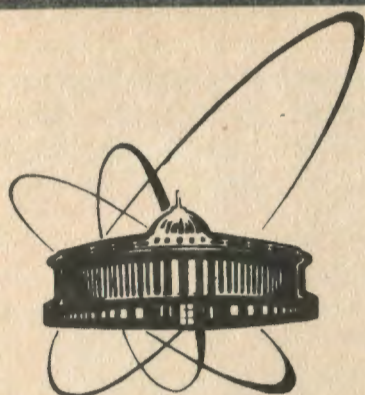


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THE MODEL OF LOW-ENERGY EXCITATIONS  
AND THE PROCESS OF PORE FORMATION  
IN POLYMERS

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## 1 General description of the process of generation of low-energy excitations

In a vitreous solid the phonon system is nearly equal to that in crystalline solids, because partially it is only slightly influenced by the disturbances in the material (see fig. 1a). But these disturbances cause local regions where charged particles or dipoles are not compensated completely. Though the solid is electrically neutral, i.e., though the sum of all charges is zero, the separate regions can have charges causing polarization. The separate regions are interconnected (see fig. 1a and b) and if there is a change of polarity in one of them the others will "feel" it.

An external disturbance like an electrical field, mechanical influence or irradiation can effect a change of polarization in a separate region by the transition of a free charge or dipole from one state of equilibrium into another. The energy barrier between these states of equilibrium is very small and so a transition from one into the other is possible. These are so called two level systems. But a transition of a charge or dipole into another state of equilibrium is connected with a change in polarization in the surrounding.

The neighbouring regions react to this change and this response can be compared with an oscillation of the regional units. (see fig.2a and 2b) These are low-energy excitations because their energy is about three orders of magnitude smaller than that of phonones. They occur in vitreous solids so that beside the phonon system there is a second, independent system of bosons.

In our case the irradiation of the polymer film produces charges around the track and leads to destruction of bonds in the macromolecules. So the structure and size of such separate units as shown in fig. 1. is changed. These charges are fixed at the macromolecule as radical electrons. The equilibrium states of the charges should be different localisations in the molecule. The transition can occur over a few bonds. The etching process leads to a change in the structure of the molecules. If a monomer unit of a macromolecule is disengaged the localisation of the charge will change and so reaction of the molecules or parts of molecules in the surrounding occurs. This reaction of the neighbouring parts of molecules can be described as a generation of low-energy excitations (see fig. 3a and b).

How it was already described in another work [7] the process of the generation of low-energy excitations has an influence on the etching behaviour of the tracks. It becomes visible in the etching curves which are received by electrical conductivity measurements during the etching process. An illustration of these etching curves and the corresponding development of the pore shape is given in fig. 4a and b.

In fig. 5a an etching curve resulting from such measurements driving the etching process of a single track of a fission fragment is shown. The dependence of the radial pore etch rate  $v_r = \frac{dr}{dt}$  on the pore radius was calculated and is shown in fig. 5b. The points represented the experimental data. The solid line corresponds to a theoretical calculated curve as it will be shown in sec.2 (eq.(9), (10),(11),(12)).

It can be noted, that up to the minimum the curve corresponds to the experimental results. After that the radial pore etch rate increases up to the value of the bulk etch rate. That means, at greater distances from the trajectory of the heavy ion other processes become decisive.

## 2 Mathematical derivation of the response function of the model of low-energy excitations

Now it is the purpose to derive this function, which describes the response of the solid. The description of the spatially or temporally depending response should be preceded by some considerations. Proceed from [1] the correlation function  $G$  of two field strengths characterizing a field  $H$  in two states of equilibrium is calculated by

$$G(x) = h_0^2 \exp\left(-2 \cdot \int_0^x dx W(x)\right) = \overline{H(0)H(x)} \quad (1)$$

with  $x = \tilde{x}' - \tilde{x}$

whereby the variables  $\tilde{x}$  and  $\tilde{x}'$  represent two different points of a generalized coordinate (spatial coordinates or time).

