Theoretical modelling and implementation of elastic modulus measurement at the nanoscale using atomic force microscope

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\textbf{Abstract.} Quantitative studies of mechanical behaviour and primarily elastic modulus are essential for material science at the nanometer scale. AFM nanoindentation is the most promising approach to address the problem. In our study we perform AFM-based nanoindentation (deflection-versus-distance curves) on a set of polymer materials with microscopic moduli ranging from 1 MPa to 10 GPa. The measurements were done with probes of different tip shapes and force levels from 100 nN to 3 \texttimes{} 10\textsuperscript{9} N. The tip geometry was evaluated from TEM and SEM micrographs and piecewise linearly interpolated for the use of analysis software; probe spring constant was determined from thermal tune data. The comparative analysis of nanoindentation data was carried out using models of Sneddon and Oliver-Pharr. We derived Sneddon's integrals in closed form for any practical tip shape using a piecewise linear interpolation. Oliver-Pharr's method to account for plasticity for the unloading curve was adapted for Sneddon's integrals. An interactive software implementation with both models was developed and applied.

1. Introduction
A need for testing mechanical properties of functional structures, whose dimensions are nowadays shrinking to the sub-micron scale, led to development of depth-sensitive force measurements with nanoindentors. Atomic force microscopy (AFM) based indenting and imaging has been increasingly used to complement conventional nanoindentors when low indentation forces and high spatial resolution are required \cite{1}. While AFM-based nanoindentation experiments involve a slightly non-vertical tip trajectory during indenting, this technique allows a unique combination of high-resolution imaging, a composition mapping and local mechanical studies with forces as small as nanoNewtons and spatial resolution down to 1 nm. These capabilities make this method invaluable for mechanical studies of ultrathin layers and coatings, interfaces in heterogeneous systems and a non-invasive testing of soft objects such as living cells, tissues and gels. In the paper we describe the results of AFM-nanoindentation of several polymer samples and their quantitative analysis. A focus was made on the evaluation of the tip shape and contact area as well as on choice of appropriate theoretical model for analysis of load-versus-penetration curves.

2. Experimental and theoretical methods
2.1. AFM nanoindentation protocol
Among practical aspects of AFM nanoindentation we outline rational choices of a probe and indentation procedure. In nanomechanical studies of homogeneous polymer samples the probe is needed to be stiff enough to make indentation of a reasonable depth. In the case of heterogeneous materials, the probe stiffness should correlate to that of the sample components. Knowledge of the
tip shape facilitates a quantitative evaluation of sample elastic modulus whereas the apex size defines a spatial resolution. When sharp tips with 5-10 nm radii are used for indentation, a truncated cone approximates their shape. In other experiments on homogeneous polymer materials and a polymer blend with relatively large domains, we sacrificed imaging resolution and chose tips with an axisymmetric shape and apex radius of 35 nm-50 nm, figure 1a [2]. Prior to imaging and indenting we characterized the stiffness of the chosen probes using the thermal tune procedure [3]. The thermal resonance of the probes was determined with a commercial vibrometer (PolyTec) and the calculated spring constants were in the 40 N/m – 50 N/m range. The tip geometry was estimated using TEM or SEM micrographs. A tip shape was obtained by a piecewise linear interpolation of its profile in the micrographs. This procedure allows calculation of the tip diameter at any current indentation depth.

![Figure 1. The steps of piecewise linear interpolation procedure: (a) Original TEM-micrograph of the parabolic-like tip (EL-HAR5, Team Nanotec GmbH), (b) the outline of the real tip shape through the suite of rectilinear segments; (c) function h(a)-contact height vs contact radius and its derivative calculated by applying Sneddon’s integral to piecewise linearly interpolated tip (6).](image)

The nanoindentation procedure was performed as follows. First we examined a sample surface in Tapping Mode and then switched to force measurements by recording “Deflection versus Z-travel” - (DvZ) curves in a predetermined force range. A grid of multiple indents were performed in different surface locations spaced far enough from each other to avoid indenting of pre-deformed places. The optical sensitivity of probe was determined by measuring DvZ traces separately on Si or sapphire substrates. The optical sensitivity and measured cantilever spring constant allows us to transform DvZ curves into “Load vs. Penetration” - (LvP) plots. A LabVIEW-based software package was applied for quantitative analysis using the Sneddon or Oliver-Pharr models (see 2.2). In practice, the models were applied depending on the type of obtained force curve, which reflects elastic or plastic deformation. Adhesion and viscoelastic effects will be considered in future.

