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Tests on silica for specimens without pre-existing stresses

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Abstract

At silica surface exposed to a water environment, the water reacts with silica. Experiments show that the hydroxyl generation has an influence on mechanical properties. We dealt with these effects in the past and could interpret them as a consequence of swelling in the surface region. A different attempt was suggested in a series of publications by Tomozawa and co-workers assuming relaxation of stresses due to presence of water.

Since any stress relaxation needs pre-existing stresses, we will here only discuss results which were obtained in the absence of any present stresses. We consider density, disk-deformation, and inert strengths. These results show a strong effect of hydroxyl content and can be understood by the effect of swelling. Finally, a suggestion is made for further studies on swelling.

Contents

1. Introduction

Water penetrated into silica reacts with the silica network according to

$$\equiv\text{Si-O-Si}\equiv +\text{H}_2\text{O} \leftrightarrow \equiv\text{SiOH}+\text{HOSi}\equiv \qquad (1)$$

with the concentration of the hydroxyl $S=[\equiv\text{SiOH}]$ and that of the molecular water $C=[H_2O]$. In the present paper we exclusively deal with the effects which are present even in the absence of stress-enhancement for reaction (1).

There exist two contrary approaches to explain mechanical effects occurring when water enters silica:

- In papers by Tomozawa et al. [1] and Lezzi et al. [2] residual curvatures after 2-point bending tests in humid air and strength increase of pre-stressed silica fibers were observed, respectively.
- In the past, the authors showed in a couple of papers the principle effects of volume swelling by hydroxyl generation in silica on mechanics and fracture mechanics properties [3,4].

1.1 Explanation by a relaxation hypothesis

The explanation given in [1,2] postulates a complete relaxation of pre-existing stresses, σ_{appl}, in the thin water containing surface layer. After unloading, these layers should show an inverse stress of $-\sigma_{\text{appl}}$. Consequently, the strength, σ_{f}, in enclosed tensile tests would increase. In bending tests, the retarding bending moment by these stresses would cause a residual curvature after unloading of previous 2-point bending tests. A discussion of the mechanical effects from this hypothesis was recently given by Tomozawa et al. [5].

Main assumption of the stress relaxation hypothesis is that in the water penetration zone near the surface any stress must completely relax. For their model, the authors claim that at the surface of a silica body under an applied stress the stress should relax in presence of water by

$$\Delta\sigma_{rel} = -\sigma_{appl}\,. \qquad (2)$$

This relaxation law should hold for all stress levels of $-0.5\ \text{GPa} \le \sigma_{\text{appl}} \le 3\ \text{GPa}$ (lower limit concluded from relaxation of compression zone in bending tests [1], upper limit from interpretation of the strength tests in [2]) and water vapour pressures of $0.6\ \text{Torr} \le p \le 355\ \text{Torr}$. It should be noted that no specific water concentration C enters eq.(2) at which the relaxation would switch on. The authors of [1,2] only distinguish implicitly between *presence* and *absence* of (molecular) water, i.e. by

$$\sigma_{rel} = \begin{cases} -\sigma_{appl} & \text{in presence of water} \\ 0 & \text{in the absence of water} \end{cases} . \tag{3}$$

The minimum value of water at which total relaxation at the surface would start can of course not be at C_w =0, because any glass will contain pre-existing hydroxyl and molecular water.

In order to determine this claimed effect, one needs of course *independent* measurements of the stress change in the surface layer. Unfortunately, to our knowledge there are no *independent* measurements available in literature from which the relaxation effect might be predicted.

In this context it seems of importance that Lezzi and Seaman [6] conclude that "*The exact mechanism by which water can enhance stress relaxation can only be postulated but not directly observed*".

On the other hand, the stress relaxation $\Delta\sigma_{rel}$ must disappear if no external stress σ_{appl} occur, i.e. if σ_{appl} =0 is selected for a suitable test.

1.2 Explanation by swelling

In the past, the authors showed in a couple of papers the principle effects of volume swelling by hydroxyl generation in silica on mechanics and fracture mechanics properties [3,4].

When *S* is the weight concentration of the hydroxyl, the volume strain in silica, ε_v, is

$$\varepsilon_v = \kappa S \ , \quad \kappa = 0.97 \tag{4}$$

This effect is experimentally proved by density measurements in literature [9-12]. Our competing explanation of the mechanical effect of reaction (1) suggested in [7], is the local swelling of the glass volume due to hydroxyl generation.

