One is usually adopted in polymer physics, where also the statistical approach to polymer chains configurations plays the major role in T_g definition. However, the statistical configurational approach of polymer physics cannot be applied directly to the inorganic glasses and also does not provide any explanation of relatively small changes in c_p values at melting point transition which sometime occur. Using the interpretation of solid state physics, the present paper intends to make a first step and bridge over the gap between these two approaches and to explain the T_g transition in dynamic terms, common to the polymers as well as to the low molecular weight substances.

Key words: Glass transition; Melting point; Anharmonic oscillations; Jump frequency at glass transition.

Extensive literature exists¹⁻⁷ providing an overall insight into the problem of T_g transition of polymers. Some authors, like for example Kaelbe⁸, emphasize the fact that for the explanation of T_g transition the concept of existence of holes does not have to be envisaged explicitly. However, the explanation of T_m phenomena by Frenkel⁹ connects T_m with the presence of about 7.5–10% of holes or vacancies. For the polymer rheologists, the notion which provides the WLF-equation for description of T_g transition and concept of holes is taken as a fundamental fact^{10,3} which is granted. In this context it is usually assumed that at T_g for 1 vacancy, about 40 particles of main chain which undergoes the diffusive jumps^{3,10} are to be taken into account. The number of the holes is then assumed to grow linearly with increasing temperature above T_g . One important fact is usually overlooked when explaining T_g transition. The origin of this fact goes back to the physics of solids in a reasoning such as is given by Kittel¹¹ or Frenkel⁹ who stated that the shapes of potential valleys in which the individual particles dwell have substantial

impact on the coefficient of thermal expansion. Substances like graphite or Invar¹² are characterized by very small coefficients of thermal expansion and also by perfect parabolic shape of potential valleys.

THEORY

It will be proved now that the change in the shape of potential valleys is accompanied by a change in the coefficient of thermal expansion as well as connected with different types of motion of individual particles. The T_g transition will be understood in this sense.

The Coefficient of Thermal Expansion

According to Einstein¹³ and Debye¹⁴, specific heats of solids are connected with the vibration of particles around their equilibrium positions. Every particle of mass m which sits in a potential hole U characterized by its parabolic shape:

$$U = U_0 + \frac{1}{2}f\xi^2 \quad (1)$$

undergoes harmonic oscillations under the influence of force

$$F = -\frac{dU}{d\xi} = -f\xi \quad (2)$$

and exhibits harmonic oscillations characterized by the frequency:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{2f}{m}}, \quad (3)$$

where U_0 is the basic level of internal energy U ; $\xi = r - r_0$ is the deviation from the equilibrium position where r_0 is defined as a distance separating two bottoms of neighbouring potential valleys. $f = d^2U/d\xi^2 > 0$ is the coefficient of the quasi-elastic force, connected with the bulk modulus K^* (ref.⁹), $K^* = f/r_0$. According to Müller¹², substances like Invar or carbon are distinguished by the harmonic oscillations according to Eqs (1) and (2), and the character of potential holes which is defined by Eq. (1) does not change with increasing temperature. The fact that in the liquid the potential hole has not the shape of a paraboloid but rather a "pan-like" shape has already been mentioned by Hirschfelder and co-workers¹⁵ and recently studied in detail by Luck¹⁶.

According to Müller¹² and Frenkel⁹, every compound needs for its thermal expansion to vary the shape of potential valleys in which the individual particles are located. The change in the shape of potential valleys is the only way how to achieve the thermal expansion of substances with temperature. Such change, however, will influence the strict character of harmonic motion of individual particles. For our purposes of T_m and T_g considerations it seems to be sufficient to add just one perturbation term to Eq. (1). This allows us to illustrate the point. We get:

$$U = U_0 + \frac{1}{2} f \xi^2 - \frac{1}{3} g \xi^3 . \quad (4)$$

We consider just the unidimensional case only. We assume that for the substances characterized by very small coefficient of thermal expansion the function $g \rightarrow 0$.