The field strength values have the value  $h_0$  in their states of equilibrium. Variable  $W$  is the transition probability from one equilibrium state into another.

If the transition probability  $W$  depends on the coordinate  $x$  as it is shown in eq.(1) this will imply that a transition of local part with a field strength value  $\pm h_0$  from one equilibrium state into another is not dependent on the behaviour of other local parts.

When applying an electrical field  $E(\tilde{x})$  at the measurement the polarization density is calculated as analog to [2] by

$$(\vec{P}) = (\vec{P}_0) + \int_{-\infty}^x d\tilde{x} \psi(\tilde{x} - \tilde{x}') E(\tilde{x}) \quad (2)$$

with  $(\vec{P})$  being polarization density in a state of equilibrium. Provided that the laws of classic statistical mechanics are valid the diagonal tensor  $\Psi(\tilde{x} - \tilde{x}')$  can be simplified as

$$\Psi(\tilde{x} - \tilde{x}') = \beta \cdot \overline{(\vec{P}_i(\tilde{x})\vec{P}_i(\tilde{x}'))}_0 \quad (3)$$

The brackets  $(\overline{\quad})_0$  indicate averaging by means of the equilibrium distribution function of the totality of local polarization fields. Variable  $\vec{P}_i(\tilde{x}')$  is the local derivation of polarization  $P(\tilde{x})$  at the position  $\tilde{x}'$ . The factor  $\beta$  is  $(k_B T)^{-1}$ , whereby  $k_B$  is the Boltzman constant and  $T$  the absolute temperature. Function  $\Psi(\tilde{x} - \tilde{x}')$  is referred to the general response function. Using correlation function (1) for response function (3)

$$\Psi(x) = 2 \beta h_0^2 W(x) \exp\left(-2 \int_0^x dx W(x)\right) \quad (4)$$

is obtained. In case of the delocalization processes of charges the transition probability  $W(x)$  depends on the coordinate  $x$ .

This dependence results from the correlation of individual local parts. Since every change yields an effect on the collective polar parts the transition probability at different positions is different. Assuming that this effect can be described by the system of independent bosons [1, 3, 4] the reaction of the collective polar system to a sudden change of a local part by emission of low-energy excitations can be calculated.

For this reason, transition probability is written in the form

$$W(x) = W_0 \exp(-\phi(x)) \quad (5)$$

with  $W_0$  representing transition probability of an uncorrelated change. The term  $\exp(-\phi(x))$  characterizes the impact of correlation. Hence, term  $\phi(x)$  takes into account processes occurring in contrast to the behaviour of "ideal" solids. The term  $\phi(x)$  is called response term. The calculation of the response term is given in [2, 5] and leads to the result

$$\phi(x) = n \cdot \text{Re}(\gamma + \ln(i\epsilon_c x) + E_1(i\epsilon_c x)) \quad (6)$$

Function  $E_1(\epsilon_c x)$  is a standard integral disappearing at high  $\epsilon_c x$ ,  $\gamma$  is the Euler's constant.

The signification of the parameter  $n$  is a measure for the influence of the low-energy excitations, or in other words, the vitreous behaviour on the general behaviour of the solid. The value  $n$  is in the range from 0 up to 1. Using the definition

$$x_0 = \frac{1}{2W_0} \quad (7)$$

the response function can be written as

$$\Psi(x) = \frac{\beta h_0^2}{e^{n\gamma} x_0 \epsilon_c^n} x^{-n} \exp\left(-\frac{x^{1-n}}{(1-n) e^{n\gamma} x_0 \epsilon_c^n}\right). \quad (8)$$

In the special case of formation of etchable tracks in polymer materials irradiated with heavy ions the general coordinates are replaced in the following way

- $x$  →  $r$  pore radius
- $\epsilon_c$  →  $k_c$  maximal wave number
- $x_0$  →  $l_0$  distance between two states of equilibrium if no correlations occurs
- $h_0$  →  $a_0$  polarization density
- $n$  →  $n$  interaction parameter

