An inverse problem for adhesive contact and non-direct evaluation of material properties for nanomechanics applications

Abstract
We show how the values of the effective elastic modulus of contacting solids and the work of adhesion, that are the crucial material parameters for application of theories of adhesive contact to nanomechanics, may be quantified from a single test using a non-direct approach (the Borodich-Galanov (BG) method). Usually these characteristics are not determined from the same test, e.g. often sharp pyramidal indenters are used to determine the elastic modulus from a nanoindentation test, while the work of adhesion is determined from a different test by the direct measurements of pull-off force of a sphere. The latter measurements can be greatly affected by roughness of contacting solids and they are unstable due to instability of the load-displacement diagrams at tension. The BG method is based on an inverse analysis of a stable region of the force-displacements curve obtained from the depth-sensing indentation of a sphere into an elastic sample. Various aspects related to solving the inverse problem for adhesive contact and experimental evaluation of material properties for nanomechanics applications are discussed. It is shown that the BG method is simple and robust. Some theoretical aspects of the method are discussed and the BG method is developed by application of statistical approaches to experimental data. The advantages of the BG method are demonstrated by its application to soft polymer (polyvinylsiloxane) samples.

Keywords
Molecular adhesion • nano-mechanics • nanoindentation • soft polymers and biological materials • inverse problems • BG method

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F.M. Borodich1∗, B.A. Galanov2†, S.N. Gorb3‡, M.Y. Prostov4§, Y.I. Prostov5¶, M.M. Suarez-Alvarez1

1 School of Engineering, Cardiff University, The Parade, Cardiff, CF24 3AA, UK
2 Institute for Problems in Materials Science, Kiev 03142, Ukraine
3 Zoological Institute of the University of Kiel, Kiel, D-24098, Germany
4 Faculty of Mechanics and Mathematics, Moscow State University, Moscow, 119991, Russia
5 Moscow State Technical University of Radioengineering, Electronics and Automation, Moscow, 119454, Russia

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∗ E-mail: BorodichFM@cardiff.ac.uk
† E-mail: galanov@ipms.kiev.ua
‡ E-mail: sgorb@zoologie.uni-kiel.de
§ E-mail: prostomi@gmail.com
¶ E-mail: prostovpro@gmail.com
E-mail: suarez-alvarezm@cardiff.ac.uk
1. Introduction

This paper deals with the phenomenon of molecular adhesion. Adhesion between elastic solids is a universal molecular phenomenon that was studied for a long period of time [1–6]. The problems related to the phenomenon are in the areas of surface physics and nanomechanics.

There are rather different definitions of nanomechanics. For example, Liu et al. [7] have specified the following three features of nanomechanics: “that are distinct from the conventional approach of macroscopic solid mechanics. They are respectively the breakdowns of continuum postulate, bridging across different scales in time and length, and mechanics-induced multi-disciplinary analysis”. On the other hand, one of the authors (F.B.) has introduced a course “Fundamentals of Nanomechanics” at Cardiff University and coined the following definition. Nanomechanics is a scientific discipline that studies (i) application of mechanical laws and solutions of problems of mechanics to objects of nanotechnology; (ii) interactions between physical objects using mechanical equations adjusted to the specific character of the interactions at nanometer length scale; and (iii) influence of nanometer scale objects and processes on meso/macroscopic phenomena. According to this definition, students studying nanomechanics have to know both the Bernoulli–Euler beam theory in order to understand the principles of work of an atomic force microscope and adhesive contact problems. Indeed, adhesion has usually a negligible effect on surface interactions at macro-scale, whereas it becomes increasingly significant as the contact size decreases. In particular, adhesion of dry surfaces plays a key role in the development of modern nanotechnology. Evidently, the division is a bit artificial. For example, it was argued by Barenblatt and Monteiro [8] that not only the chemical reactions take place at the Ångström length scale, but this scale has a fundamental physical meaning in nanomechanics and should be included in the list of governing parameters when the scaling laws are derived. However, to separate nanomechanics from other branches of mechanics, we will not consider quantum mechanical background of van der Waals forces but will consider models based on the concepts of the work of adhesion (w).

Here we consider molecular adhesion caused by van der Waals forces and we do not consider chemical bonding. The distinction of these forces is somewhat artificial, because all of these forces are electrical in nature [2], however, this distinction is very convenient. The same distinction is usually introduced for studying adsorption phenomena, where chemisorption and physiosorption are considered. Note that it is rather difficult to determine experimentally the values of the work of adhesion for contacting solids and, therefore, w is not a well-known quantity for many modern materials [9].

