

Motion of Segment Dislocations as a Model for Glass Relaxation

W.R. Pechhold and B. Stoll

Abt. Angewandte Physik, Universität Ulm, Oberer Eselsberg, D-7900 Ulm, Federal Republic of Germany

Presented at the Third International Seminar on Polymer Physics "Molecular Mobility and Energy Transfer in Polymer Systems", High Tatras, CSSR, April 1982

Summary

The meander model of polymer melts assumes nearly parallel packing of molecular chains and therefore invites to describe shear deformation processes by "dislocation" motion in analogy to metals. Examination of the glass relaxation data for 12 amorphous polymers leads to reasonable values for the energy and the Burgers vector of segment dislocations which are also consistent with thermal properties of the glass transition.

Introduction

By heating a glassy polymer, the volume-temperature-curve shows a bend at the glass transition temperature T_g . It is widely accepted, that this is due to the formation of voids in the neighbourhood of which a cooperative movement of chain segments occurs, but there are still many discussions about the size and the energy of these voids, and there is no detailed model of the chain motions which lead to mechanical deformations. In this communication a molecular model is presented which may give an answer to these questions. It is supposed that the macromolecules in amorphous polymers form a mixture of nearly parallel conformations and are arranged in bundles with a thickness of some nm and that these bundles are folded back and forth to little cubes as fig. 1a shows (PECHHOLD 1980). If you imagine the molecules in a bundle to be quasi hexagonally packed, shear deformations of the bundle are performed most likely by moving dislocations. A general type of deformation includes both, the motion of screw dislocations

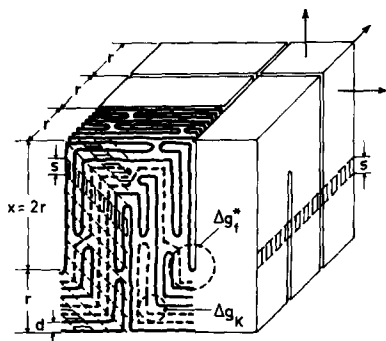


fig.1a: meander cube

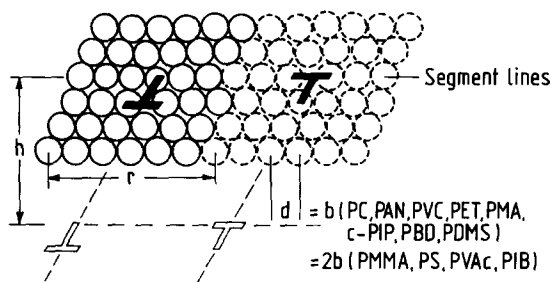


fig.1b: cross section of two bundles with dislocations

and of edge dislocations. As the screw dislocations presumably have a lower activation energy, the deformation rate will be controlled by the edge dislocation parts. Two edge dislocations of opposite sign are shown in a drawing of two bundle cross sections in fig. 1b (PECHHOLD et al. 1979). From metal physics it is known that dislocations tend to associate to dislocation walls (NABARRO 1967). Two of such walls are indicated in fig.1b. According to the molecular model used here, which includes the application of cluster-entropy-hypothesis (PECHHOLD 1980), the probability of finding a chain segment of length s within a dislocation wall, is approximately $\exp(-\epsilon_s/kT)$, where ϵ_s is the dislocation wall energy per segmental area $s \cdot d$, given by (NABARRO 1967, PECHHOLD et al. 1979):

$$\epsilon_s = \frac{0,3 G b^2 d}{4\pi (1 - \nu)} \tag{1}$$

G = shear modulus, b = Burgers vector, ν = Poisson's ratio
 d = chain distance

Relaxation time

In this model, cooperative motions of chain segments leading to mechanical and dielectric relaxation, are only possible, if each segment line of a meander cube does contain at least one segment in a dislocation wall. The probability for this to happen is multiplied with the relaxation frequency of the isolated segment to give the expression inserted in fig.2, which may be taken as the glass relaxation frequency for a segment to reorientate in an electric field. Curves according to this formula are fitted in fig. 2 to experimental dielectric relaxation data. The parameters used in fig.2 are summarized