By mechanical boundary conditions, the swelling strains result in swelling stresses proportional to the amount of hydroxyl concentration. Strength predictions on this basis [8] were in suitable agreement with the strength results by Lezzi et al. [2]. The same holds from the curvature measurements in [1].

At a free surface, the stress state is plane stress and, consequently, also stresses caused by swelling are equi-biaxial ($\sigma_{sw,x}$=0)

$$\sigma_{sw,y} = \sigma_{sw,z} = -\frac{\varepsilon_v E}{3(1-\nu)} = -\frac{\kappa E}{3(1-\nu)} S \tag{5}$$

where *E* is Young's modulus and ν is Poisson's ratio.

2. Effects in the absence of pre-existing stresses

We consider here only experiments on samples which did not show any stress already existing before the experiments. Consequently, these tests cannot in principle be influenced by the postulated relaxation, since there was nothing available that could relax.

2.1 Density decrease by swelling

A swelling effect in water-containing silica at high temperatures was early reported by Brückner [9,10], Shackelford [11] and Shelby [12]. As a consequence of the high temperature the diffusivity of water is very high, so that the water is homogeneously distributed. Consequently, mechanical stresses cannot exist. The authors [9-12] showed that the density ρ decreased by reaction (1) at high temperatures according to

$$\frac{\Delta\rho}{\rho_0} = -\chi C_w \tag{6}$$

where C_w is the weight fraction of water and ρ_0 is the density of the anhydrous material. At the high temperature >1000°C all water is in form of hydroxyl *S*. From the definition of the density as the quotient of mass *m* and volume *V*, $\rho = m/V$, it follows for the volume swelling strain ε_v (using logarithmic derivation)

$$V = \frac{m}{\rho} \;\Rightarrow\; \varepsilon_v = \frac{\Delta V}{V} = \frac{\Delta m}{m} - \frac{\Delta\rho}{\rho} \tag{7}$$

Since the density decreased when the water content increased, the volume must increase too.

Figure 1 represents data from [9-12]. The data by Shackelford for fictive temperatures of T_f=1000°C, T_f=1100°C and T_f=1200°C were directly taken from the original paper [11] transforming the “water” content (wt% OH) in water content (wt% H_2O) using the factor (18/17)/2 where 18/17 reflects the different molar weights of OH and H_2O.

By a least-squares fit over all the scattering individual data points for 1100°C exclusively, we obtained [13] the coefficient κ in (4). The corresponding dependency is introduced in Fig. 1 by the dash-dotted straight line.

The effect of the water-silica reaction is the generation of *swelling strains*. *Swelling stresses* are a consequence of the mechanical boundary conditions. A volume element in a thick plate that undergoes swelling cannot freely expand. If the diffusion zone is small compared to the component dimensions, expansion is completely prevented in the plane of the surface and can only take place normal to the surface plane. In the absence of externally applied stresses no preference in swelling strains is given and therefore *isotropic swelling* in all directions has to be expected.

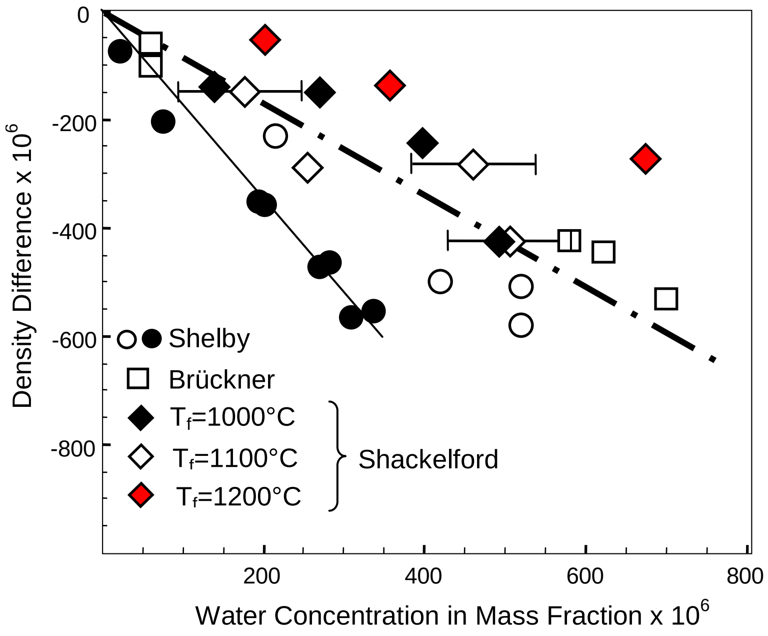

Fig. 1 Effect of water concentration on density of vitreous silica, results by Shelby [12], Brückner [9, 10], and Shackelford [11]. The dash-dotted straight line serves as a guide-line for the eyes. The open symbols are for a fictive temperature of T_f=1100°C, the black symbols for T_f=1000°C and the red ones for T_f=1200°C. The circles represent results by Shelby [12] with the water produced in silica saturated with hydrogen and then gamma-irradiated.