The well established classic theories of adhesive contact that include the JKR (Johnson–Kendall–Roberts) theory, the DMT (Derjaguin–Muller–Toporov) theory, and the Maugis transition solution between the JKR and DMT theories, propose methodologies to predict the adhesion force between surfaces. To give quantitative predictions of the adhesive forces, one needs to know both the work of adhesion and the effective contact elastic modulus (E*) of contacting materials [5].

Various methods were introduced to determine the surface energy of a sample. For example, it was proposed to measure contact angle for several liquids and to employ the Young–Dupre and Dupre equations [10, 11]. However, these equations were derived for liquids, while it is known that the breach of adhesive connection between solids, as a rule, goes in a non-equilibrium way and the techniques based on the transfer of these equations to solids is rather questionable [2].

Work of adhesion is usually determined by experimental techniques based on direct methods. These methods vary depending on the device and the theory used. For example, in 1954, Derjaguin and his co-workers published a description of a surface forces apparatus (SFA) consisting of a hemisphere and a surface of polished quartz [12]. The hemisphere and the surface could be brought into close proximity that could be measured by interferometry, while the force was measured by an elaborate feedback mechanism. A modified SFA [13] was used for direct measurement of molecular level adhesion forces between biaxially oriented solid polymer films [14]. Currently the most popular approach for measurement of the work of adhesion is based on measurements of pull-off force of a sphere and the use of the JKR model [15]. However, the direct measurements of the critical force (−Pc) (in the framework of the JKR model it is also referred to as the pull-off or adherence force) and the absolute value (δc) of the maximum tensile displacement by the P − δ diagram are rather difficult. Indeed, the direct measurements are unstable due to instability of the load–displacement diagrams P − δ at low tensile loads, in particular, the directly measured values of the adherence force F ado, have poor reproducibility because the tensile (adhesive) part of the load–displacement diagram may be greatly influenced by surface roughness and the spring stiffness of the measuring device. Hence, one needs to have a number of measurements to estimate w properly using direct approaches.

Using the connection between depth-sensing indentation by spherical indenter and mechanics of adhesive contact,
it has been shown how the values of work of adhesion and elastic contact modulus of materials may be quantified by the non-direct BG method (the Borodich-Galanov method) based on an inverse analysis of a stable region of the force-displacements curve [16]. One can expect that the compressive branch of the adhesive $P - \delta$ curve is not sensitive to small surface roughness. Therefore, the classic models of adhesive contact derived for contact of smooth spheres are applicable. It has been shown recently that the BG method is robust [17]. Here some theoretical aspects of the method are discussed and the BG method is developed by application of statistical approaches to experimental data.

The paper is organized as follows:

In §2 we give some preliminary information concerning mechanics of adhesive contact and depth-sensing indentation.

In §3 various approaches to overdetermined systems are discussed. It is shown that the popular semi-empirical $L$-curve method does not work in application to the DMT contact model.

In §4 it is shown using numerical simulations that the BG method is simple and robust. To emphasize the crucial difference between this method and the standard experimental techniques based on the direct measurements of pull-off force, the BG method has been applied only to compressive parts of the force-displacement diagrams. This removes the major obstacle of the direct approaches because at compression the diagrams are stable. Actually, an ideal JKR curve is considered and some Gaussian noise is added to its compressive part. Using the data, the elastic and contact characteristics have been extracted.

In §5 the work of adhesion and the elastic modulus of soft polymer (polyvinylsiloxane) samples are extracted from experimental load-displacement diagrams. The method is applied to experiments that were using relatively large sapphire sphere (the radius $R = 1$ mm). To solve the overdetermined problem for each experiment, statistical approaches are employed. Since the experimental results were within the applicability of the JKR model, there was a problem of finding the origin of the $P - \delta$ coordinate system, while the shift of the origin may greatly affect the values of seeking parameters. It is shown how to find the origin. It should be noted that due to inhomogeneity of material properties of polymers at micro/nanoscale, the extracted values of both adhesive contact characteristics vary within the same polymer sample and hence, the results may vary from one experiment to another.

2. Preliminaries

2.1. Depth-sensing indentation and adhesive contact

Currently depth-sensing indentation (DSI) techniques that is the continuously monitoring of the $P - \delta$ curve where $P$ is the applied load and $\delta$ is the displacement (the approach of the distant points of the indenter and the sample), are widely used in materials science. Originally both depth-sensing nanoindenters introduced by Kalei [18] and atomic force microscopes (AFM) introduced by Binnig et al [19] were based on the use of sharp pyramidal probes. However, currently the DSI techniques with spherical probes are also widely used. Various devices such as nanoindenters, AFM and other devices with spherical probes attached to the end of cantilever beams are widely used to study non-traditional materials such as polymers, pharmaceutical and biological materials [20, 21].

