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Principy nanoindentace na heterogenních systémech

Principals of Nanoindentation on Heterogeneous Systems

Summary

In the past decade, the investigation of heterogeneous materials on different length scales has made a significant progress from experimental as well as theoretical points of view. Some new experimental techniques and approaches have been established. One of the most powerful micromechanical tools includes nanoindentation which, nowadays, can be successfully used also for the analysis of inhomogeneous solids. Several experimental approaches are introduced in this contribution in conjunction with numerical and statistical evaluation, such as statistical grid indentation, deconvolution algorithms or pointed indentation.

Nanoindentation can be successfully used for analyzing of complicated structural materials like cementitious composites or materials based on alternative aluminosilicate binders, e.g. alkali-activated fly ash. For these kinds of materials, intrinsic mechanical properties of distinct material phases are usually treated with the aid of statistical nanoindentation. Some material phases, such as clinkers, or high-density C-S-H, can be measured by direct method, i.e. pointed indentation. Results need to be examined together with the knowledge of chemistry and other supplementary measurements like porosimetry, ESEM and EDX analyses, etc. Up-scaling of intrinsic micromechanical properties to upper level can be performed for a composite using simple analytical or numerical homogenization tools.

Nanoindentation plays an indispensable role in identifying of phase properties of heterogeneous materials and its application to structural materials open a path to wide variety of interesting research topics that can be hardly solved by using of some other mechanical tests.

Souhrn

V minulém desetiletí jsme byli svědky prudkého rozvoje experimentálního i teoretického výzkumu heterogenních materiálů na různých úrovních materiálu. Došlo k rozvoji nových experimentálních technik a postupů. Mezi nejužitečnější nástroje mikromechnické analýzy lze počítat i nanoindentaci, která může být úspěně využita též pro analýzu nehomogenních látek. V tomto příspěvku je představeno několik experimentálních postupů ve spojení s numerickou a statistickou analýzou jako je statistická maticová indentace, dekonvoluční algoritmy nebo cílená indentace.

Nanoindentace může být úspěně použita pro studium komplikovaných stavebních materiálů jako jsou cementové kompozity nebo materiály na bázi alternativních aluminosilikátových pojiv, např. alkalicky aktivovaného popílku. Pro tyto materiály lze nanoindentaci použít ke stanovení skutečných mechanických vlastností jednotlivých fází materiálu a to často s pomocí statistické nanoindentace. Některé materiálové fáze, jako jsou slínky nebo vysokohustotní C-S-H gel, mohou být měřeny přímo cílenou indentací. Výsledky musí být zkoumány též se znalostí chemického složení a dalších podpůrných měření jako např. porozimetrie, ESEM, EDX analýza, apod. Promítnutí skutečných mikromechanických vlastností na vyšší úroveň lze u kompozitu zajistit pomocí jednoduché analytické nebo numerické homogenizace.

Nanoindentace hraje nezastupitelnou úlohu při identifikaci vlastností jednotlivých fází heterogenního materiálu a její aplikace na staveb-ní materiály otvírá cestu k širokému spektru výzkumných témat, které těžko mohou být vyřešeny za pomoci jiného mechanického testu.

Klíčová slova

nanoindentace, heterogenní materiály; cementové kompozity; statistická dekonvoluce; homogenizace

Keywords

nanoindentation; heterogenous materials; cement composites; statistical deconvolution; homogenization

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1 Introduction

Analysis of complicated engineering materials always brought an attention of many researchers and scientists. Significant progress has been made through the past years in this field. Current trends in civil and material engineering put high demands on engineers with the final aim to produce:

- Safe buildings
- Durable buildings
- Cost and energy efficient buildings
- Buildings that contribute to the reduction of CO_2

In order to fulfill these goals it is necessary to develop improved materials with optimized strength and stiffness, with dense microstructure, with balanced permeability, and with other important engineering properties. Nowadays, investigations are performed with the effort to understand the material microstructure and material behavior on microlevel which leads to the optimization of components, mixture and analysis of component properties at microlevel. Final aim is to control resulting macroscopic properties through the changes made on the material microstructure.

Many experimental tools have been devepoled to access material microlevel. Let us summarize some of them in three groups. The first group includes techniques measuring material microstructure and composition such as: electron microscopy (ESEM), atomic force microscopy (AFM), fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), X-ray diffraction (XRD) and others. The second group covers very important thermal analyses like differential thermal analysis (DTA) or calorimetry. The third group involves micromechanical analyses. The unique position between these methods is occupied by nanoindentation which is the only micromechanical tool that can access nano/microlevel properties of material components.