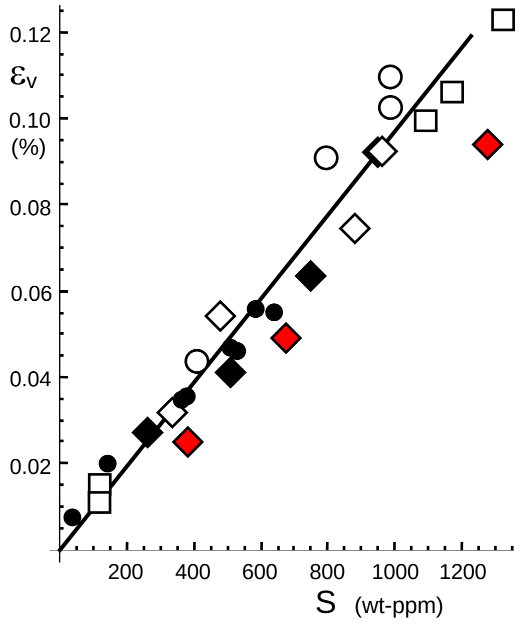

Fig. 2 Volume expansion vs. hydroxyl concentration *S*, from [14,15].

Finally, the volume increase ε_v is plotted in Fig. 2 as a function of the hydroxyl concentration *S* for all measurements in Fig. 1. The symbols in Fig. 2 are the same as in Fig. 1. The straight line, introduced in Fig. 2, represents the coefficient κ=0.97 according to (4). The good agreement with all the data is evident.

2.2 Deformation of water-soaked disks

Swelling stresses were derived in [7] by measuring the change of the curvature of silica disks after hot-water soaking. At the heart of this study is an experiment in which water is diffused into one side of thin vitreous silica disks. This technique has been used earlier to determine the volume change caused by the penetration of water into silica coatings on silicon wafers [16]. The consequent volume expansion at the glass surface results in a bending of the disks, which are no longer flat after exposure, but concave-shaped [17]. By measuring the radius of curvature at the surfaces of the curved disks and by understanding the mechanism of water migration, the surface stress can be calculated. The technique can also be used to calculate the diffusivity of water in silica glass.

Two different experimental procedures were applied in [7] for tests at 90°C and 200°C. Here the procedure for the higher temperature may be addressed exclusively. At this temperature bare silica disks were heat-treated on both sides and after cooling to room temperature stepwise etched from one side in a buffered HF solution. After each etching step the change of curvature was determined resulting in the released bending moment versus total removed surface layer d, $\Delta M_b(d)$ for different soaking times, determined by

$$\Delta M_b(d) = \frac{EW^3}{12(1-\nu)}\left(\frac{1}{R} - \frac{1}{R_0}\right) \tag{8}$$

where R is the actual and $R_0 \approx 0$ the initial curvature and W the thickness of the plate. The asymptotically reached value is the total bending moment ΔM_b. Figure 3a shows results for soaking at 196°C for 2.2h and 20h.

The bending moment M_b caused by a thin swelling layer after one-side soaking was computed in [7]. In terms of the hydroxyl concentration S the moment reads

$$M_b = -\kappa \frac{W}{2}\frac{E}{3(1-\nu)} \cdot \frac{m_s}{2} \tag{9}$$

where m_S is the mass of the hydroxyl water as was determined in [7] via IR-absorption measurements.

An example for the predicted bending moment is shown in Fig. 3a for 20h soaking time by the horizontal straight line at $M_b = -0.0145$ Nm/m. From the measurements an asymptotically reached moment of $M_b \cong -0.017$ Nm/m is concluded.

In Fig. 3b all predictions (squares) and measurements (circles) are compiled. The predicted data are within the 95% error limits of the measurements supporting the insight that only the ≡SiOH contributes to the volume expansion.

