THE ANHARMONIC CHARACTER OF T_g AND T_m TRANSITION

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SUMMARY: The idea of anharmonic oscillations has been extended to explain the glass transition or melting point. All ideas of free volume, vacancy transport, etc., have been respected but are treated as minor phenomena relative to harmonic–anharmonic vibration transition. A simple model of coupled oscillators is studied. It is shown that coupled anharmonic oscillators can produce vibrations on entirely different levels of amplitudes, which explains the highly different coefficients of thermal expansion and c_p values for solid and liquid states. At higher temperatures, for polymers in the rubber-like zone, the theory of anharmonic coupled oscillators brings certain justification for the theories of De Gennes, Doi and Edwards or Rouse. The solid–liquid transition seems to be connected on microlevel mainly with the enlargement of vibrational amplitudes of monomer or dimer units in polymer chain as the temperature increases.

Introduction

For a long time it has been presumed that the problem of T_g transition is mainly related to the conformational changes of entropy[1-7]. The physicists working in the area of polymers have even made up their own definition for the coefficient of thermal expansion α and its change $\Delta\alpha$ at T_g. For the definition of specific heat coefficient, c_p, these authors[5-7] used a linear oscillator concept (which brings $\alpha = 0$). For the definition of change in Δc_p at T_g, the trivial Eq. 1 has been used[5]:

$$\Delta S = \int_{T_1}^{T_2} \frac{\Delta c_p}{T} dT = \Delta c_p \ln \frac{T_2}{T_1} \qquad (1)$$

In this form, the entropy change ΔS can have a conformational as well as the vibrational origin. This fact has been discussed extensively in a recent work by Hlaváček and co-workers[8,9]. The traditional approach[1-7] has never been able to cope with the fact that c_p, after passing through a peak reminding the Dirac's delta function at T_m, can reach the lower level at temperatures above $T_m + \Delta T$ (where $\Delta T > 0$) with respect to its original level before reaching the melting point[10,11] $T_m - \Delta T$. In this contribution, we would like to concentrate our effort on the explanation of the T_g transition through the anharmonic vibrations and drastic amplitude

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changes in the T_g vicinity. We have to note here that the use of anharmonic oscillators has been mentioned by many authors in the past[12-18] in connection with the characterisation of the T_g transition[12-15].

Furthermore, regarding the explanation of tunnelling state phenomena[16,17], the boson peak[17,18] or the Johari–Goldstein β-maxima[19], the non-linear shape of potential valleys of particles has been considered, too.

These authors, however, have never used, to full extent, the mathematical possibilities which the non-linear anharmonic oscillator can offer[8,9]. The isolated non-linear oscillator will show the double frequencies and pulses which can interfere with the nucleation of crystals[9]. If the individual oscillators can interact on the similar frequencies, then the individual particles can undergo a discontinuity in amplitudes (the amplitude jumps)[8,9]. Such an amplitude jump of a monomer or dimer unit will push aside the particles in its vicinity in a liquid state, forming thus the vacancy opening space.

The enlargement of the amplitude can be detected through the methods of neutron scattering[20] which can provide the information about the average vibrational amplitude (the Debye–Waller factor).

However, even more information about the free volume can be provided by the PASCA (positron annihilation spectroscopy) measurements[21-33], which can even detect the distributions of vacancies in the matrix space.

Theory

The basic misapprehension which has sometimes been passed on in the early works dealing with T_g transition has its source in the disregard of two facts: one of them results from the omission of solid state physics definition of "α" [34-37]; the other stems from the fact that the meaning of the conformational part of entropy in Eq. (2) was overemphasised in the vast majority of cases:

$$S = k \ln W_{conf} + k \ln W_{therm} \qquad (2)$$

where k stands for the Boltzmann constant.

This reality was well understood by Goldstein[12,13] who presumed the following partition function:

$$P = P_{vib} \cdot P_{conf} \qquad (3)$$

In our theory, we will presume that the T_g transition is associated with release of vibrational motion of monomer or dimer units in the rotational sense as, e.g., is the rotation of a benzene ring around the CH_2CH_2 group in polystyrene chain. The vacancy thus created can have a size larger than 100 $Å^3$ above the T_g area[26]. For inorganic glasses, the substructure of SiO_4 tetrahedron is supposed to be released in the T_g vicinity[38,39]. Below (T_g – 52) K, only a very small part of particles can undergo a finite displacement.

So Buchenau[17] presumes only 10^{-5} tunnelling states per atom and about 10^{-3} states connected to boson peak at very low temperatures. If we disregard the motion of side chains, then below T_g, Eq. 2 will have the form:

$$S \cong k \ln W_{therm} \tag{4}$$

as a consequence of $W_{conf} \cong 1$.