2 Heterogeneity and multiscale materials

Standardly, some fine materials are considered, measured and also modeled as homogeneous. But their homogeneity must be viewed

from the perspective of different length scales. For example, if we consider the whole structure of a building, the material like steel or concrete can be considered as homogeneous without any problems. But if we downscale our view to a structural element we can see joints, layers, material inhomogeneity etc.

In case of analyzing the material the situation is very much the same. Strictly speaking, every material is heterogeneous at certain length scale. In case of a structural material like concrete it is usually treated as so called multiscale material in which we can distinguish some typical length scale levels (e.g. [1, 2, 3, 4]). On these separate levels the material is considered as homogeneous. So we split the material to levels (e.g. Fig. 1) that are assumed to be homogeneous or the homogeneous properties are computed from intrinsic properties of their components using some homogenization technique to obtain its effective overall property (see [5] for review).

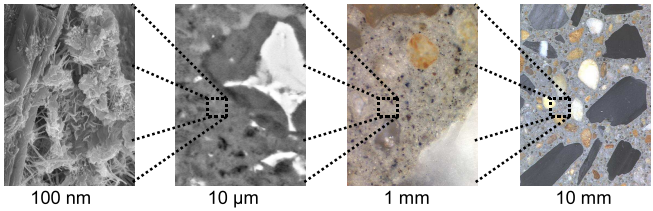

Figure 1: Concrete viewed as a multiscale material.

3 Nanoindentation

Nanoindentation is a powerful experimental technique which is being developed for more than a decade together with precise device fabrication, characterization of lower scale physical laws, theories and small scale numerical modeling. Nowadays, it is fairly widely used for assessing of mechanical properties of small material volumes at nano and micrometer range.

The principle of nanoindentation lies in bringing a very small tip to the material surface producing an imprint. It is used for obtaining material parameters like elastic modulus, hardness, plastic or viscous parameters from experimental readings of indenter load and depth of penetration. Forces involved are usually in the mili or micronewton

range and the depth in the order of nanometers. Different kinds of probes can be used for making an imprint into the material surface [6].

The main advantage compared to classical mechanical tests is that a very small material volumes having typically the order of several tens of nanometers can be accessed with the tip of the nanoindenter and material properties can be evaluated for such a small piece of the material. When testing such small volumes one should realize which material or structural feature can be affected. For illustration, some typical ones are summarized in Table 1.

Table 1: Length scales of some typical features.

Feature	Typical dimension
Concrete aggregate	10 – 100 mm
Sand particle	0.1 – 1 mm
Human hair	50 – 100 μm
Cement clinker grain	10 – 100 μm
Gel structures in hydrated cement	$\approx$ 10 – 100 nm
C-S-H gel globules [7]	$\approx$ 5 nm
Carbon nanotubes SWNT	$\approx$ 2 nm
Water molecule	3.1 nm
Atom of carbon	0.1 nm

4 Principle of nanoindentation

Nowadays, nanoindentation is probably the only experimental technique that can be used for direct accessing mechanical properties at material microlevel. It is based on the measurement of the load versus penetration relationship using a very small (usually diamond) tip pressed into a material (Fig. 2). With this method, it is possible to assess bulk elastic properties, such as Young's modulus, hardness and viscosity of material volumes with dimensions on the nanometer scale. Therefore, nanoindentation offers results in the point-wise estimates of locally homogenized data (in nm scale). Nanoindentation has been widely used for metals, glass or ceramics. However, its use for heterogeneous and porous materials such as cementitious composites, where it could disclose micromechanical properties of individual cement components, interfacial zones, fibers, aggregate, etc., is rare. For

instance, Velez et al. [8], determined intrinsic properties of individual cement clinkers, Constantinides and Ulm [9] investigated elastic properties of two types of C-S-H gels in cement paste and their chemical degradation.

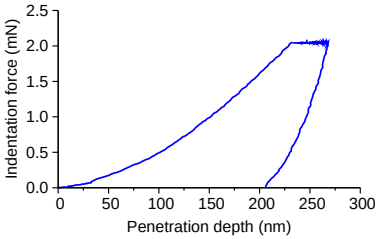

Figure 2: Typical load versus penetration diagram from nanoindentation.