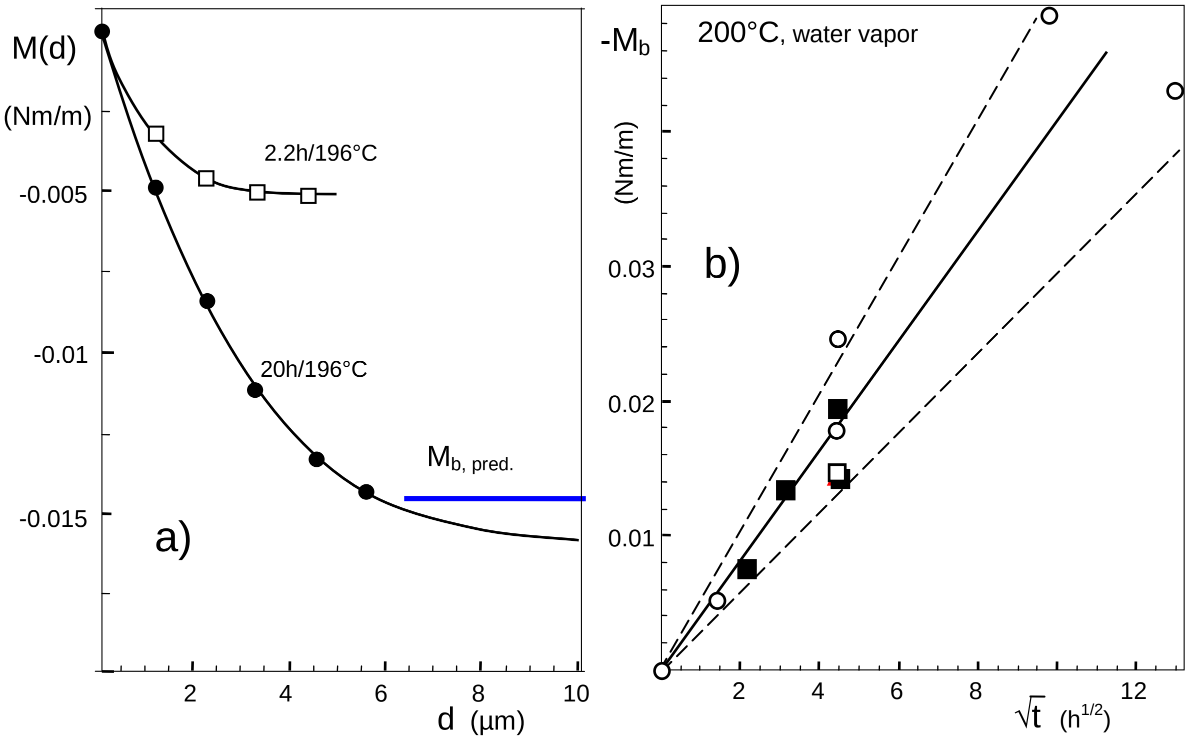

Fig. 3 a) Measured change of bending moments at θ≅200°C, b) comparison of measurements (circles) and predictions based on measured IR-data (open square) and data reported by Zouine et al. [18] and Helmich and Rauch [19] (solid squares). The dashed lines represent the 95% error limits of measurements.

2.3 Change of inert strength

The process of swelling sets up a negative stress intensity factor that shields the crack tip and enhances the strength of the specimen. Because diffusion rates increase with temperature, crack tip shielding should also increase as the temperature is increased, as should the specimen strength.

Strength measurements at 250°C are in principle known from literature. Li and Tomozawa [20] soaked silica bars for up to 4 days soaking time and tested the strengths in dynamic bending tests under subcritical crack growth conditions. To the authors' knowledge, so far no really inert strength measurements are available for water-soaked silica.

We studied the strength behaviour of the silica glass EN08NB (GVB, Herzogenrath) containing 99.98% SiO_2. Cylindrical bending bars of 45 mm length were cut from silica rods of 4 mm diameter maintaining the original surface from manufacturing. Then all specimens were annealed for 1h at 1150°C in vacuum in order to eliminate pre-existing residual surface stresses. To avoid any water contact, the series foreseen for strength measurements in an inert environment were immediately, after cooling down, stored in fresh silicon oil as proposed by Sglavo and Green [21] as an inert medium. The soaking conditions and surface zone parameters are given in Table 1.

b (µm)	S (wt%)	ε_v	$\sigma_{sw,0}$ (MPa)
17.7	0.74	0.72%	-209

Table 1 Parameters of specimens soaked for 192 h in liquid water of 250°C, $\sigma_{sw,0}$ calculated due to eqs.(4) and (5).