So the response function get the form

$$\Psi(r) = \frac{\beta a_0^2}{e^{n\gamma} l_0 k_c^n} r^{-n} \cdot \exp\left(-\frac{r^{1-n}}{(1-n) e^{n\gamma} l_0 k_c^n}\right). \quad (9)$$

The eq.(9) is not the finished form of the response function describing the pore formation, because in this special case there is a external disturbance, the irradiation, but the generation of the low-energy excitations occurs because of a mediator. This is the etching process. That means, the generation of the low-energy excitations is influenced by the etching rate and an expression for that fact is the parameter  $m$ , the so called activation parameter. With the relation

$$r_p = \frac{1}{k_p} = \left((1-n) e^{n\gamma} l_0 k_c^n\right)^{\frac{1}{1-n}} \quad (10)$$

$\Psi(r)$  can be written as

$$\Psi(r) = \frac{(1-n) \beta a_0^2}{r_p} \left(\frac{r}{r_p}\right)^{-n} \cdot \exp\left(-\left(\frac{r}{r_p}\right)^{1-n}\right). \quad (11)$$

If  $\frac{r}{r_p}$  is replaced by  $\left(\frac{r}{r_p}\right)^m$  the response function becomes the finished form:

$$\Psi(r) = \frac{(1-n) \beta a_0^2}{r_p^m} \left(\frac{r}{r_p}\right)^{-m \cdot n} \cdot \exp\left(-\left(\frac{r}{r_p}\right)^{m(1-n)}\right). \quad (12)$$

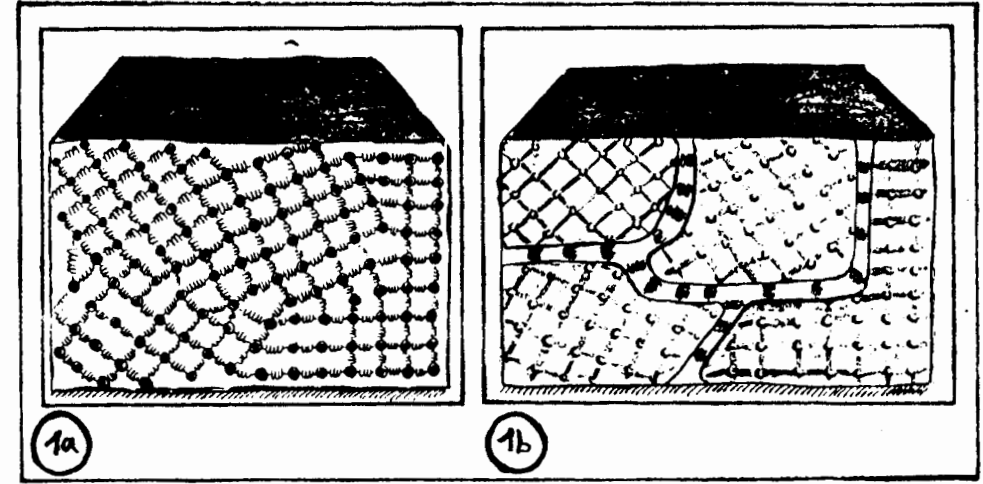


Figure 1: A schematic illustration of a disturbed solid

- a - The springs show the coupling between the atoms and molecules
- b - The fat springs show the coupling between local regions, formed due to the disturbances in the solid.