As already mentioned, the principle of nanoindentation lies in bringing a very small tip to the material surface producing an imprint (Fig. 3). Two basic parameters are monitored in the apparatus: force and displacement (i.e. penetration depth). In the simplest case, the test includes loading and unloading as shown in Fig. 4. From nanoindenter, just one axial deflection in the vertical axis can be utilized. So, the surrounding surface deflections must be deduced by other means (by independent measurements or modeling). Residual imprints can be visualized, for example, by atomic force microscope (AFM, Fig. 5).

The loading diagram can be modified for different solids. Elastoplastic materials do not exhibit time-dependent behavior and thus loading/unloading can be sufficient for describing their behavior while time-dependent materials exhibit also viscous flow during loading process and thus additional segments such as holding periods are often included in the loading diagram (Fig. 6) to measure creep, for instance.

5 Standard evaluation of experimental results for homogeneous bodies

Standardly, the elastic and inelastic materials' constants are derived from nanoindentation test data using analytical solutions typically applicable to homogeneous and isotropic half-space with a flat surface. The limitations of such solutions are further corrected by calibrations

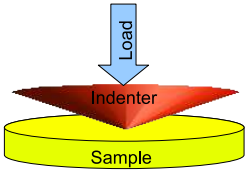

Figure 3: Principle of nanoindentation.

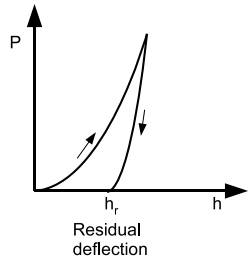

Figure 4: Loading diagram.

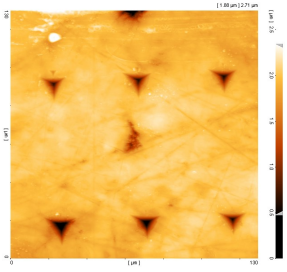

Figure 5: AFM image of imprints in cement paste after nanoindentation.

and semi-analytical factors for real geometries of a punch.

An elastic contact problem was solved already in the far history by Hertz [10] in 1881 when he found solution of elastic contact of two spheres with different radii. In 1885, Boussinesq [11] solved stresses and displacements in an elastic body loaded by a rigid axisymmetric indenter. In 1965, Sneddon [12] formulated a general relationship between load, displacement and contact area for any punch described as a solid of revolution of a smooth function.

If we analyze the loading diagram of the real material that is usually not only elastic we can apply this solution to the unloading part which, in many cases, can be successfully supposed to be elastic (Fig. 7). The situation under the indenter at maximum deflection and after unloading is described in Fig. 8. Two elastic constants are usually derived from experimental data: hardness and elastic modulus. The problem with analyzing of experimental data is in the description of the unloading branch and contact area under the indenter. Probably the

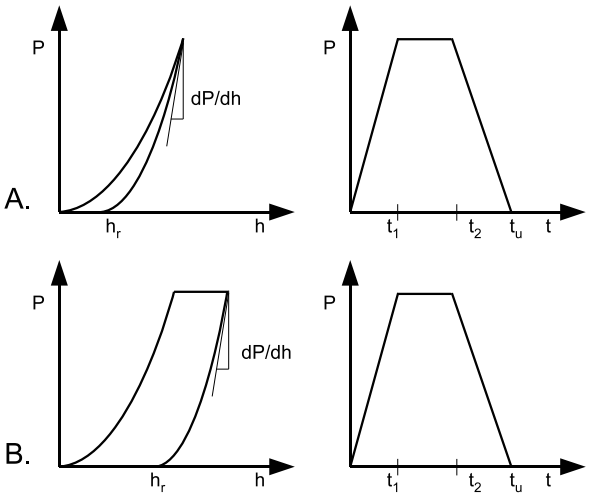

Figure 6: A. Load-depth and load-time plots for elastic-plastic solid, B. Load-depth and load-time plots for visco-elasto-plastic solid.

most popular evaluation methodology was elaborated by Oliver and Pharr [13].