For the choice of thermal energy $U_0 = 0$, the energy U has to be equal to energy kT of thermal motion, where k is the Boltzmann constant. We get:

$$U = \frac{1}{2} kT = \frac{1}{2} f \overline{\xi^2} , \quad (5)$$

where $\overline{\xi^2}$ is the average of the square of deviation from the bottom of potential valley. The average value of the distance between the particles remains constant and equals to r_0 since the mean value of $\overline{\xi}$ vanishes. That gives:

$$\overline{\xi^2} = \frac{kT}{f} . \quad (6)$$

Let us now consider the case of anharmonic force F acting in a nonideal case on a particle sitting in a potential valley given by Eq. (4).

$$-\frac{dU}{d\xi} = F = -f\xi + g\xi^2 \quad (7)$$

Putting its mean value equal to zero gives:

$$F_{AV} = 0 = -f\overline{\xi} + g\overline{\xi^2} . \quad (8)$$

Equation (8) provides a relation connecting the average deviation $\overline{\xi}$ with the shape of potential valley for real substances. We get:

$$\bar{\xi} = \frac{g}{f} \bar{\xi}^2 \neq 0 . \quad (9)$$

For harmonic oscillations $\bar{\xi}$ would be zero. It can be seen that due to anharmonic character of thermal motion the average position of particles $\bar{\xi}$ has been shifted.

Provided that the particles have been separated by distance r_0 and the change in character of motion for the temperature change dT has been characterized by increase in g from $g' \rightarrow 0$ to g , then for the relative displacement D_r and coefficient of thermal expansion α it is:

$$D_r = \frac{\bar{\xi}}{r_0} . \quad (10)$$

Substitution from Eq. (6) into (9) and (10) will give:

$$\alpha_1 = \frac{1}{r_0} \frac{d\bar{\xi}_1}{dT} = \frac{1}{r_0} \frac{g'}{f^2} k \quad (11)$$

$$\alpha_2 = \frac{1}{r_0} \frac{d\bar{\xi}_2}{dT} = \frac{1}{r_0} \frac{g}{f^2} k , \quad (12)$$

where α_1, α_2 are the coefficients of thermal expansion for two different levels of the perturbation function g', g in the solid-liquid transition.

$$\Delta\alpha = \frac{1}{r_0} \frac{d\Delta\bar{\xi}}{dT} = \frac{1}{r_0} \frac{g-g'}{f^2} k , \quad \text{where} \quad \Delta\alpha = \alpha_2 - \alpha_1 . \quad (13)$$

From the Eqs (8)–(13) it can be seen that the coefficient of thermal expansion can be associated with the anharmonic character of thermal vibrations. Its sudden change thus is associated also with different characteristics of the thermal motion of particles. In that transition not only the rigidity of substance plays role for a change in α which is expressed by the presence of function f , but also the perturbation function $g - g'$ regarding the shape of potential valley makes the sudden change in α possible. We can now associate the change in α in Eq. (13) with the change in α for polymers at T_g which is about the same⁴:

$$\Delta\alpha T_g = (\alpha_L - \alpha_G) T_g = 0.115 \quad (14)$$

$$\Delta\alpha = \frac{0.115}{T_g} \quad (15)$$

$$\Delta\alpha \approx \frac{g - g'}{f^2} . \quad (16)$$

With the Eqs (15) and (16) we arrive at a new point of view upon T_g transition which associates the T_g transition with an onset of new form of vibrations, which is pertinent to every particle of the system. Let us discuss this point of view in the following text.

The Change in the Characteristics of Vibrational Frequency

From Eqs (8)–(16) it can be seen that the T_g transition can be envisaged as a sudden variation in the function g . If the substance is taken as an ensemble of vibrating harmonic oscillators which move with characteristic frequency ν under T_g

$$\nu = \frac{1}{2\pi} \sqrt{\frac{f}{m}} , \quad (17)$$

where m means mass of individual particles, then above T_g (where we assume that the anharmonic character of motion is taking place) a new term appears in the solution for ξ (ref.²⁴).