Usually, the indentation by sharp pyramidal indenters is used to estimate the elastic modulus of a tested material by measuring the slope $S$ of the unloading branch of the diagram and employing the BASh (Bulychev-Alekhin-Shorshorov) formula or its modifications [22, 23]

$$S = \frac{dP}{d\delta} = C \frac{2\sqrt{A}}{\sqrt{\pi}} E^*,$$

where $A$ is the area of the contact region and $C$ is a constant depending on the boundary conditions of the contact [24].

We have to note that strictly speaking the assumptions of the Hertz contact theory are not valid for contact between a sharp indenter and a plastically deformed surface of the material sample having an inhomogeneous field of residual stresses. Hence, the use of the BASh formula is not as mathematically justified as it is usually assumed. In fact, (1) is a semi-empirical formula for an exact expression $S = 2CE^*a$ for a convex axi-symmetrical punch having contact radius $a$ and an external load $P$.

For adhesive contact of smooth spheres, models are well established. These models include the JKR, DMT, and Maugis models [4, 5]. Further, only the techniques based on DSI of spherical probes are considered and developed because there is no currently any established model of adhesive contact for pyramidal indenters. In addition, the real probes are not ideally sharp [25], hence the exact shape of a sharp probe is often unknown. Measurements of the pull-off force may be used for estimations of $w$ in the framework of theoretical models of adhesive contact, e.g. it follows from
the JKR model that measuring directly the adherence force $P_{adh}$ between a sphere of radius $R$ and an elastic half-space one can calculate

$$w = -\frac{2}{3} \frac{P_{adh}}{\pi R}.$$  

(2)

Reviews of methods for measurement of the contact modulus and elastic modulus of materials can be found in [26, 27]. Although the above mentioned techniques for determination of $E^*$ and $w$ are very popular, they have a number of drawbacks. In particular, the plastic residual stresses are ignored in (1) [23], while the $P_{adh}$ values obtained by direct measurements have poor reproducibility because the tensile (adhesive) part of the load-displacement diagram may be greatly influenced by surface roughness and the spring stiffness of the measuring device [15]. Indeed, in the case of a solitary contact, even slight damage of the contact due to the presence of contamination or surface irregularities will immediately lead to contact breakage, similar to the crack propagation in bulk material [28]. Hence, one needs to have a number of measurements to estimate $w$ properly using (2). On the other hand, it is known that the non-adhesive contact problems have some features of chaotic systems: the trend of the compressive $P - \delta$ curve (the global characteristic of the solution) is independent of fine distinctions between functions describing roughness, while the stress field (the local characteristic) is sensitive to small perturbations of the punch shape [29]. One can expect that the same observation is valid for adhesive contact, i.e. the compressive branch of the adhesive $P - \delta$ curve is not sensitive to small surface roughness. Therefore, the classic models derived for contact of smooth spheres are applicable and, in turn, we can use the non-direct BG method for estimations of both mechanical and adhesive properties of contacting materials [16].

The BG method is based on an inverse analysis of all points at a bounded interval of the force-distance curve obtained for a spherical indenter. It is assumed that this branch is described by a known functional expression

$$F\left(\frac{P}{P_c}, \frac{\delta}{\delta_c}\right) = 0, \quad P_c \geq 0, \quad \delta_c \geq 0.$$  

(3)

where $P_c$ and $\delta_c$ are characteristic scales of the contact problem for the force and the displacement respectively at low loads and small displacements. The scales can be chosen arbitrary using the problem governing parameters $R, w$, and $E^*$. Here we use the Maugis notations

$$P_c = \frac{3}{2} \pi w R > 0, \quad \delta_c = \frac{3}{4} \left(\frac{\pi^2 w^2 R}{(E^*)^2}\right)^{1/3} > 0.$$  

(4)

For the DMT and JKR models, the functional expression (3) has respectively the following forms

$$F\left(\frac{P}{P_c}, \frac{\delta}{\delta_c}\right) \equiv \frac{P}{P_c} - \frac{1}{\sqrt{3}} \left(\frac{\delta}{\delta_c}\right)^{3/2} - \frac{4}{3} = 0$$  

(5)

and

$$F\left(\frac{P}{P_c}, \frac{\delta}{\delta_c}\right) \equiv \left\{ \begin{array}{l} (3\chi - 1) \left(\frac{1 + \chi}{\chi}\right)^{1/3} - \frac{1}{\chi} = 0, \quad \chi \geq 0, \quad \delta/\delta_c \geq -3^{-2/3}, \\ -(3\chi + 1) \left(\frac{1 + \chi}{\chi}\right)^{1/3} - \frac{1}{\chi} = 0, \quad \chi \geq 0, \quad -1 \leq \delta/\delta_c < -3^{-2/3}, \end{array} \right.$$  