6 Heterogeneity of structural materials

Structural materials exhibit several types of heterogeneity at microscale. The first type of heterogeneity comes from mixing of components that do not chemically react in the matrix like sand, fibers, and other additives. Such heterogeneity is usually known in advance and is given by the mixing proportions. The second type of heterogeneity comes from chemical reactions that are evolving after the mixing of components. As a result of these reactions, new phases are produced and it is hard to rigorously define their volumes and distribution. Formation of the new phases includes fully reacted matrix, unreacted grains of the raw material and interfacial zones with different chemical and also mechanical properties (e.g. [14, 15, 16, 17]) and porosity. Structural materials based on cement (like cement paste, concrete) or waste materials (like fly-ash, furnace slag, etc.) usually include both types of the heterogeneity. An example of two structural materials is shown

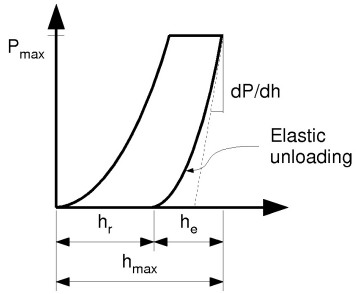

Figure 7: Loading diagram.

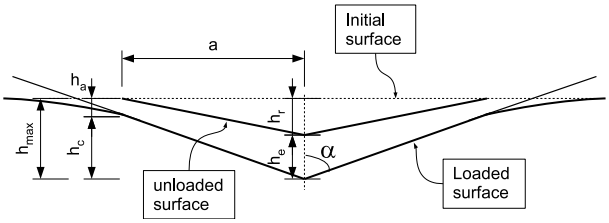

Figure 8: Situation under the indenter.

in Figs 9 and 10. It can be seen from these ESEM images that we are facing high degree of heterogeneity at and even below the micrometer range.

Therefore, micromechanical analysis of any heterogeneous material involves several subsequent steps that cannot be omitted. The first step includes microstructural observations and determination of phases. This step can be performed with the aid of many experimental techniques. Among others, the most common technique is an electron microscopy (ESEM) and atomic force microscopy (AFM). These techniques allow qualitative as well as quantitative investigation of individual material phases at small volumes near or at the sample surface. As a complementary computational technique, image analysis can give valuable results for the phase distribution based on the separation of pixel colors.

The second step includes the measurement of intrinsic properties of individual material phases. It can be provided exclusively by nanoindentation which is the only technique that can directly access me-

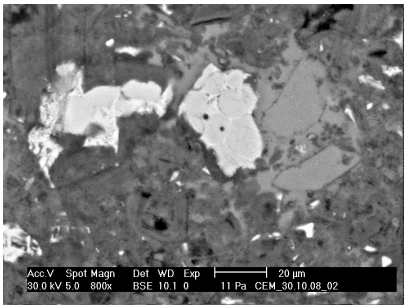

Figure 9: ESEM image of hydrated cement paste. Dark areas= pores; dark grey= C-S-H gels; light grey= Portlandite; light areas= unreacted clinker.

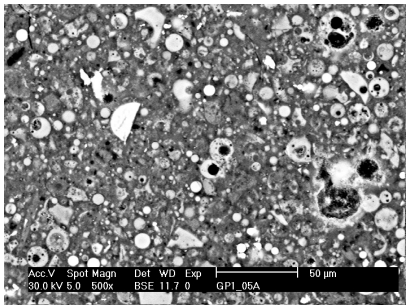

Figure 10: ESEM image of alkali-activated fly ash. Light and light grey areas= unreacted or partly reacted fly-ash grains; dark grey areas= polymer zone; dark areas= pores.

chanical properties at small dimensions starting from several tens of nanometers (depending on the sample and the probe).

The third step involves up-scaling of the properties to the higher level (meso/macrolevel). Several analytical or numerical homogenization techniques can be employed to reach this goal, e.g. [5, 18, 2].

In contrast to usual indentation on homogeneous glass, films, coatings, metals or ceramics, structural materials like cement paste are much more complex. Their heterogeneity is further complicated also by their loading time dependence, aging and property fluctuations due to temperature or humidity [19].

The evaluation methodology however, is currently restricted to homogeneous systems. Its direct application to multiscale materials poses several difficulties, as the underlying analysis relies on the self-similarity of the indentation test which holds only for homogeneous materials [20]. The interaction of phases in multiscale materials is unavoidable but depending on the length scales it can be more or less important as will be discussed in the next section.