The Kauzman paradox of negative entropy (the so-called entropy crisis) can never occur, because just one part of entropy under T_g disappears. For polymers, the value of c_p per atom is approximately[40] k or 2k and forms a sort of analogy to the Dulong–Petit rule for metals[41]. In his early work Gibbs[1] avoided the thermal entropy contribution[9] completely. Later Di Marzio and co-workers[2,7] have coped with this insufficiency and took a correction considering the vibrational part of entropy as well. They were referring to a work by Einstein[42] which can lead to correct prediction of specific heat c_v, but cannot correctly predict the coefficient of thermal expansion α.

The potential valley, in which the individual particle is assumed to undergo a vibrational motion, in the following form,

$$U - U_0 = \frac{1}{2} kT = \frac{1}{2} f\xi^2 \tag{5}$$

$$\frac{kT}{f} = \xi^2 \tag{6}$$

will always result[8,9,43] in the coefficient of thermal expansion $\alpha = 0$.

In Eq. (5), the U_0 is the reference energy level which can be taken as equal to zero; $\xi = r - r_0$ is the deviation from the bottom of potential valley; r_0 is a distance separating two bottoms of potential valleys; k is the Boltzmann constant and f is related to the bulk compressibility modulus; $K^* = f/r_0$.

For the non-linear form of potential valley,

$$U - U_0 = \frac{1}{2} f\xi^2 - \frac{1}{3} g\xi^3 \tag{7}$$

the non-zero coefficient of thermal expansion can be defined[8,9,37,43] as

$$\alpha = \frac{1}{r_0}\frac{g}{f^2} k = \frac{1}{r_0}\frac{d\bar{\xi}}{dT} \tag{8}$$

It is evident that even this definition does not have to be perfect. However, as it has been already shown by Kittel[34], the inclusion of a higher term in the power series development, in analogy to Eq. (7), will not bring any difference into the definition of α.

$$U - U_0 = \frac{1}{2} f\xi^2 - \frac{1}{3} g\xi^3 - \frac{c}{4}\xi^4 \tag{9}$$

This type of potential valley is generally considered in physics of inorganic glasses[16-18,20]. Usually the authors do not consider any possible interactions of particles with the particles located in the neighbourhood. The interactions with neighbours can bring the isolated particle on a completely different level of $\bar{\xi}$ for which the particle, if left subsequently isolated, has to be associated with the different anharmonicity level characterised through a completely different ratio of g/f^2 functions. This stems from Eqs (6) and (8) as well as from the expression for the average force acting on the isolated particle ($F_{AV} = f\bar{\xi} - g\overline{\xi^2} = 0$ and $\bar{\xi} = \frac{g}{f}\overline{\xi^2}$). The non-linearity can be also considered through the variations of coefficients of the second order differential equation[8,9] together with the addition of the right-hand side to Eq. (10). A variety of particles interactions can be considered.

For the particle motion in the potential valley we get

$$m\frac{d^2\xi}{dt^2} + F\left(\xi; \frac{d\xi}{dt}\right)\frac{d\xi}{dt} + \frac{\partial U}{\partial \xi} = A\left(\xi; \frac{d\xi}{dt}\right)\cos pt \tag{10}$$

where the angular frequency p is presumed to be close to the characteristic (eigen) frequency ω of free vibrations. The right-hand side of the equation stands for the particle interactions with its neighbours.

By using the mathematical methods described by Minorsky[44] or Tockstein[45], the non-linear system of the second-order differential equation can be turned into two separate differential equations of the first order with variables A_1, A_2 (corresponding to $A_1 = d\xi/dt$ and $A_2 = f(A_1, \xi, t, \alpha_{11}, ...,$etc.) for example) and subsequently even the time dependence can be eliminated.

We thus get

$$\frac{dA_1}{dt} = \alpha_{11}A_1 + \alpha_{12}A_2 \tag{11}$$

$$\frac{dA_2}{dt} = \alpha_{21}A_1 + \alpha_{22}A_2 \tag{12}$$

and choosing

$$-a_1 = \alpha_{11} + \alpha_{22} \tag{13}$$

$$a_2 = \alpha_{11}\alpha_{22} + \alpha_{12}\alpha_{21} \tag{14}$$

we can arrive at the time-independent amplitude representation of the problem (See Figs 1, 2, 3) where the type of the motion is defined through different ratios of constants a_1 and a_2. Providing that we can choose the point C in Fig. 1 as the point of small spatial vibrations $\xi_{max} \rightarrow 0$, then the curves a and b in Fig. 1 will reflect the different levels of amplitude fluctuations. In Fig. 2, we can see (expressed by the dashed line) the particular amplitude shrinkage and in Fig. 3, the amplitude enlargement (both accompanied by $a_1 \neq 0$).