For $\omega = 2\pi\nu$ for the anharmonic oscillator we get according to Kittel and co-authors²⁴:

$$\xi = A \left(\cos \omega t - \frac{1}{6} \frac{g}{f} \cos 2\omega t \right) . \quad (18)$$

The solution for the anharmonic oscillator is characterized by two different frequencies. The influence of the second term depends upon the ratio of g/f .

We can see that the phase transition T_g on microlevel has a dynamic character and opens new opportunities for mechanical movement for every particle in the sample. This can explain the stepwise change in the c_p at T_g (ref.¹⁷). The presence of holes does not affect the c_p too much in T_m vicinity as it is shown in variation of c_p data for inorganic and organic substances⁹ as well as for the polymers data^{18,19} in T_m areas. The substances undergo a much larger change regarding the volume (stepwise change) at T_m where a much larger amount of holes are created. A question arises whether the concept of holes is realistic. Here it must be emphasized that Hirshfelder¹⁵ assumes the number

of vacancies to reach the number of particles even at critical conditions. We can envisage the structure which will have even higher amount of vacancies at that point (see Figs 1 and 2).

As we will show in the Example below and in Appendix, the coefficient of thermal expansion α can be distantly related to T_c of the envisaged subsegment which undergoes the thermal jumps motion above T_g , pointing thus to the physical background of function g .

We can conclude that the holes contribute to the combination entropy at T_m or at T_c (ref.⁹) where the specific heat c_p curves look like the Dirac delta functions in shape.

FIG. 1

The notion of critical state according to Hirschfelder¹⁵ and Curtiss²⁰. The notion which explains the fact that in critical state there are so many vacancies that the liquid phase is loosing its continuity in the two-dimensional model pictured. According to this notion there is, at the critical state, about the same number of holes as particles. The total volume contains about 50% of holes. (Note: $V_c = 2b$; for a Dieterici Eq.)

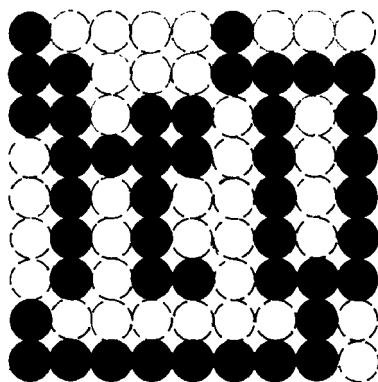


FIG. 2

The extrapolation of two-dimensional case of Hirschfelder, Curtiss^{15,20} and Bird¹⁵. If it is assumed that the increase in number of holes will cause the interruption of the phase in the vicinity of T_c , then the number of holes will exceed the number of particles in the ratio of 1 : 2. In the area of typical p_c pressures 20–200 atm the holes appear to be almost incompressible⁸. (Note: $V_c = 3b$; for the van der Waals Eq.)

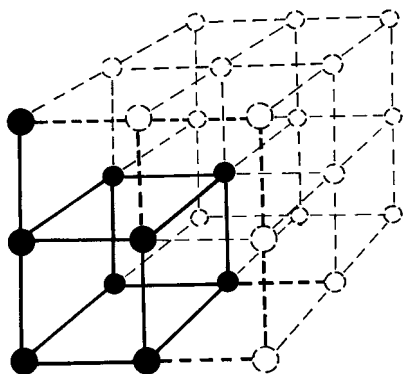


Table I shows that many substances change c_p after melting only little or not at all (see Table II). It is also seen that the presence of about 10% of holes above T_m does not result in a big change in c_p values. Therefore at T_g , where the number of holes (according to Ferry⁴, Bueche³ or Greasley¹⁰) is much smaller than at T_m , the change in c_p can also be explained differently, which our concept of Eqs (13)–(18) does seem to accomplish.

In the case of Table II the solution of the anharmonic oscillator has to be searched in the form of Eq. (18) for two different values of g ($g \neq g'$) for the liquid–solid transition. The change in the second term in the bracket of Eq. (18) brings the change in c_p values.