(6)

where $\chi = \sqrt{1 + \frac{P_c}{w}}$. The BG method reduces the problem to finding the scale characteristics $P_c$ and $\delta_c$ using only the experimental points of the chosen interval of the stable unloading branch of $P - \delta$ curve. If $P_c, \delta_c$ have been found then using (4) $w$ and $E^*$ can be obtained

$$w = \frac{2P_c}{3\pi R}, \quad E^* = \frac{P_c}{4} \sqrt{\frac{3}{R\delta_c^3}}.$$  

(7)
3. Adhesive contact and inverse problems

If \((P_i, \delta_i), i = 1, \ldots, N\) are respectively experimental values of the compressing load \(P \geq 0\) and corresponding values of the displacement \(\delta \geq 0\) then there is the following system of non-linear equations for determining the two unknown values \(P_i\) and \(\delta_i\)

\[
F \left( \frac{P_i}{P_{i}}, \frac{\delta_i}{\delta_{i}} \right) = 0, \quad P_i \geq 0, \quad \delta_i \geq 0.
\]  

(8)

The above problem is ill-posed according to Hadamard’s definition (see, e.g. [30]) because the system (8) is overdetermined for \(N > 2\). For a non-linear ill-posed problem, it is possible that there exists no solution in the classic sense. In addition, there is a possibility of high sensitivity of the solution of the inverse problem to noise in the measured data.

3.1. Inverse problem to adhesive contact and approaches to overdetermined systems

An inverse problem may be considered using probabilistic formulation, when two covariance matrices: \(C_i\) that represents the a priori uncertainties on the model parameters (input data), and \(C_O\) that represents the uncertainties on the output parameters are studied (see, e.g. [31]). If one assumes that all uncertainties of both the input and output data are independent Gaussian with zero mean and standard deviations \(\sigma_i\) and \(\sigma_O\) respectively, and if both \(C_i\) and \(C_O\) are diagonal and isotropic, i.e. \(C_i = \sigma_i^2 I\) and \(C_O = \sigma_O^2 I\) where \(I\) is an identity matrix, then the probabilistic formulation of an inverse problem may be reduced a regularization problem [30, 31].

The most popular approach to the ill-posed problems is the use of the regularization techniques. The techniques were introduced independently in many different contexts. They became widely known from their application to various equations by Tikhonov (see, e.g. [30]). The determination of the regularization parameter \(\alpha\) (that is also known as the Tikhonov parameter) is one the main difficulties in regularization of ill-posed problems. According to this method, the solving of the system (8) is reduced to the problem of minimization of the following functional

\[
\Phi_\alpha(x) = ||F(x)||^2 + \alpha||x||^2,
\]  

(9)

where

\[
x = (P_i, \delta_i), \quad F = (F_1, \ldots, F_N, F_{N+1}, F_{N+2}),
\]

\[
F_i(x) = F \left( \frac{P_i}{P_{i}}, \frac{\delta_i}{\delta_{i}} \right), \quad i = 1, \ldots, N, \quad F_{N+1}(x) = \frac{|P_i| - P_{i}}{\sqrt{2}}, \quad F_{N+2}(x) = \frac{|\delta_i| - \delta_{i}}{\sqrt{2}},
\]  

(10)

\(\alpha > 0\) is the regularization parameter, and \(|| \cdot ||\) denotes the Euclidean norm of the vector. The components \(F_{N+1}\) and \(F_{N+2}\) reflect the inequalities in the system (8) that can be represented by the following equations

\[
\frac{|P_i| - P_{i}}{\sqrt{2}} = 0, \quad \frac{|\delta_i| - \delta_{i}}{\sqrt{2}} = 0.
\]  

(11)

It is assumed that the functional \(\Phi_\alpha\) is written in a dimensionless form because the physical dimensions of the load and the displacement are different. To avoid undesirable instability of the seeking solution, one has to minimize simultaneously the squares of the norms of the discrepancy vector \(F\) and the solution vector \(x\). For any value of \(\alpha\), there is a corresponding vector \(x_\alpha = (P_\alpha^o, \delta_\alpha^o)\) that gives a minimum to the functional \(\Phi_\alpha\).

Since sensitivity has not been analyzed, a general Tikhonov regularization approach will be employed in this paper. To find the regularization parameter \(\alpha\) many methods were introduced, in particular, the discrepancy principle (see, e.g. [30, 32]) and the L-curve method (see, e.g. [32]). There are many other methods for choosing the regularization parameter \(\alpha\).