Inert bending strength tests were carried out in liquid nitrogen in a 3-point test. The results for unsoaked specimens (open circles) are shown in Fig. 4 in Weibull representation (see e.g. [22]). The distributions of the unsoaked specimens show the usually expected Weibull straight–line. Applying the Maximum Likelihood procedure (for details see [23]) the obtained Weibull parameters are m = 6.6 MPa and σ_0 = 250 MPa. It should be noted that even if the initial strength is Weibull-distributed, the strength of specimens under swelling stresses do no longer result in a Weibull distribution [22].

Even the strengths of the unsoaked specimens appear rather large. The reason for this is of course the 3-point bending loading with its reduced effective surface compared to 4-point bending tests and on the other hand the circular cross section of the specimens, that reduces the effective surface once more. The strength could be approximated roughly by Weibull distributions. Table 2 shows the related Weibull parameters. From the strengths in the untreated state and the fracture toughness of K_{Ic}=0.8 MPa√m [24], the initial crack depth can be concluded.

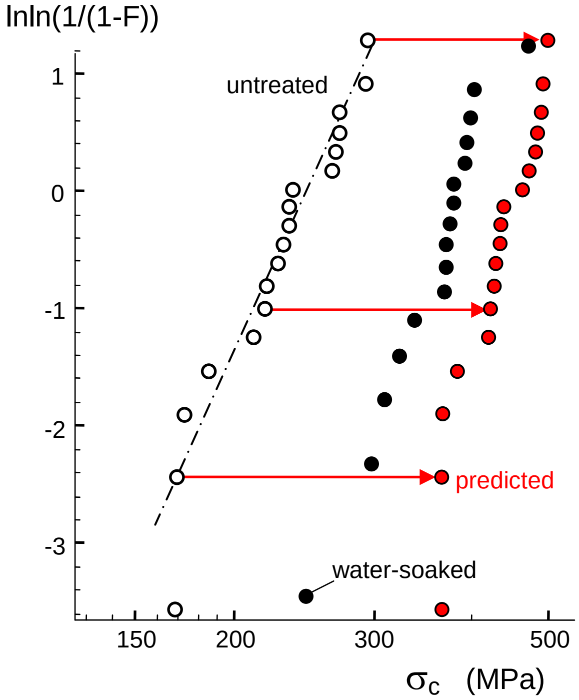

Fig. 4 3-point bending tests in liquid nitrogen: Strength of untreated silica (open circles), liquid water treated at 250°C (full circles).

	$\sigma_{c,0}$ (MPa)	*m*
untreated	250	6.6
Water soaked	395	4.5

Table 2 Strength results, represented by the Weibull parameters.

An extended comparison of results predicted via swelling has been given in Section 9 of [15] and best agreement between measurements and predictions could be stated.

Here we have addressed in Section 2 only experiments on samples which did not show any pre-existent stress existing before the experiments. Although these tests can never be affected by the postulated relaxation [1], they show mechanical responses which are fully consistent with the predictions based on volume swelling.

3. Suggestions for the determination of volume swelling

In future work we plan to determine the volume swelling strain via AFM-measurements. Two possible procedures may be applied:

3.1 Profile measurements at specimen ends

The plane of a silica specimen end is measured with AFM, Fig. 5a. Then, the sample is soaked in water vapour at high temperature (no liquid water in order to avoid change of the surface by dissolution). Finally, the surface profile is measured again, Fig. 5b, and the displacements determined from the difference between measurements of Fig. 5a and 5b. If the polished planes do not end sufficiently sharp (possibly rounded by the polishing procedure, also a fractured specimen (not soaked before) can be used.

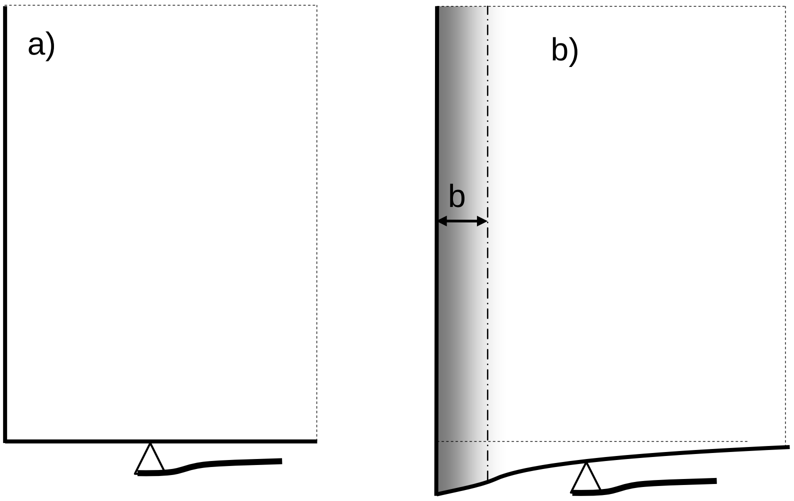

Fig. 5 Swelling strain for diffusion zones without stress enhancement, a) rectangular end of a polished specimen before and b) after soaking in water vapor.