For the character of T_m transition let us quote Frenkel⁹: “We must finally stress the well-known fact that the specific heat of condensed bodies is only very slightly affected by fusion, being somewhat greater just above the melting point than below it. That means that the character of the heat motion in liquid bodies at least near crystallization point, remains fundamentally the same as in solid bodies, reducing mainly to small vibrations about certain equilibrium positions and in case of diatomic and more complex molecules, to rotational oscillations about certain equilibrium orientations”.

From Table I and by assuming the presence of about 10% of holes above T_m it can be concluded that the vacancy itself does not carry any substantial heat capacity alone and behaves like a particle in the combination sense only, and even though for the creation of the vacancy the evaporation energy of the particle approximately is needed.

TABLE I

The c_p values of some compounds^{9,19} for which vibrational character of thermal motion does not change substantially at melting point. LDPE and HDPE stand for low-density and high-density polyethylenes, respectively

Compound	Na	Hg	Pb	Zn	Al	LDPE	HDPE
$c_{p(s)}$, cal/mol	7.6	6.7	7.2	7.2	6.8	0.4 ^a	0.35 ^a
$c_{p(l)}$, cal/mol	8	6.7	7.7	7.9	6.8	0.35 ^a	0.35 ^a

^a cal/g.

TABLE II

Example of the compounds for which the T_m transition is accompanied by a larger change in c_p values

Compound	N ₂	Cl ₂	Br ₂	CH ₄	NH ₃	C ₆ H ₆
$c_{p(s)}$, cal/mol	11.3	14	14.1	10.6	12.2	26.6
$c_{p(l)}$, cal/mol	13.1	16.2	17.1	13.5	18.4	30.1

EXAMPLE

To relate the function g to the thermodynamic state variables, the van der Waals equation can be rewritten into the following form:

$$V = b + \left(\frac{bp + RT + pV}{a} \right) V^2, \quad (1E)$$

where the constants a , b have the usual meaning.

If one neglects the cubic and quadratic terms in this equation, the solution of the remaining linear equation will be a crude approximation to the lowest root of the original equation, a root that must correspond to the volume of the liquid. This crude approximation, which is the lowest possible value that V could approach, is simply $V = b$.

A substitution of this approximation into the right-hand side of Eq. (1E), then yields a better approximation,

$$V = b \left(1 + \frac{bRT}{a} \right) = b(1 + \alpha T). \quad (2E)$$

Putting $\frac{b}{a}$ as $\frac{1}{27p_c b}$ we get α as:

$$\alpha = \frac{R}{27p_c b}. \quad (3E)$$

(As it is shown in Appendix, the p_c for the polymer subsegment can be related to the cohesive energy density of the given polymer or to the solubility parameter ($p_c \approx \delta^2$).

Comparing with Eqs (11)–(13): $\alpha = \frac{1}{r_0} \frac{gk}{f^2}$ and keeping in mind

$$r_0 K^* = f, \quad (4E)$$

where K^* is the bulk modulus⁹, we can get:

$$\alpha = \frac{1}{r_0^3 (K^*)^2} gk = \frac{1}{r_0^3} \frac{gk}{(K^*)^2} \quad (5E)$$

$$\alpha = \frac{R}{27p_c b} = \frac{N_A k}{27p_c b} = \frac{1}{r_0^3} \frac{gk}{(K^*)^2} \quad (6E)$$

and taking $N_A r_0^3$ as approximately equal to nb we get:

$$\frac{k(N_A r_0^3)}{27p_c b} = \frac{knb}{27p_c b} = \frac{kn}{27p_c} = \frac{gk}{(K^*)^2}, \quad (7E)$$

where n will be a multiplication constant reflecting the local packing. Furthermore:

$$g = \frac{(K^*)^2}{p_c} \frac{n}{27} \quad (8E)$$

or taking into account that:

$$\frac{p_c V_c}{RT_c} = Z_c \quad (9E)$$

we get:

$$g \approx \frac{(K^*)^2 V_c}{Z_c RT_c}. \quad (10E)$$

Taking into account that for the majority of liquids the bulk modulus in compression is approximately the same, we can say that, for low-molecular substances, the ratio of critical volume to critical temperature will play the essential role in determination of function g . For the polymers then we can assess the size of the subsegment which starts to move and be mobile at T_g because, according to Hirschfelder, for the low-molecular substances¹⁵ it is $T_m/T_c = 2/5$ and, according to Brydson¹⁸, for the subsegment which is trapped into the crystal the approximate relation between T_g and T_m is $T_g/T_m \approx 2/3$; thus for the determination of g we can approximately write:

$$g \approx \frac{(K^*)^2}{Z_c R} \frac{4V_c}{15T_g} \quad (11E)$$

or simply, since $V_c = 3b$, we can write:

$$g \approx \frac{\text{rel. size of the subsegment}}{T_g}. \quad (12E)$$

Note that this ratio already appears at the left-hand side of Eq. (7E) where the term $p_c b$ is expressed properly.

The relative size of the subsegment can be estimated from the polarizabilities of individual atoms. Keeping in mind that the polarizability of carbon atom is $0.93 \cdot 10^{-24} \text{ cm}^3$, we express the individual relative size of atoms as it follows²¹:

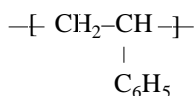
(taking C = 1) C as 1; H as 0.4; Cl = 2.2; O = 0.8; N = 0.9. Furthermore, we can compare the relative size of polystyrene monomer unit (which is taken as a standard) with the relative sizes of subsegments for the other polymers which presumably can play the equivalent role in T_g transition. We are keeping in mind that only for the most rude approximation the van der Waals coefficient b can be calculated by the addition of individual atomic polarizabilities τ (ref.²²): $b = 18.6 \tau_{\text{mol}} N_A$ where τ_{mol} stands for the sum of the individual atomic polarizability contributions. This is the most simple formula. For more precise calculations a correction must be made for the presence of double and triple bonds, molecular geometry, intermolecular interactions, as well as for the electrons of free pairs.

We can compare the polystyrene monomeric unit with the polybutadiene monomeric unit and PVC dimeric unit exactly:

Polystyrene:

Relative size of monomeric unit is 11.6; $T_g = 373 \text{ K}$;

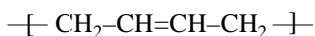
rel. size/ $T_g = 3.10 \cdot 10^{-2}$.



1,4-Polybutadiene:

Relative size of *cis*-1,4-polybutadiene monomeric unit is 6.4; $T_g = 202 \text{ K}$;

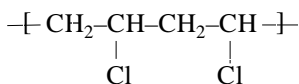
rel. size/ $T_g = 3.07 \cdot 10^{-2}$.



PVC:

For dimer: Relative size of dimeric unit is 10.8; $T_g = 351 \text{ K}$;

rel. size/ $T_g = 3.16 \cdot 10^{-2}$.

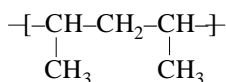


Here we can see that the size of the opening for T_g transition must reach twice the size of monomer unit in order to accommodate the proper values of T_g . However, for polypropylene a strange torso of dimer has to be taken as the basic unit to be released at T_g . It is a dimer minus $\text{---CH}_2\text{---}$ group:

Polypropylene:

Relative size of dimer torso is 9; $T_g = 273$ K;

rel. size of unit/ $T_g = 3.28 \cdot 10^{-2}$.

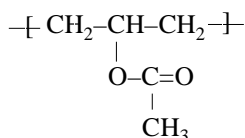


The size of an average hole at T_g transition for the polypropylene system seems to be larger than is the size of monomer unit but smaller than is the dimer unit. The release of units smaller than indicated in the torso unit, if they occur, must take place at much lower temperature than is T_g , or otherwise, the intermittent unit must "wait" for its release till the larger vacancy above T_g (or in vicinity of T_g) is created and larger blocks are released. The release of smaller units can probably be associated with the existence of the so-called beta or gamma maxima. Here seems to be the origin for different values of T_g reported for polyethylene in literature¹⁸ where the groups of different size $\text{---}(\text{CH}_2)_{n>1}\text{---}$ can be involved. Thus Brydson has reported eleven different values of T_g 's for polyethylene from a range of $T \in \langle -130$ °C; $+60$ °C). Just an opposite effect was observed with poly(vinyl acetate) where the group pictured gives the correlations for T_g transition (monomer plus $\text{---CH}_2\text{---}$ group):

Polyvinyl acetate:

Relative size of the unit is 9.8; $T_g = 301$ K

rel. size/ $T_g = 3.16 \cdot 10^{-2}$.