7 Scale separation

Indentation analysis of homogeneous materials is independent on length scales and so on the indentation depth h [21]. In order to describe heterogeneous systems and their effective properties in a statistical

sense, representative volume element (RVE) have been introduced [22, 23]. The transition from a heterogenenous material at a lower level to a homogeneous material at a higher level is ensured by a scale separation inequality:

$$d << L << (h, D) \tag{1}$$

where d is the characteristic size of the largest microstructural inhomogeneity, L is the RVE size and D is a characteristic microstructural length scale. If the Eq. (1) is satisfied, an indentation experiment performed to an indentation depth h gives access to the material properties that are characteristic of the material at a length scale of L including all underlaying inhomogeneities. In case of a structural material, these inhomogeneitites can be porosity or internal polymeric structures, etc.

As already mentioned, standard nanoindentation data processing (Oliver and Pharr [13]) is based on homogeneous-like solutions with no scale limit, where the self-similarity applies. Therefore, the properties extracted from indentation data of a heterogeneous solid are averaged quantities dependent on the depth h. For example, the effective volume affected by an indent can be estimated as three times of the penetration depth h for the Berkovich indenter [24]. Therefore, the choice of an indentation depth directly determines the length scale of the material RVE.

Composite structural materials are multiphase materials in which distinct phases are intermixed spatially and chemically. Taking the microstructural heterogeneity into account one can formulate basically three testing strategies to obtain mechanical properties of a composite or its phase properties.

1. Averaged (effective) composite properties can be found if the indentation depth is larger than the characteristic phase dimension ($h >> D$). In this case, a phase compound is indented and thus, physically averaged properties are obtained. This strategy does not give access neither to distinct phases' properties nor to their volume fractions.

2. Another possibility is to perform pointed indentation to a specific material phase with indent's dimension smaller then the characteristic dimension of the tested phase ($h << D$). In this case, intrinsic properties of the distinct phase (but including intrinsic phase porosity, for example, which lies below the tested

size h) are obtained. This strategy can be used, provided the material phase can be distinguished prior to indentation by some other means (e.g. optical microscope, ESEM) which is not always the case. It gives access to the distinct phase properties but not to volume fraction of the phase compared to other phases.

3. The last one, but for structural materials probably the most powerful technique, is based on the statistical (massive grid) indentation in which indents are produced over a large area to capture the sample heterogeneity but the dimension of a single indent is still smaller than the characteristic dimension of an individual phase ($h << D$).

   In this case, the results provide information on all phases' properties as well as their volume ratios but without any knowledge which indent belongs to which phase. The properties can be evaluated in terms of property histograms for which subsequent deconvolution techniques can be employed and individual phase properties assessed [20].

All the approaches are schematically shown in Fig. 11 for a three phase medium. Different property histograms are received and, as explained, they must be viewed from the perspective of proper scale separation.

However, the methodologies described in items #2 and #3 can provide the access to intrinsic phase properties only in case that the indentation response of one phase is not influenced by another. It means that not only the geometrical factor of indentation depth but also mechanical properties of distinct phases matter. As a rule of a thumb, the indentation depth is usually chosen as $1/10$ of the characteristic size D [25, 26]. The situation of phases with different stiffnesses was studied for thin films placed on a substrate (e.g. Gao et al. [27]). It was shown by Gao that the substrate effects are negligible for stiffness mismatch ratio $E_s/E_f \in [0.2, 5]$ as long as the indentation depth h is smaller than 10% of the film thickness. The layered substrate–film system is not completely equivalent to the disordered structural multiphase materials but it can be succesfully used as the first estimate.

In many cases, material phases can hardly be distinguished. For example, C-S-H gels of different densities (low and high) are intermixed with Portlandite zones in hydrated cement matrix. There is no exact means of chemical or optical differentiation between them and therefore pointed indentation (item #2) is not possible in this case. Hence, the assessment of intrinsic phase properties leads to using of

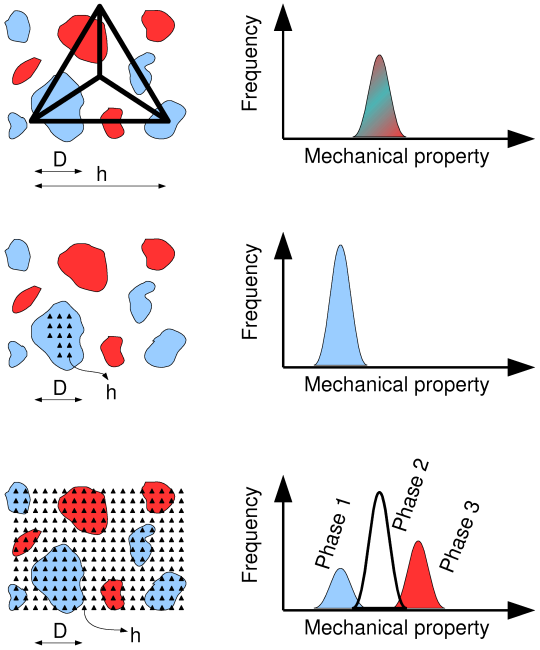

Figure 11: Schematic representation of three testing strategies. Top: Large indent producing average properties. Middle: Small indents pointed into one phase. Bottom: Large grid of small indents produced over large sample area. The overall property histogram is a convolution of results from several phases in this case.