3.2. Application of L-curve approach to the DMT model

In this method one has to plot a graph of the norm of the regularization solution \(||x_\alpha||\) versus the norm of the corresponding discrepancy \(||F(x_\alpha)||\) for the entire range of valid values of the regularization parameter \(\alpha\). In a number of cases the shape of the \(||x_\alpha||; ||F(x_\alpha)||\) graph is in the form of an “L” and hence it is referred to as the L-curve. The seeking value of \(\alpha\) is taken at the point of maximum curvature of the graph.
Let us write the system that corresponds to the DMT model

\[
3^{1/3} \left( \frac{P_i}{P_c} + \frac{4}{3} \right)^{2/3} - \frac{\delta_i}{\delta_c} = 0, \quad P_c \geq 0, \quad \delta_c \geq 0, \quad i = 1, \ldots, N. \tag{12}
\]

It can be shown that the equations for the unknown value \( P_c \) can be separated from equations for determination of \( \delta_i \) [16]. One can use some straightforward calculations and represent the system (12) in the following form

\[
a_i P_c - b_i = 0, \tag{13}
b_i \delta_i - \delta_i = 0,
\]

where the coefficients

\[
a_i = \frac{4}{3} \left[ 1 - \left( \frac{\delta_i}{\delta_c} \right)^{3/2} \right],
b_i = \left( \frac{\delta_i}{\delta_c} \right)^{3/2} P_i - P_1
\]
do not depend on \( P_c \) and \( \delta_i \), and the coefficient

\[
c_i = 3^{1/3} \left( \frac{P_i}{P_c} + \frac{4}{3} \right)^{2/3}
\]
depends only on \( P_c \). This representation means that the value of \( P_c \) can be found independently of \( \delta_i \) and the value of \( \delta_c \) should be determined after evaluation of the \( P_c \) value.

Let \( P_c \geq 0 \), then we have

\[
\Phi^2 = \Phi^2(P_c) = \frac{1}{N} \sum (a_i P_c - b_i)^2 + P_c^2 - P_c P_c = \frac{1}{N} \left( \sum a_i^2 \right) P_c^2 - \frac{2}{N} \left( \sum a_i b_i \right) P_c + \frac{1}{N} \left( \sum b_i^2 \right),
\]

\[
\Phi^2 = \Phi^2(P_c) + \alpha P_c^2.
\]

Let us introduce the following notations

\[
S = \frac{1}{N} \sum a_i^2, \quad T = \frac{1}{N} \sum a_i b_i, \quad U = \frac{1}{N} \sum b_i^2.
\]

Then we have

\[
\Phi^2_a = S P_c^2 - 2 T P_c + U + \alpha P_c^2 = (S + \alpha) P_c^2 - 2 T P_c + U.
\]

Since

\[
P_{ca} = \frac{\sum a_i b_i}{N \alpha + \sum a_i^2} = \frac{\sum a_i b_i}{N (\alpha + \frac{1}{N} \sum a_i^2)} = \frac{1}{N} \sum a_i b_i = \frac{T}{\alpha + S},
\]

we obtain

\[
\alpha = \frac{T}{P_{ca}} - S. \tag{16}
\]

Hence, it follows from (15) and (16) that

\[
\Phi^2(P_{ca}) = \Phi^2_a - \alpha P_{ca}^2 = \left( S + \frac{T}{P_{ca}} - S \right) P_{ca}^2 - 2 T P_{ca} + U - \left( \frac{T}{P_{ca}} - S \right) P_{ca}^2
\]
or

\[ \Phi^2 = SP^2_{\alpha} - 2TP_{\alpha} + U. \]

Therefore,

\[ \Phi^2 = S \left( P_{\alpha} - \frac{T}{S} \right)^2 + U - \frac{T^2}{S} \]

or

\[ \frac{\Phi^2}{S} - \left( P_{\alpha} - \frac{T}{S} \right)^2 = \frac{US - T^2}{S}. \]  

(17)

Since \( S > 0 \), we obtain that (17) is a hyperbola. It is well known that a hyperbola has the maximum curvature at its vertex, i.e. at the point \( P_{\alpha} = T/S \) where \( \Phi = 0 \). This point corresponds to \( \alpha = 0 \). If \( \alpha \) increases then the curvature decreases.

Hence, in the case of applicability of the DMT model the point of maximum curvature of L-curve corresponds to \( \alpha = 0 \) and the functional depends on \( P_{\alpha} = T/S \) as a hyperbola.