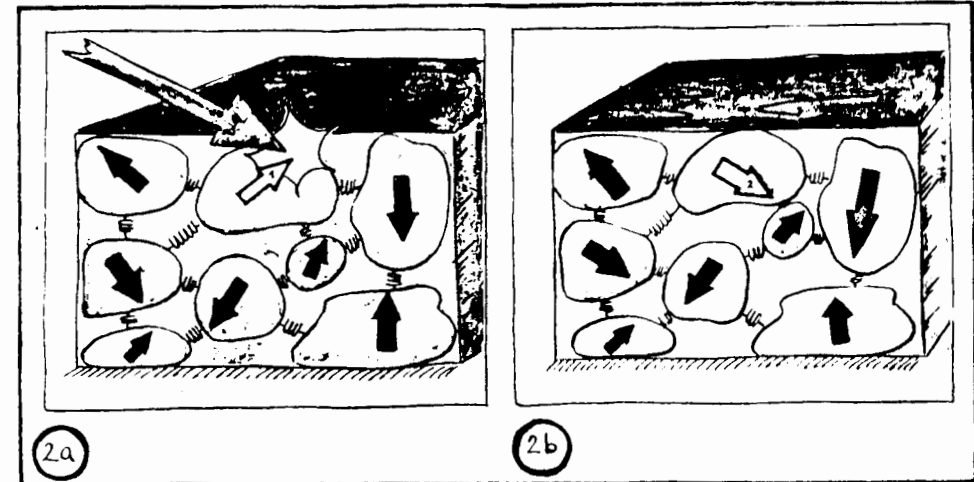


Figure 2: The same solid like in Figure 1, in a more abstract manner

- a - An external disturbance occurs (big arrow).
- b - One local region passes from one state of equilibrium into another (see arrow (1) in (a) and arrow (2) in (b)).

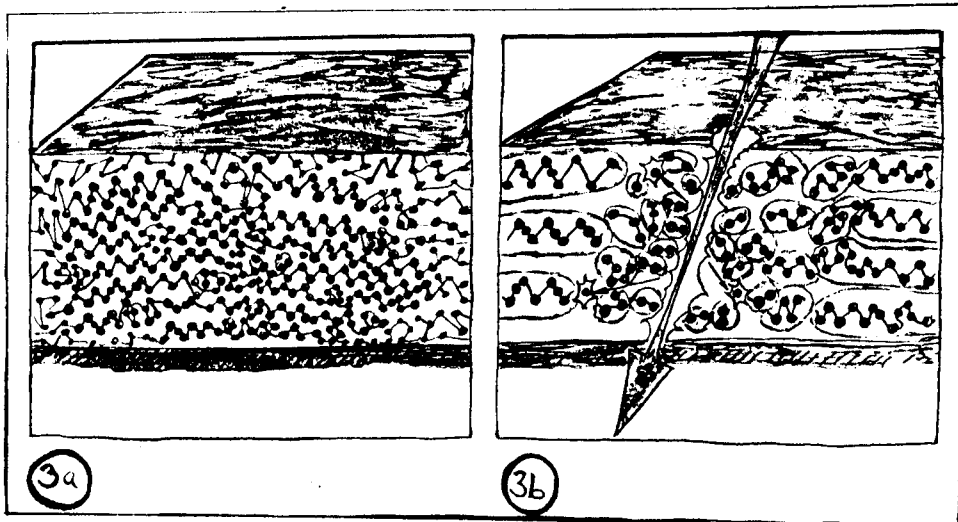


Figure 3: A polymer foil in a schematic manner  
 a - The foil consists of macromolecules.  
 b - After an irradiation exists an ensemble of the disturbed macromolecules. Due to the irradiation a lot of charges are produced around the tracks. So the process causes there the building of local polarized regions.