approach #3. However, in such a case, properties received from grid indentation have to be deconvoluted into distinct phase distributions.

8 Statistical Deconvolution

For heterogeneous materials, individual phase properties can be determined by the statistical deconvolution applied to histograms of any mechanical property like E modulus, for example. The deconvolution procedure here was adopted from [24] but different minimizing criteria and a different generation of random sets of probability functions were used as will be demonstrated in the following.

Experimental histograms are constructed from all measurements whose number is N^{exp}, using equally spaced N^{bins} bins of the size b (see Fig. 12). Each bin is assigned with a frequency of occurrence f_i^{exp} that can be normalized with respect to the overall number of measurements as f_i^{exp}/N^{exp}. From that, we can compute the experimental probability density function (PDF) as a set of discrete values:

$$P_i^{exp} = \frac{f_i^{exp}}{N^{exp}} \cdot \frac{1}{b}. \tag{2}$$

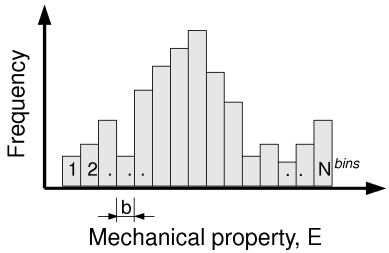

Figure 12: Construction of property histogram with bin size b.

The task of deconvolution into M phases represents finding $j = 1 \dots M$ individual PDFs related to single material phases. If we assume normal (Gauss) distributions, the PDF for a single phase can be written as:

$$p_j(x) = \frac{1}{\sqrt{2\pi s_j^2}} exp \frac{-(x-\mu_j)^2}{2s_j^2} \tag{3}$$

in which μ_j and s_j are the mean value and standard deviation of the j-th phase computed from n_j values as:

$$\mu_j = \frac{1}{n_j} \sum_{k=1}^{n_j} x_k \qquad s_j^2 = \frac{1}{n_j - 1} \sum_{k=1}^{n_j} (x_k - \mu_j)^2 \tag{4}$$

and x is the approximated quantity, i.e. the E modulus in our case. The overall PDF covering all M phases is then:

$$C(x) = \sum_{j=1}^{M} f_j p_j(x) \tag{5}$$

where f_j is the volume fraction of a single phase:

$$f_j = \frac{n_j}{N^{exp}} \tag{6}$$

It was proposed to find individual distributions by minimizing the following error function:

$$min \sum_{i=1}^{N^{bins}} \left[\left(P_i^{exp} - C(x_i) \right) P_i^{exp} \right]^2 \tag{7}$$

in which quadratic deviations between experimental and theoretical PDFs are computed in a set of discrete points that is further weighted by the experimental probability in order to put emphasis on the measurements with a higher occurrence.

For practical computations, the number of mechanically distinct phases M must be known in advance to reduce the computational burden and to give the results a physical meaning. It is usually assessed by some independent measurements, using the knowledge of sample chemistry or simply by detection of several significant peaks in the property histogram. Also the bin size b have to be chosen in advance. Higher value of b leads to more fuzzy histograms with the peaks being smoothed whereas low value of b leads to more precise distributions but the distinction between the phases may be harder. In case of structural materials included in this work a reasonable bin size was find to be $b = 1$ GPa and the number of distinct phases M was 1 to 5 depending on a sample.

The minimization in Eq. (7) was based on the random Monte Carlo generation of M probability density functions. They have to satisfy the compatibility condition:

$$\sum_{j=1}^{M} f_j = 1. \tag{8}$$

There is an infinite number of possibilities that can satisfy the condition Eq. (8). So, completely random generation of the sets can lead to a time consuming procedure. In order to guarantee the convergence of the algorithm and to minimize the computational effort, it is suggested in this work to use the set of M PDFs in Eq. (3) generated from the experimental dataset of all E moduli. Separation of the dataset into M randomly spaced successive intervals can be done in a straightforward way (see Fig. 13). Mean values, standard deviations in Eq. (4)

and volume fractions in Eq. (6) are then computed in these intervals from corresponding E moduli and used in Eq. (5). Then, finding of the set satisfying condition Eq. (7) is a question of a few seconds on a regular PC.