The applicability of the L-curve approach to the DMT model was discussed earlier [16]. However, only an approximate estimation of the regularization parameter was obtained. It was suggested to take respectively \( \alpha = 0.001 \) to determine the adhesion characteristics \( P_c \) and \( \alpha = 0.002 \) to determine the adhesion characteristics \( \delta_c \), while it is followed from the above consideration that the parameter has to be taken as \( \alpha = 0 \). The errors of the determined values of the scaling parameters were less than 0.1% and because the experiments considered were out the applicability of the DMT model even these approximate values were not used.

We can conclude that the popular semi-empirical L-curve method does not work in application to the DMT contact model.

![Fig 1. The theoretical P - \( \delta \) JKR curve whose compressive part is contaminated by normally distributed noise 10% of \( P_c \) and 0.1% of \( \delta_c \) values. The units for displacements and force are respectively \( \mu m \) and \( \mu N \).](image)

4. Robustness of the BG method

The least-squares method that is a particular case of the regularization techniques. Because of its simplicity, it is widely used for the resolution of inverse problems. The only drawback of the least-squares approach is the lack of robustness, i.e., there is a possibility that the least-squares method has strong sensitivity to a small number of large outliers in a data set [31].

Let us consider the following numerical algorithm for checking the validity of the BG method. It can be described as follows:

(i) prescribe \( E^* \) and \( w \) of a material and \( R \) of an indenter;
(ii) calculate \( P_c \) and \( \delta_c \) by (4);
(iii) plot the \( P - \delta \) graph for these \( P_c \) and \( \delta_c \) according to an appropriate classic model (JKR (6) or DMT (5));
(iv) take a part of the \( P - \delta \) graph and add to it some Gaussian noise;
(v) take only the compressive part of the disturbed data;
(vi) solving overdetermined problem, calculate the estimations \( \hat{P}_c \) and \( \hat{\delta}_c \);
(vii) calculate estimations \( \hat{E}^* \) and \( \hat{w} \) by (7);
(viii) compare the initial values \( E^* \) and \( w \) and their estimations \( \hat{E}^* \) and \( \hat{w} \), and calculate the error of the BG method.

The application of the BG method shows that the obtained estimations of the elastic modulus and work of adhesion have very small error even for rather contaminated data. For example, let us consider a sphere of radius \( R = 3mm \) and a material with the given values \( w = 5.66 \cdot 10^{-2}N/m \) and \( E^* = 1.218MPa \). The corresponding scaling parameters of the problem are respectively \( P_c = 800\mu N \) and \( \delta_c = 3.0\mu m \). Results obtained using our method from data (\( N = 500 \)) for a corresponding truncated JKR curve whose compressive part is contaminated by normally distributed noise 10% of \( P_c \) and 0.1% of \( \delta_c \) (Fig. 1), were respectively \( \hat{P}_c = 852\mu N \) and \( \hat{\delta}_c = 3.098\mu m \), \( \hat{w} = 6.02 \cdot 10^{-2}N/m \) and \( \hat{E}^* = 1.235MPa \), i.e. the errors are 6.5% for \( w \) and 1.4% for \( E^* \).

For disturbance 5% of both \( P_c \) and \( \delta_c \) (Fig. 2), the results were respectively \( \hat{P}_c = 822\mu N \), \( \hat{\delta}_c = 3.043\mu m \), \( \hat{w} = 5.82 \cdot 10^{-2}N/m \) and \( \hat{E}^* = 1.226MPa \), i.e. the errors are 3% for \( w \) and 0.6% for \( E^* \). Hence, the method is not only fast but it is also robust.

5. Experimental studies

Polyvinylsiloxane (PVS) was used for experimental studies. PVS is a silicone elastomer that is often used in dentistry as an impression material. The BG method was applied to experiments that used a relatively large sapphire sphere. The interacting force between two surfaces is recorded as a force versus displacement curve.

5.1. The experimental tests

The specimens were prepared in a similar way to the fibrillar specimens tested in [20]. They were produced at room temperature by pouring two-compound polymerizing polyvinylsiloxane into the smooth template lying on a smooth glass support. After the polymerization process, the cast of the smooth glass was obtained. Two PVS samples were used in the experiments: the first sample had the surface as it was received after preparation (the fresh sample), while the second surface was washed to remove possible contamination and the oxides (the washed sample).

PVSs have also been used for production of gecko and insect inspired synthetic brushed and mushroom shaped microstructured adhesive surfaces [33]. Physical properties of PVSs can be modulated by variation of fillers, in particular,
they can have various viscosities.