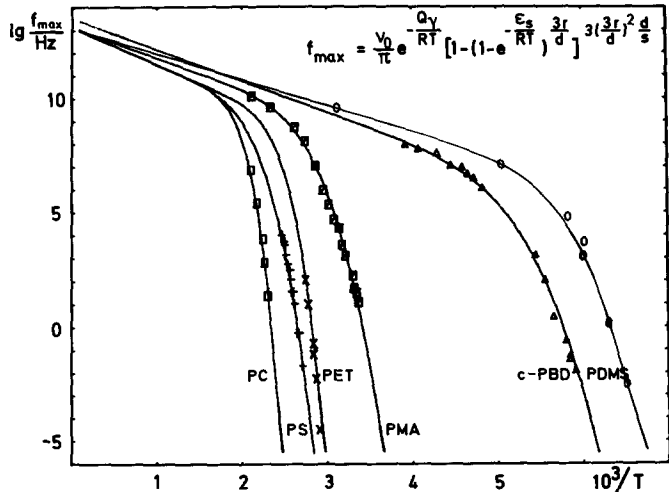


fig. 2: Curves according to the inserted formula, fitted to experimental dielectric relaxation data

in table 1. The values of ϵ_s thus obtained were used to calculate the Burgers vector from equation [1] and the results are listed in table 1. The Burgers vector is in remarkable agreement with either the chain distance d or with one half of it

| | PC | PMMA | PS | PAN | PVC | PET | PVAC | PMA | PIB | c-PIP | c-PBD | PDMS |
|--|------|------|------|------|------|------|------|-------|------|-------|-------|------|
| $Q_V / \frac{\text{kcal}}{\text{Mol}}$ | 7.5 | 15 | 7.5 | 8.2 | 11.3 | 7.5 | 10.0 | 6.2 | 9.7 | 7.0 | 6.3 | 3.0 |
| $\nu_D / 10^{13} \text{ Hz}$ | 4 | 1 | 4 | 10 | 4 | 4 | 4 | 4 | 50 | 2 | 10 | 4 |
| $\epsilon_s / \frac{\text{kcal}}{\text{Mol Segm}}$ | 1.60 | 1.42 | 1.22 | 1.0 | 1.51 | 1.32 | 1.03 | 0.945 | 0.63 | 0.72 | 0.595 | 0.55 |
| $\frac{3r}{d} (r_{\text{max}})$ | 30 | 21 | 18 | 9 | (50) | 30 | 20 | 18 | 18 | 25 | 26 | 24 |
| $\frac{3r}{d} (J_{eN}^0)$ | | (10) | 20 | | | | 19 | 20 | 21* | 22 | 21 | 21 |
| $G(T_g) / 10^9 \text{ Pa}$ | 1.7 | 1.8 | 1.3 | 1.3 | 1.5 | 1.1 | 1.8 | 0.5 | 1.7 | 1.0 | 1.2 | 0.5 |
| $b(T_g) / \text{\AA}$ | 5.6 | 4.3 | 4.5 | 5.0 | 5.8 | 6.2 | 3.8 | 7.1 | 3.4 | 5.1 | 4.6 | 5.9 |
| b/d | 0.97 | 0.52 | 0.52 | 0.85 | 0.98 | 1.04 | 0.50 | 0.94 | 0.51 | 0.94 | 1.03 | 0.95 |

Table 1: Parameters used in figure 2. ϵ_s obtained are evaluated according to equ. [1]

(for PMMA, PS, PVAC, PIB). The latter fact may be understood by considering the average cross section of the chains to exhibit two potential minima. The values for $3r/d$ in table 1 are compared with evaluations from the relaxation strength J_{eN}^0 in the shear compliance (fifth line in table 1). The value of $3r/d = 10$ for PMMA was set in brackets, because from intramolecular potentials it is known that the molecules are slightly bent and it is to be expected that the bundles are twisted; if this is true, the dislocation motion should be confined to the bundle boundaries and the shear compliance should be reduced by a factor d/r . A similar restriction exists for PVC from the small crystalline content probably inside the bundles. As the crystallinity is temperature dependent in the range 120...190°C, $3r/d$ from shear compliance data on PVC has not yet been evaluated. For plotting the curves in fig. 2 ϵ_s was taken to be temperature independent with one exception: in PMMA the temperature dependence of the unrelaxed shear modulus is relatively strong and therefore the temperature dependence of ϵ_s was taken into account. For PVC this effect is expected to be of similar importance, but it has not hitherto been corrected for and therefore the value $3r/d=50$ is set into brackets.