Because of the absence of precise data regarding the bulk modulus whose square enters into g function formula and also because of the approximate value of the Z_c coefficient we will stop our considerations at this point, hopefully showing just the direction for possible g function analyses and evaluation.

The constant values in the above-mentioned ratios are not accidental and can be obtained using an independent way.

According to Bueche³ "It appears that the segmental jump frequency is essentially the same for all materials as their glass temperatures". The viscosities η at T_g reach the values of 10^{13} poise. Kauzman²³ referring to Eyring's theory stated "The rate k_0 at which its molecules jump from one equilibrium "lattice position" in the liquid state to another is given by

$$\frac{1}{\eta} = \frac{\lambda^2 A}{kT} k_0, \quad (13E)$$

where k is the Boltzmann constant, T is the absolute temperature, λ and l are lengths of the order of molecular dimension, and A is of the order of such dimensions squared". For $A = \lambda l$ and $\eta = \text{const.}$ at T_g we get:

$$\frac{1}{k_0} \approx \frac{\lambda^3}{kT_g} \quad (14E)$$

which is an analogous expression to Eq. (12E).

However, we have to say at this point that, as a result of certain "arbitrariness" in the choice of the subsequent size λ^3 in the above-mentioned examples, the Bueche's assumption can be fulfilled just roughly or, on the other hand, the satisfying of Bueche's assumption would mean that the monomeric unit need not necessarily be the unit "release" for the diffusion jump motion at T_g .

Thus the analyzes leading to Eq. (12E) have been roughly confirmed.

CONCLUSIONS

Using the simple idea about the shape of potential valley in which the individual particles of substances undergo their thermal vibrational motions, it was possible to provide semiquantitative approximate approach which allows slightly different understanding of T_g transition. According to the method presented, the change in α at T_g is associated with deformation of potential valleys in which the thermal motions take place and also with linear growth in number of vacancies above T_g . The c_p change is then associated with an onset of anharmonic motion in the whole field of particles which form the system.

It is stated, that at T_g only a very small amount of vacancies is created which itself cannot be responsible for the constant increase in the c_p values above T_g . (The stepwise change in c_p at T_g .)

The onset of anharmonic motion above T_g is connected with increase in the average amplitude of vibrational motion as well as with the onset of motion which is characterized with a different frequency. This change, which results in a sort of wobbling motion, affects every particle of the system. This would affect also the sharp change in fluidity of the system above T_g which can hardly explain the "static" notion about the imperfections or defects in lattice structure (1 hole per 40 particles). The perturbation term g must, in the course of time, always compensate the shape of the bottoms of potential valleys in such a way that for a very small displacement of particles the term $dU/d\xi = 0$, which seems to be a characteristic of liquid state.

APPENDIX

The Polymers and the Concept of a Liquid State

For amorphous low molecular weight substances the liquid state can be defined above the Vogel's temperature between the points of T_g on one side of the temperature interval and for the point of T_c on the other side of the temperature scale.

In this context the T_c temperature is defined as such a temperature above which the liquid phase cannot exist under elevated pressures. The reason for this behaviour is usually not connected with any particular picture or model. In our approach, which is pictured in Figs 1 and 2, however, the disintegration of liquid phase at T_c takes place as a result of abundance of holes. This can be envisaged by visual models as well as seen from the equations of state where for a Dieterici equation we get $V_c = 2b$ or, for example, for a Peng–Robinson equation²⁵ $V_c = 3.9b$. The relation $V_c = 2b$ agrees well with experiment for the substances with low T_c such as is helium¹⁶, for example, but for the hydrocarbons with higher T_c level¹⁶, the Peng–Robinson relation²⁵ $V_c = 3.9b$ fits the experimental data much better.