The forces and displacements of a smooth spherical probe \( (R = 1\, \text{mm}) \) contacting a flat polymer surface (Fig. 3) were continuously measured. As can be seen in Fig. 3, the loading and unloading branches are very close to each other and, hence the contribution of viscosity to the \( P - \delta \) curve of the tested samples was very low.

The displacement of the sphere attached to a glass cantilever beam with known spring constant was detected by the fiber-optic sensor. The interacting force between the sphere and the sample is recorded as a force versus time curve. One can find a detailed description of the used force tester (Tetra GmbH, Germany) in [20]. The tester was used previously for adhesion measurements of the attachment pads of insects. All experiments were carried out at room temperature \((22 - 24\, ^{\circ}\text{C})\) and at a relative humidity of 47-56 %. An accuracy of about 10 \( \mu \text{N} \) was achieved for force measurements. The spring constant was determined with an accuracy of approximately \( \pm 2^5 \text{N/m} \). Since the surface asperities are squashed during loading, only unloading branches were studied, where the classic models of smooth adhesive contact are applicable.

Since the sphere was attached to the end of the cantilever beam (the spring constant of the beam was \( k_1 = 147 \text{N/m} \) ), the real displacement \( \delta \) of the contacting sphere is \( \delta = \delta_c - P_c/k_1 \), where \( P_c \) and \( \delta_c \) are the recorded force and displacement respectively. After the jump out of the contact, the displacement is \( \delta = \delta_c. \) However, the points of the graph near the jump out of the contact value were not used. Hence, \( \delta = \delta_c - P_c/k_1 \) versus \( P_c \) graphs are presented in Fig. 3. The experimental points for an experiment with a washed sample are presented in Fig. 4. Since our results show that the obtained results are quite stable, the least square method can be applied [31]. This method was used for solving overdetermined problems.

5.2. The coordinate origin of the load-displacement curve

Note that in the framework of the JKR model, the origin of the displacement coordinate is not readily extracted from the experiments. On the other hand, this reference point is very important because the solution of the overdetermined problem (8) is quite sensitive to the shifting of the \( \delta \) values. For the JKR model, as it follows from (6), \( P(0) = -(8/9)P_c \) for \( \delta = 0 \).

Let us consider the coordinate system \( O'\delta'P \) that can be chosen arbitrary with respect to the displacement coordinate origin. This means that the origin is shifted by the same value \( \delta_c \) with respect to the true coordinate system \( O\delta P \) that was used to derive the JKR equation. If \( \delta_c > 0 \) then the JKR curve is located on the right from \( O' \) and in turn if \( \delta_c < 0 \) then the JKR curve is located on the left from \( O' \). If \( \delta' = \delta_c \) then the point \( (\delta_c, -(8/9)P_c) \) belongs to the JKR curve. For \( \delta_c > \delta_c \), the origin \( O' \) is taken at a point where \( P = 0 \). In this case the system (6) can be written as
An inverse problem for adhesive contact

Fig 4. The experimental loading-unloading branches of the $P - \delta$ curve for a washed sample loaded by a sphere $R = 1\, \text{mm}$. The BG method is applied to the unloading curve. The solid line is the JKR curve that corresponds to the found values of the scaling parameters.

\begin{equation}
F \left( \frac{P}{P_c}, \frac{\delta' - \delta_c}{\delta_c} \right) = \begin{cases} 
(3\chi - 1) \left( \frac{1 + \chi}{\chi} \right)^{1/3} - \frac{\delta' - \delta_c}{\delta_c} = 0, & \chi \geq 0, \quad \frac{(\delta' - \delta_c)}{\delta_c} \geq -3^{-2/3}, \\
-(3\chi + 1) \left( \frac{1 + \chi}{\chi} \right)^{1/3} - \frac{\delta' - \delta_c}{\delta_c} = 0, & \chi \geq 0, \quad \frac{(\delta' - \delta_c)}{\delta_c} < -3^{-2/3}, \\
\frac{2}{3} \geq \chi \geq 0, & -1 \leq \frac{(\delta' - \delta_c)}{\delta_c} < -3^{-2/3}, 
\end{cases}
\end{equation}

where $\delta = \delta' - \delta_c$. It follows from (18) that the overdetermined system instead of (8) is written as $i = 1, 2, \ldots, N, \quad N > 3$

\begin{equation}
F \left( \frac{P_i}{P_c}, \frac{\delta'_i - \delta_c}{\delta_c} \right) = 0, \quad P_c \geq 0, \quad \delta_c \geq 0.
\end{equation}

The condition $N > 3$ has been added because we have three unknowns: $P_c, \delta_c$ and the shift of the coordinate origin $\delta_c$.