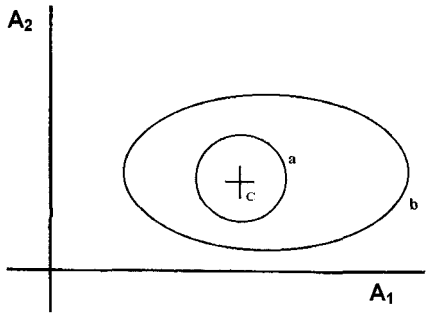

Fig. 1 The shifted amplitude coordinate for the anharmonical oscillations, where the point C represents the origin of coordinates. Curve a represents the smaller amplitude of vibrations (solid state) and curve b the liquid state ($a_1^2 - 4a_2 < 0$, $a_1 = 0$)

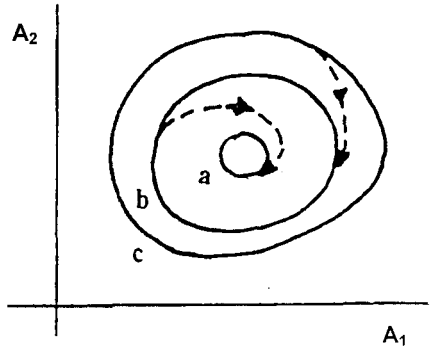

Fig. 2 A schematic representation of the amplitude diminution proceeding in stages from curve a toward b and, finally, c ($a_1^2 - 4a_2 < 0$, $a_2 > 0$, $a_1 \geq 0$).

In such a way, a passage from the solid to liquid phase or from the liquid to gas phase can be treated[9]. In polymers, we have to concentrate our effort on T_m or T_g transition only because the gas phase, as the consequence of entanglements, cannot be considered. The question which

can be raised at this point is: Can we find any experimental support, for "the amplitude switch" at T_m or T_g transition, to justify our approach to the phase change ?

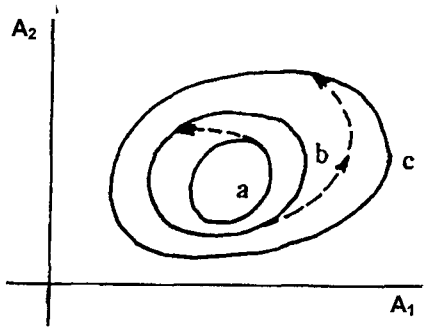

Fig. 3

A schematic representation of the amplitude enlargement proceeding in two stages ($a_1^2 - 4a_2 < 0$, $a_2 > 0$, $a_1 \geq 0$).

Experimental support for the theory presented

The neutron scattering data[20] present the most convincing evidence of the average amplitude rise in the T_g vicinity. The average amplitude of vibrations starts to rise slowly at Vogel's temperature, and at $T = T_{cr}$ (T_{cr} is the so-called crossover temperature; $T_{cr} \approx 1.2\ T_g$), the constant slope of the average amplitude rise is established for area of $T \geq T_{cr}$. It has clearly been shown by Buchenau and Zorn[20] that the average amplitude rise has a continuous character, which implies either that the individual particles enter the higher-level amplitude in one-by-one sequence or that the rise of amplitude itself has a continuous character. At T_m, a discontinuity in the average amplitude was reported[20]. This would indicate a sudden discontinuity in amplitude for groups of particles.

We assume that the vacancies are created in the liquid matrix through the high-amplitude motion of the particles. In such a case, the vibrating particle is able to push aside the neighbouring particles in its vicinity. The PASCA measurements[21-33] give us the complete evidence about the excited particles only because in their vicinities, the actual vacancies are assumed to be created.

The vacancy size is proportional to the amplitude of vibrating unit $\bar{\xi}_{AV}$. In Fig. 4, we can see the radius of the average vacancy, in Fig. 5, the average vacancy volume for 1,4-*cis*-poly(butadiene), based upon the outstanding experimental work by Bartoš[26] and co-workers.

In Fig. 6, we can see the characteristic curve for an electric circuit with high ohmic resistance described by Martiensen[46], which has been used as an analogous device for the description of amplitude switch in the T_g vicinity[9], where a very high viscosity[47] occurs.