The polymers in rubberlike state contain slightly more than 10% of vacancies above their melting points and slightly more than 2.5% of vacancies for amorphous phase at the temperatures above T_g . If polymer is heated up to the boiling point of its monomer, about 30% of holes (by volume) will be present. This is essentially the same amount which would be expected for a monomer where the amount of holes at boiling point depends on the separation of the boiling point from the T_c or T_g points. Polymers differ from low molecular weight substances only in one characteristic feature which causes that the polymer (as a result of mutual segmental connection and entanglements) cannot form a gas phase. Therefore the point of T_c for a polymer has an only illusory meaning without any practical significance. Not mentioning the fact that every known polymer also thermally disintegrates at much lower temperatures. However, the critical pressure of a subsegment has a connection to the solubility parameter²⁶ and therefore to the density of cohesive energy. The critical pressure of a subsegment has a quite real meaning for the amorphous polymers. Some authors which work in the polymer science in the theory of solubility²⁷ are working quite comfortably with the "envisaged T_c extrapolations" for a polymer or its segment and also mainly with p_c values for polymeric subchains. According to Lyndersen²⁸, the corresponding value of p_c for any particular subchain of the polymer can be calculated by using the additive rule formula. For low molecular weight substances Hildebrand²⁶ stated that $\delta = 1.25 p_c^{1/2}$, where p_c is in atm and δ is the solubility parameter in $(\text{cal}/\text{cm}^3)^{1/2}$.

In analogy to the calculations presented in this paper the polymer chain segment can be selected and its "hypothetical" p_c calculated²⁸ on the basis of the Hildebrand²⁶ formula as well. The segments which can fit Hildebrand's formula can be taken as basic

segments which take part in the process of polymer chain diffusion in the rubber like state area.

This segment which was determined through such a procedure does not have to coincide with the subsegment presented in above Example, where we have tried to satisfy the rule of constant frequency of diffusion jumps at T_g .

To conclude this Appendix, we can say that the polymer segments in rubber like zone are in the state of a liquid with all its attributes, only with an exception which stems from the polymer disability to form a gas phase, as a result of segmental connections and entanglements.

SYMBOLS

a, b	constants of van der Waals equation a (energy volume), b (volume)
c_p	specific heat at constant pressure
f	proportionality constant of harmonic force (energy/length ²)
g	function of potential valley distortion (energy/volume)
k	Boltzmann constant
k_0	the rate at which the molecules jump from one equilibrium position to the other
l	length of the molecular dimension
m	mass of the particle
n	multiplication constant
r	the rate of molecular jumps in liquids
p_c	critical pressure
A	the surface of approximate size $A = \lambda l$
F	force acting on the particle
K^*	modulus of the material in compression
N_A	Avogadro number
R	universal gas constant
T	temperature, K
T_m	melting point temperature
T_g	glass transition temperature
U	energy connected with attractive forces
U_0	lowest level of energy U of attractive forces
V_c	critical volume
V	molar volume
Z_c	$Z_c = p_c V_c / RT_c$
α	coefficient of thermal expansion
α_1	the coefficient of thermal expansion in the glassy state (based on Eqs (10), (11))
α_2	the coefficient of thermal expansion above T_g (based on Eqs (10), (12))
$\Delta\alpha = \alpha_2 - \alpha_1$	
α_L	coefficient of thermal expansion above T_g (based on experiment)
α_G	coefficient of thermal expansion below T_g (based on experiment)
η	viscosity
λ	length of the molecular dimension
ξ	the coordinate signifying the deviation of particle from the bottom of potential valley
$\bar{\xi}$	the average value of coordinate

$\bar{\xi}_1$	the average value of the oscillations of the individual particle below T_g
$\bar{\xi}_2$	the average value of the oscillations of the individual particle above T_g
ν	frequency of the particle oscillations below T_g
ν^*	frequency of the particle oscillations above T_g

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