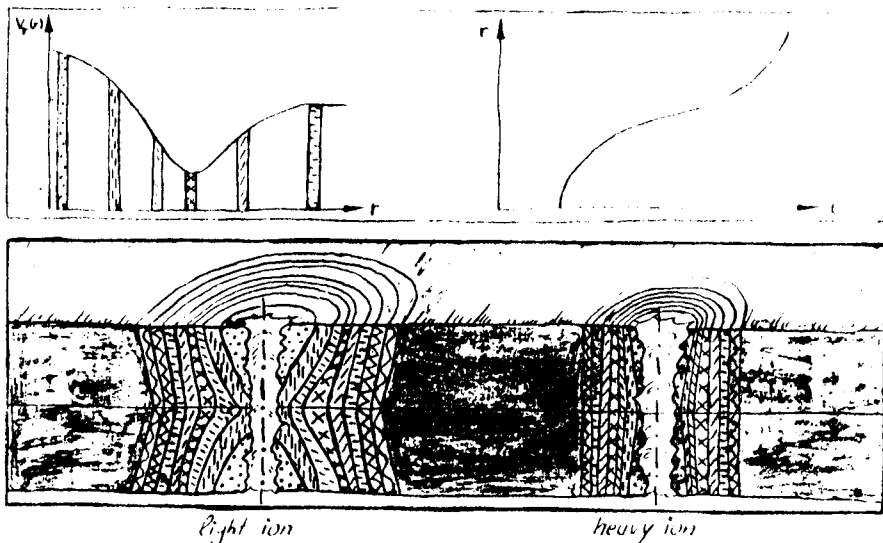


Figure 4: An illustration of the etching process in a polymer foil and the corresponding development of the pore shape. The value  $v_r$  is the pore etch rate,  $r$  is the mean cylinder radius of the track and  $t$  is the etching time.

In the case of the etching process of irradiated polymer films the pore growth is caused by a degradation of ester bonds. Analog to the kinetics of chemical reactions the pore growth is determined as

$$\frac{dr}{dt} = K \cdot a_{OH^-} \cdot a_{H_2O} \quad (13)$$

As it is a reaction of a solid the reaction rate constant  $K$  is determined by the structure of the polymer like crystallinity or average molecular weight of the macromolecules.  $a_{OH^-}$  and  $a_{H_2O}$  are the activities of the hydroxyl ions and the water molecules in the etchant. But as it was already shown in the range around the trajectory of the heavy ion the disturbances caused by the heavy ion leads to a change in the structure and polarity which cause the generation of low-energy excitations during the etching process. The response of the parts of molecules around the place where a monomer unit is disengaged has an influence at the reaction rate. This response can be described with the model of low-energy-excitations. That means eq.(13) changes to

$$\frac{dr}{dt} = K_r \cdot \Psi(r) \cdot a_{OH^-} \cdot a_{H_2O} \quad (14)$$

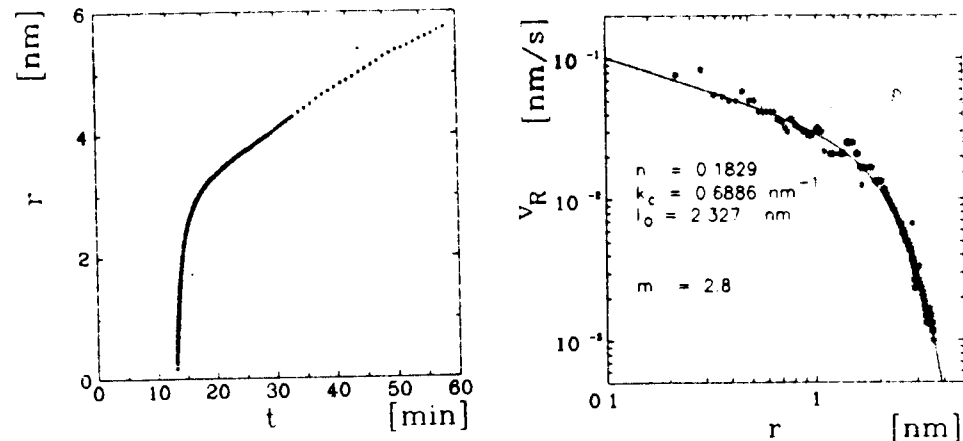


Figure 5: a - Typical shape of the etching curve describing the dependence of the pore radius on the etching time.  
 b - Representation of the radial pore etch rate. The solid line corresponds to a theoretically calculated curve.

### 3 Conclusions

The present work should give an illustration of the processes in polymer films irradiated with heavy ions. It is assumed as an addition to further works where these problems were discussed [5, 6, 7].

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