The basic conclusion of the theory is that the amplitude change (Figs 1-6) will play a major role in the definition of the liquid state and in its transition into the solid or the gas state. The vibrational amplitude rise will be the major cause for the solid or the liquid volume enlargements. These enlargements can proceed either through continuous changes or through a sharp discontinuity. In such a way, the non-linear mutually interactive oscillators system can successfully cope with the first-order as well as with the second-order transitions in the liquid state.

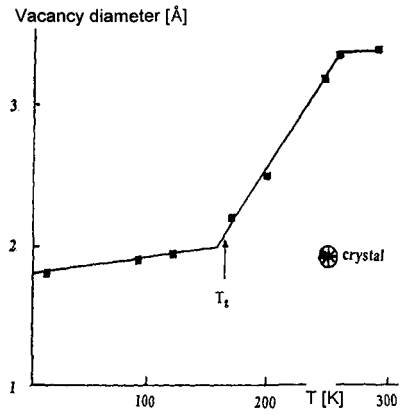

Fig. 4 The most probable vacancy diameter of *cis*-1,4-poly(butadiene) as a function of temperature (T_g = 168 K)[26].

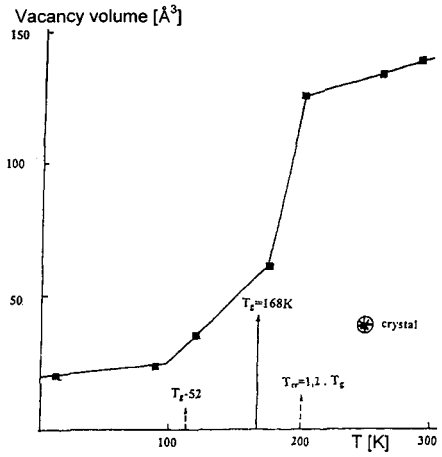

Fig. 5 The volume of the highest occurrence of vacancies of *cis*-1,4-poly(butadiene) as a function of temperature.

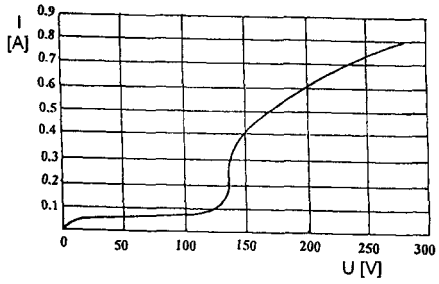

Fig. 6 The current vs voltage dependence for a non-linear electric circuit[46] with additional 200 Ω resistance in series, reported recently[9]. The high ohmic resistance in electrical circuit corresponds to high viscosity damping force in a mechanical analogous device. (The viscosity of 10^{13} poise is expected to occur in the T_g vicinity.)

The implication of the theory for polymer rheology

In polymers, it is interesting to note that the conformational statistic approach in true sense comes into play immediately above the T_g temperature. The directional character of the

coordinative motion is usually characterised by the soft dumb-bell distribution of relaxation time according to the Rouse theory[48].

The polymer chain can be represented as springs and beads connected in series. The springs will represent the randomly agitated spots in liquid, while the beads represent the stagnant areas, which seems to fit very well our concept of mutually interactive oscillators. Such a system will always produce the randomly agitated spots in the liquid matrix as well as the "anchors" or stagnant areas. The same can be stated about the theories of de Gennes[49] and Doi and Edwards[50]. De Gennes, who claimed that a chain can move along its own tunnel in the form of reptation from its snake-like character and diffuse freely in its own tunnel in the rubber-like zone, was quite correct because different parts of a macromolecule, at constant temperature, will be undergoing a different level of thermal agitations in the course of time. The fluctuations in level of thermal vibrations will, from time to time, give the extra energy to any part of the segment to get "self-dislodged" out of its local energy barrier or entanglement. The level of thermal agitation along the chain will fluctuate in time for individual chain segments and the polymer chain will show up strong time-changing inhomogeneities on the level of local thermal agitations. The inhomogeneities in thermal agitations will not be fixed in one position, but will be created and annihilated randomly along a chain in the course of time. At the same time, the stagnant areas can work as anchors not allowing the agitated parts to get lost too far away from the tube area.

The terms like 'reptation', 'tube length fluctuations' and 'constraint release' will be understandable in this context.

Beside the support for the theories of de Gennes[49], Doi and Edwards[50], the vibrational amplitude fluctuations theory also falls in line with the experimental evidence, which suggests a sharp rise in fluidity above T_g, where the system has just slightly more than 2.5 % vacancies. Such an increase can hardly be explained by the static perception of structural deficiencies only.

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