2.2. Sneddon’s integrals for linearly interpolated tip’s shape.

The majority of nanoindentation procedures are based on Sneddon’s integrals [4] describing a contact between a plane surface of the sample and an axisymmetric tip. An axisymmetric tip can be determined by height, \( h \), versus radial position, \( \rho \), function

\[
h = w(\rho) \tag{1}
\]

Having this shape, Sneddon’s integrals are the following [4]:

\[
\begin{align*}
h(a) &= \int_0^a f'(x) \frac{dx}{\sqrt{1 - x^2}} \\
kD(a,E) &= \frac{2Ea}{(1 - \nu^2)} \int_0^a x^2 f'(x) \frac{dx}{\sqrt{1 - x^2}}
\end{align*}
\tag{2}
\]

where \( a \) is a contact radius between the tip and the surface; \( E \) is the elastic modulus of the sample; \( \nu \) is the Poisson ratio of the sample; \( h(a) \) is the tip penetration that relates to the contact radius \( a \) according to Sneddon’s theory; \( k \) is the spring constant of the cantilever; \( D(a,E) \) is deflection of the cantilever, and \( kD \) is the force of tip-sample interaction; \( f(x) = w(\alpha x) \), where \( w \) is the function describing a tip’s shape, defined in (1).

The popular Oliver-Pharr [5] method has its origin in Sneddon’s theory [4] and is based on the following formula [6]:
\[
\frac{E}{1 - v^2} = \frac{S}{2a}, \quad \text{where} \quad S = \frac{kdD(h)}{dh}
\]

stating that the reduced modulus is the slope of the \(LvP\) curve \(S\) over the contact diameter \(2a\).

Sneddon’s integrals can potentially be solved to find the reduced modulus from experimental AFM \(LvP\) curves. However, the main obstacle, namely the necessity to iteratively solve the system of nonlinear equations with numerical integration in the loop, reduces the practical applicability of this method to only some special cases [4]. In this article, we present a way to overcome this limitation. Our utilization of the linear interpolation of the tip widens the application of equations (2) to the majority of practical cases.

Sneddon [4] has proposed several cases where integrals in (2) can be presented in closed form. The most general case is the Segedin’s formulae for the tip shape approximated by a polynomial. Unfortunately AFM tips often cannot be accurately approximated by polynomials due to the small opening angles and tip radius as well as possible shape irregularities. There is, however, a simple analytical representation - piecewise linear interpolation that is adequate to approximate the tip and allows the calculation of the integrals in (2) in closed form. This approach is given here.

Piecewise linear interpolation can be formulated by the following formula:

\[
w(\rho) = k_i \rho + d_i, \quad \rho_0 \leq \rho < \rho_{i+1}
\]

\[i = 0, \ldots, N; \quad \rho_0 = 0, \rho_N = \infty\]

where \(k_i\) and \(d_i\) are slope and intercept of the \(i\)-th linear piece. In this case,

\[
f(x) = k_i ax + d_i, \quad x_i(a) \leq x < x_{i+1}(a)
\]

\[i = 0, \ldots, N_a - 1; x_i(a) = \frac{\rho_i}{a}; \rho_{N_a - 1} \leq a < \rho_{N_a}\]

where \(N_a\) is the number of pieces needed to cover the interval \([0,a]\) that includes the contact radius \(a\).

Using formulas:

\[
\int \frac{dx}{\sqrt{1-x^2}} = \arcsin x + C; \quad \int \frac{x^2 dx}{\sqrt{1-x^2}} = \frac{\arcsin x - x\sqrt{1-x^2}}{2} + C
\]

and substituting function \(f\) from (5) to the first formula in (2), we get

\[
\begin{align*}
\frac{d}{da} \left[ k_{y_{i-1}} \frac{\pi}{2} + \sum_{i=1}^{N_a} (k_i - k_{i-1}) \arcsin x_i(a) \right] \\
\frac{d h}{da} = \frac{h(a)}{a} + \sum_{i=1}^{N_a-1} (k_i - k_{i-1}) \frac{x_i(a)\sqrt{1-x_i^2(a)}}{4}
\end{align*}
\]

These formulas can be used to solve the equation:

\[
h(a) = h
\]

for \(a\), given experimental value of \(h\) by the Newton-Raphson method that requires a formula for the derivative \(dh/da\). Then the reduced modulus is calculated using the closed-form of the integral in the second equation in (2):

\[
\frac{E}{1 - v^2} = \frac{kD}{a h(a) + \sum_{i=1}^{N_a} (k_i - k_{i-1}) x_i(a)\sqrt{1-x_i^2(a)}}
\]

where \(D\) is the deflection corresponding to penetration \(h\) according to the experimental \(LvP\) curve.

It was proven theoretically and experimentally that for a majority of tips with axisymmetric shape the equation (7) has a unique solution and the Newton-Raphson method converges to the solution in only a few iterations, making the described procedure a reliable tool. This Sneddon approach is applicable and desirable for analyzing the initial part of the loading curve before the onset of plastic deformation. It does not, however, cover cases involving plastic deformation.