Specific heat

Having data on the concentration of dislocations and its temperature dependence, it is possible to calculate the contributions to the specific heat, ΔC_p , to the volume expansion coefficient $\Delta\alpha$, and to the isothermal compressibility ΔK caused by dislocations. These relaxation strengths may be calculated by irreversible thermodynamics (see e.g. PECHHOLD et al. 1979) from the free energy g^* per segment which may be written (for one lateral direction):

$$\frac{g^*}{2} = \sum_i x_i \epsilon_s + kT \left[\sum_i x_i \ln x_i + (1 - \sum_i x_i) \ln(1 - \sum_i x_i) \right] + p s d^2 \sum_i x_i \bar{\theta}_i \quad [2]$$

x_i being the mole fraction of segments to which an intermolecular defect of ϵ_s is attached; p = pressure; $\bar{\theta}_i$ denotes the mean contribution of volume dilatation (caused by anharmonicity) which is approximately given by (NABARRO 1967, PECHHOLD et al. 1979)

$$\bar{\theta}_i = i \frac{0,3 d^2 G}{8\pi(1-\nu)s^2 K} \left(1 - \frac{\partial \ln G}{\partial \ln V}\right) \quad \begin{array}{l} K = \text{bulk modulus} \\ V = \text{volume} \end{array} \quad [3]$$

For many materials (metals and polymers) the quantity $m = -\partial \ln G / \partial \ln V$ is in the range 5..10. Evaluation of the relaxation strengths using suitable approximations (which hold for the range of ϵ_s given by table 1) for the case $p \rightarrow 0$ yields

$$\Delta C_p \approx 1,86 R \frac{M_m}{M_g} [1 + m \alpha_g T_g]^2 \quad \Delta \kappa \approx 0,0023 \frac{M_s}{M_m} \frac{V_g}{RT_g} \quad \Delta \alpha \approx \frac{0,065}{T_g} [1 + m \alpha_g T_g]$$

with R =gas constant, M_m (and M_g) = molecular weight of a monomer (and a segment), the index g refers to the glass. For $m = 10$, a comparison with experimental data (see literature cited in PECHHOLD et al. 1979) is shown in table 2.

| | | PC | PMMA | PS | PAN | PVC | PET _a | PVAC | PMA | PIB | c-PIP | c-PBD | PDMS |
|--|-----|------|------|------|----------------|----------------|------------------|------|------|------|-------|-------|------|
| units/segment j | | 6 | 4 | 4 | 6 ^g | 6 ^g | 7 | 4 | 4 | 4 | 4 | 4 | 4 |
| M_g/M_m | | 1 | 2 | 2 | 3 ^g | 3 ^g | 1 | 2 | 2 | 2 | 1 | 1 | 2 |
| T_g/K | | 420 | 380 | 370 | 350 | 350 | 340 | 302 | 278 | 200 | 203 | 170 | 150 |
| $\alpha^g/10^{-4}K^{-1}$ | | 2.2 | 2.5 | 2.4 | 2.4 | 2.2 | 2.5 | 2.6 | 3.3 | 1.4 | 2 | 2 | 4 |
| $\frac{\Delta \alpha^g}{10^{-4}K^{-1}}$ | exp | 3.4 | 3.3 | 3.7 | 3.4 | 3.2 | 3.2 | 4.2 | 4 | 4.0 | 4.0 | 5.5 | 6.5 |
| | th | 3.0 | 3.3 | 3.3 | 3.4 | 3.3 | 3.5 | 3.8 | 4.5 | 4.2 | 4.5 | 5.1 | 6.9 |
| $\frac{\Delta C_p^g}{\text{cal Mol}^{-1}K^{-1}}$ | exp | 15 | 7.5 | 7.4 | 6.8* | 4.3 | 14 | 8.6* | | 3.9 | 7.4 | 7 | 5-7 |
| | th | 14 | 7.1 | 6.6 | 4.2 | 3.9 | 13 | 5.9 | 6.8 | 3.1 | 7.4 | 6.7 | 4.8 |
| $\frac{\Delta \chi^g}{10^{-9}Pa^{-1}}$ | exp | | 0.13 | 0.17 | | 0.1 | | 0.16 | | | 0.09 | | |
| | th | 0.14 | 0.13 | 0.15 | 0.11 | 0.11 | 0.12 | 0.13 | 0.14 | 0.16 | 0.10 | 0.09 | 0.24 |

Table 2: Relaxation strengths of the thermal properties at T_g . (* The high values of ΔC_p are probably due to a breakdown of dipolar order and traces of water (PVAC))

References

- F.R.N.NABARRO, Theory of crystal dislocations, Oxford, Clarendon 1967
W.PECHHOLD, Colloid & Pol.Sci., 258, 269 (1980)
W.PECHHOLD, E.SAUTER, W.v.SODEN, B.STOLL and H.P.GROSSMANN, Makromol. Chem., Suppl.3, 247 (1979)