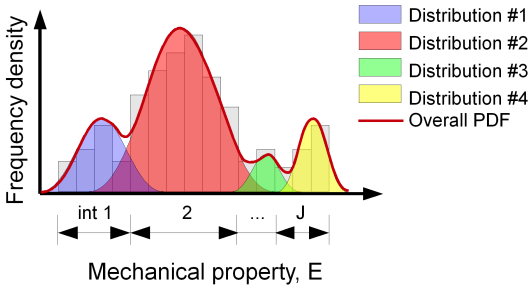

Figure 13: Separation of the experimental dataset to $j = 1 \dots M$ intervals and construction of M probability density functions.

9 Up-scaling of mechanical properties

Up-scaling of mechanical properties from microscale to the macroscopic level relies on homogenization techniques in which microscopically inhomogeneous body is replaced by a fictitious homogeneous one which behaves globally in the same way. Continuum mechanics uses mainly the concept of representative volume element (RVE) that obeys the scale separation condition Eq. (1) for a multilevel material. Preliminary results in the field of homogenization techniques were obtained for the first time by Voigt in 1887 who postulated the 'rule of mixtures' and in 1929 by Reuss (Reuss estimate). In early 1960s the basis of continuum micromechanics was found by Hill [28]. Continuum micromechanics seeks for the solution of the localization (or concentration) problem for a given spacial distribution of phases in RVE. The localization problem of the mechanical modeling of interactions between the phases which is associated with the local stress or strain fields is solved from global macroscopic stress and strain on the RVE. This problem cannot be solved in general, so additional assumptions need to be done in order to derive some estimates or bounds. Moreover, the boundary conditions are generally unknown so the prob-

lem is firstly transformed into simpler one by assuming homogeneous boundary conditions on the RVE [22, 23].

Various estimates of stiffness tensors trying to express at best the specific morphology of the material can be found in literature. For example, the simple rule of mixtures, the Mori-Tanaka method [29] devoted to composites with continuous matrix reinforced with discontinuous inclusions or the self-consistent scheme [28] in which the reference medium points to the homogenized medium itself, etc. Other methods have been developed for layered spherical inclusions in a matrix [30] which can be successfully used e.g. for the homogenization of ITZ zones [31]. Upper and lower limits of the homogenized elastic constants are often estimated using bounds, such as *Voigt* and *Reuss* bounds, *Hashin-Strikman* [32] or *Hashin-Strikman-Walpole* bounds [33].

Cement-like composites usually obey the condition of morphologically significant matrix phase filled with differently shaped inclusions. The proper homogenization method can, therefore, be Mori-Tanaka scheme. It appears also from other studies [9] that this scheme is a simple but effective homogenization tool that can be used on several material levels.

Besides the aforementioned analytical methods there are also many numerical homogenization methods searching for the stiffness tensor of the homogenized medium. These methods are usually based on the concept of eigenstrains [18], finite element computations [34, 35] or fast Fourier transformation [36, 33].

10 Conclusions

In this contribution, the principles of nanoindentation on heterogeneous materials were presented with the comparison to homogeneous ones. The main three experimental approaches for finding of intrinsic material properties on the microlevel using nanoindentation were discussed and can be summarized as follows.

1. Averaged (effective) composite properties of the phase compound can be found if the indentation depth is larger than the characteristic phase dimension.

2. Pointed indentation to a specific material phase with indent's dimension smaller then the characteristic dimension of the tested phase gives access to intrinsic properties of the distinct phase. Limited usage of this method on cementitious composites is given

by the impossibility of morphological or other means of distinction between the phases.

3. Statistical (massive grid) indentation provides information on all phases' properties as well as their volume ratios but without any knowledge which indent belongs to which phase. In this method, indents are produced over a large area to capture the sample heterogeneity but the dimension of a single indent have to be smaller than the characteristic dimension of an individual phase.

The method of statistical deconvolution, which is needed for the evaluation of intrinsic properties from grid indentation, was described in some details and up-scaling of materials properties to upper level applicable to cement based composites introduced.

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