The results obtained for the fresh PVS sample are given in Table 1. Hence, one has

\[
\max w / \min w = 1.35.
\]

Table 1. The results extracted by the BG method for the fresh sample tested by a sphere with $R = 1\, \text{mm}$.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$R$, mm</th>
<th>$E^*$, MPa</th>
<th>$w$, J/m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>2.150</td>
<td>5.469</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>2.099</td>
<td>5.217</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>2.016</td>
<td>7.068</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>2.452</td>
<td>5.250</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>2.296</td>
<td>5.366</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>2.496</td>
<td>5.368</td>
</tr>
</tbody>
</table>

For the corresponding determined values of the contact modulus, we have

\[
\max E^* / \min E^* = 1.24.
\]
For the washed PVS sample, the obtained values are given in Table 2. Hence, one has
\[ \max w / \min w = 1.40. \]

For the corresponding determined values of the contact modulus, we have
\[ \max E^*/ \min E^* = 1.30. \]

**Table 2.** The results extracted by the BG method for the washed sample tested by a sphere with \( R = 1 \text{mm} \).

<table>
<thead>
<tr>
<th>n</th>
<th>( R, \text{mm} )</th>
<th>( E^*, \text{MPa} )</th>
<th>( w, J/m^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>2.925</td>
<td>5.926</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2.680</td>
<td>6.812</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>2.294</td>
<td>6.537</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>2.531</td>
<td>4.871</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>2.319</td>
<td>5.170</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>2.253</td>
<td>6.018</td>
</tr>
</tbody>
</table>

It can be seen from the Tables 1 and 2 that elastic modulus and the work of adhesion of polymer materials can be reliably extracted using the enhanced statistical approach (\( n \) is the test number). One can also see that the washing of the sample does not affect the contact properties of materials (see also Fig. 5). The results of similar experiments for spheres of radius 3 mm have been recently published [17].

![Graph](image)

**Fig 5.** The experimental \( P - \delta \) curve for a washed sample loaded by a sphere \( R = 1 \text{mm} \) superimposed on the experimental curve for a fresh sample.

Calculating the Tabor–Maugis parameter [4],
\[ \mu = \left( \frac{R_d w^2}{(E^*)^2 z_0} \right)^{1/3}, \]

where the effective radius is equal to the radius of the sphere, \( R_d = R \), and \( z_0 \) is the equilibrium distance between atoms of contacting pair, that is usually between 0.3 - 0.5 nm, one can easily check that all experiments were in the range of applicability of the JKR model.
6. Conclusions

At the macroscale adhesive interactions between surfaces have usually a negligible effect on contacting solids. However, these interactions are very important at micro/nano scales and small things are very sticky due to these interactions. To solve many problems of nanomechanics one needs to know the values of the work of adhesion of contacting materials. It has been argued that these values may be quantified using the recently proposed BG method for non-direct determination of adhesive and elastic properties. The BG method is based on an inverse analysis of a stable region of the force-displacements curve obtained from the depth-sensing indentation of a sphere into an elastic sample. It has been proven using both numerical simulations and experimental testing of PVS samples that the BG method is fast and robust.

An inverse problem for adhesive contact and experimental evaluation of material properties for nanomechanics applications have been studied. Various approaches to overdetermined systems have been discussed. It has been shown that the popular semi-empirical $L$-curve method does not work in application to the DMT contact model. It has been noted that in the framework of the JKR model, the origin of the displacement coordinate is not readily extracted from the experiments. A way for solving a very important problem of experimental finding the origin of the $P - \delta$ coordinate system has been described.

Currently, the modern depth-sensing nanoindentation tests are based on the use of the BASh formula (1) that has several drawbacks. On the other hand, although the BG method is targeted mainly to determination of the work of adhesion, the estimations of $E^*$ by (7) may be a good alternative to the BASh approach. We believe that soon the BG method will be widely used by the materials science community.

It has been argued that the standard experimental techniques for measurements of the work of adhesion based on the direct measurements of pull-off force, are unstable. To emphasize the crucial difference between our method and the standard experimental techniques, it has been shown that the BG method may be applied only to compressive parts of the force-displacement diagrams. This removes the major obstacle of the direct approaches because at compression the diagrams are stable.

Evidently, the extracted values of both characteristics vary within the same polymer sample. However, the variations of the obtained results may be caused not only by the errors of the measurements or the method but also by the physics of the polymers. Indeed, polymer molecules are rather long and the contact area may have interacting molecules in various orientations, i.e. it may contain groups that are permanently electron-rich or electron-poor. This phenomenon may affect the seeking values and the results may vary from one experiment to another.

Acknowledgments

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References