3.2 Measurement in distance *y*>>*b* from the specimen end

A bar is soaked and then fractured, Fig. 6. The two fracture surfaces are measured with AFM. The difference of the displacements is then twice that of procedure 3.1, i.e. the reference plane is the sum of the two measurements (displacement signs at the upper and lower fracture surface different). The diffusion or swelling zone was modelled by a zone of thickness *b* with a constant volume strain ε_v. The results are plotted in Fig. 7. The sign of the displacements is here negative because the lower surface was modelled with the expansion *against* the *y*-direction.

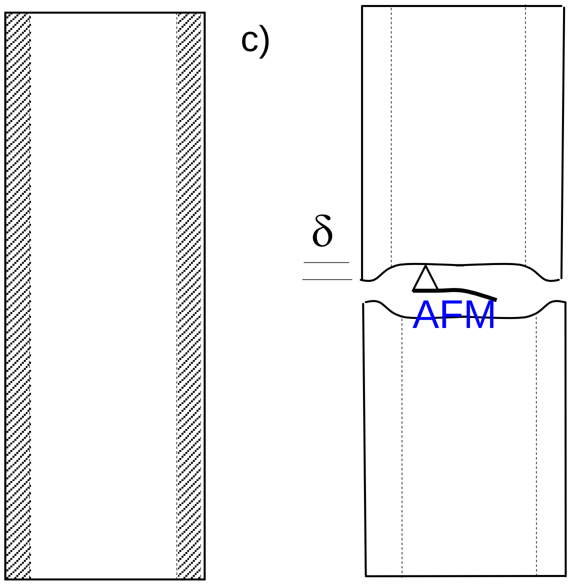

Fig. 6 Swelling strain for diffusion zones without stress enhancement, measurements on both sides of a specimen fractured after soaking.

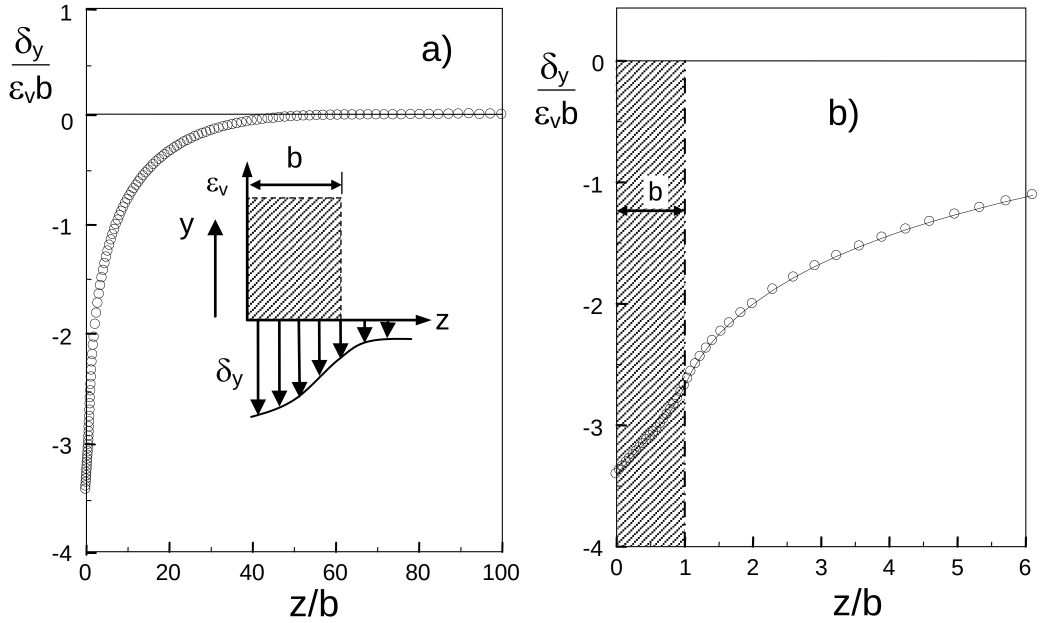

Fig. 7 Displacements at the end of a specimen undergoing the volume swelling ε_v.

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