2.3. Extension of the Sneddon integral-based model to elasto-plastic materials

The Oliver-Pharr’s method to estimate modulus of elastoplastic materials uses the unloading curves and heuristic plastic correction based on the value \(h_f\) called “the residual hardness impression” in [5]. Formula (3) is the direct derivation from Sneddon’s integrals (2) but the
Oliver-Pharr method applies this formula to the unloading curve and makes an estimation of the contact radius corrected for plastic deformation [5]. For our goal to adapt the Oliver-Pharr approach for plasticity to Sneddon integrals it is appropriate to rewrite formula (3) as:

\[
\frac{E}{1-v^2} = \frac{S}{2a^\text{pl}_c}, \quad a^\text{pl}_c = \sqrt{\frac{A(h^\text{pl}_c)}{\pi}}
\]  

(9)

where \( h^\text{pl}_c \) is a contact depth evaluated according to the Oliver-Pharr method (Ref. [5] and other papers use notation \( h_c \), but we add superscript “pl” denoting ‘plastic’ for more clarity); \( A \) is an area of contact as a function of the contact depth. In a similar way we can rewrite second equation of (2) to derive-Sneddon’s analog of the Oliver-Pharr method for elastic-plastic systems:

\[
\frac{E}{1-v^2} = \frac{kD}{2a^\text{pl}_c} \left[ \int_0^1 x^2 f'(x)dx \right]^{-1}
\]

(10)

where the numerator is the slope of the (unloading) force-penetration curve, i.e. \( S \).

Then the value \( a^\text{pl}_c \) in (10) can be calculated by the heuristic Oliver-Pharr method: (1) For a given \( x = h-h^\text{pl} \) find \( a=a^\text{pl}_c \) by solving \( h(a) = x \); (2) Calculate the corresponding \( h_c \) using the tip shape function (1) (for piecewise linear interpolation, this reduces to (4)); (3) Calculate plastic correction for contact height \( h^\text{pl}_c = h^\text{el}_c + h^\text{pl}_c \) ; (4) Calculate corresponding \( a^\text{pl}_c \) using tip shape function (1) (for piecewise linear interpolation, this reduces to formula (4)).

3. Results and Discussions

Practical value of the developed approach in the AFM nanoindentation was verified in studies of large number of samples of homogeneous polymer materials, whose macroscopic elastic modulus varies in the 1MPa – 10GPa range. The Lvp data are summarized in figure 2a, where the curves obtained for different polymers, show pure elastic responses as well as those with plastic deformation using sharp indenters. High reproducibility and accuracy of the indentation data was checked in the experiments with large number of indents up to 400 (figure 2b, c).

Figure 2. (a) Lvp curves for: DP8-150 - polydimethylsiloxanes (Dow Corning) with different degree of polymerization between cross-links; SiLK™ – semiconductor dielectric film (Trademark of The Dow Chemical Company); PS64 and PS292 - polystyrene with 64K & 292K molecular weight. (b) Height image of SiLK™ surface (10µm scan) with 400 leftover imprints; (c) Statistical data treatment of DP25 sample: top - loading and unloading indentation traces on 400 locations, middle and bottom - calculated modulus and its statistical distribution, respectively; (d) Height image (3 µm scan) recorded after indentation using a probe with a spherical tip.

The software panel with the results of statistical treatment of 400 curves for DP25 sample (figure 2c) shows that the deviation in the elastic modulus values obtained on the freshly prepared surface of homogeneous sample did not exceed 2 %. The height image of PS surface (figure 2d) shows the leftover indents made with the spherical tip. They exhibit fairly circular shape verifying that non-vertical tip trajectory during indentation has been minimized.
Study of the polystyrene (PS) and low-density polyethylene (LDPE) blends proved the unique capability of the AFM nanoindentation. Figure 3 shows the elastic modulus changes with respect to morphology of the unmodified blend (figure 3a) and modified one (figure 3b) with a compatibilizer - styrene-(ethylene-butylene)-styrene triblock copolymer (SEBS). Indents were made on the microtomed surfaces of the blends across matrix, several domains and interfaces using a spherical indenter.

Figure 3. A combination of phase images (bottom) and the elastic modulus profiles (top) measured across matrix and several domains in the locations with the leftover indents for: blend of PS and LDPE without a compatibilizer (a) and the same blend modified with SEBS (b). Bright and dark contrast on the phase images corresponds to PS-matrix and LDPE domains, respectively.

The distinctive areas of PS-matrix and PE-regions in both cases are clearly recognized by different modulus levels and by phase image contrast. A partial pooling of the LDPE domains from the matrix during the cutting procedure indicates a poor interfacial binding of the unmodified blend (figure 3a). In this sample, the changes of elastic modulus are quite abrupt at the interfaces. When a small amount of the compatibilizer (5 wt%) was introduced into the blend, the changes of elastic modulus at the interfaces became gradual and pulling of LDPE domains was not observed. This finding indicates on strengthening of the interfaces yet the understanding of large width (up to 300 nm) of the transitional locations (figure 3b) requires additional studies.

Analysis of nanoindentation data will be further developed to include integration of the Sneddon model with adhesion and viscoelasticity [7] and to address limitations of the Sneddon and Oliver-Pharr approaches outlined in [8].

4. Conclusions
We presented the methodology of quantitative analysis of AFM indentation of polymers, which includes the cantilever spring constant calibration, tip geometry estimation through piecewise linear interpolation (TEM image or shape reconstruction), transformation of DvZ curves into LvP curves and the expansion of Sneddon and Oliver-Pharr methods for modulus calculation accompanied by statistical analysis. The methodology was verified in studies of various homogeneous polymers and polymer blends.

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