Iterative control approach to high-speed force-distance curve measurement using AFM: Time-dependent response of PDMS example

Kyong-Soo Kim\textsuperscript{a}, Zhiqun Lin\textsuperscript{b}, Pranav Shrotriya\textsuperscript{a}, Sriram Sundararajan\textsuperscript{a}, Qingze Zou\textsuperscript{a,*}

\textsuperscript{a} Mechanical Engineering Department, Iowa State University, Ames, IA 50011, USA
\textsuperscript{b} Materials Science and Engineering Department, Iowa State University, Ames, IA 50011, USA

1. Introduction

In this article, we illustrate the implementation of a novel inversion-based iterative control technique [1] to achieve high-speed force curve measurement on a commercial atomic force microscope (AFM). As an example of application, the high-speed force curve measurements are then utilized to measure the time-dependent properties (e.g., elastic modulus) of poly(dimethylsiloxane) (PDMS). Force-curve measurements using AFM [2–4] have opened the door to experimentally study material properties [5] as well as physical and/or chemical interactions between materials [6]. However, such interrogations are currently hindered by the low-speed operation of AFM, as numerous force-curve measurements usually need to be obtained, particularly in the so-called force-volume imaging [7–11]. In force-volume imaging, a mapping of force-curves distributed over a sample area is obtained. Since numerous force-curves need to be acquired while the sample is scanned with a raster pattern, currently force-volume imaging is time-consuming [12]. More fundamentally, the low-speed of force-curve measurements encumbers the study of time-dependent material properties/interactions at micro-/nano-scale [13,14]. For example, force-volume imaging has been used to obtain the force-mapping [15] or the strain-stress mapping of a live cell [16]. Large temporal errors, however, can occur in the obtained mapping if the force-curves are acquired at low-speed while the cell is moving—as the force-curves at the first and at the last sample point are acquired at much different time instants. Another example is the study of stress-induced chemical bond breaking of siloxane elastomers in the high force regime. To verify the theoretical prediction results [17] obtained from molecular dynamics simulation, the force-curves of single molecule need to be measured at a daunting retraction (unload) rate of nearly \(m/s\) range, which is far beyond the achievable rate on current AFM. Clearly, there exist needs for high-speed AFM force-curve measurement.

The speed of force-curve measurement can be increased by using the force-modulation technique [12,18,19], where a sinusoidal force signal (i.e., AC signal) of small amplitude is augmented with the displacement driven signal, and applied to the tip during the force-curve measurement. Then the amplitude change and the phase shift of the tip oscillations, relative to the input driven force, are acquired and used to measure the elastic stiffness of the material [18,19]. Although the modulation frequency can be changed from a few Hz to \(200\text{Hz}\) [12,18], the equivalent push-in (load) and retraction (unload) rate are still low (<\(6\mu m/s\)) due to the small oscillation amplitude (<\(30nm\)). The push-in/retraction rate is further limited because only sinusoidal...
signal can be applied—methods to increase the rate by using other shape of trajectories [14] cannot be implemented. Moreover, the force-modulation technique requires extra hardware and a complicated parameter calibration process [12,18], and its efficiency is inherently limited because a de-modulation process is needed to accurately measure the amplitude and phase shift, which is time consuming. Therefore, techniques need to be developed to achieve high-speed force-curve measurement.

Recently, advanced control techniques (see, e.g., the tutorial paper [20] and the references therein) have been proposed to improve the throughput of AFM imaging, or more generally, the nanopositioning of piezoelectric actuators [21]. For example, system-inversion-based techniques [22–24] have been developed to find the output-tracking, feedforward control input by feeding the desired output trajectory through the inverse of the system dynamics model and/or hysteresis model. Feedback control design [25] based on robust control theory has also been proposed. Recently, efforts to combine these two approaches, the feedforward with the feedback control, have been pursued for AFM applications [26,27]. The efficacy of these control developments in improving the lateral scanning [24,28,29] as well as the vertical AFM-tip positioning [26] for AFM imaging have been successfully demonstrated. To the best of our knowledge, however, no advanced control techniques have been developed for high-speed force-curve measurements.

In this article, we present a novel enhanced inversion-based iterative control (EIIC) technique [1] for high-speed force-curve measurements. The EIIC technique seeks an appropriate feedforward control input through iterations to eliminate, during high-speed force-curve measurements, the adverse effects of the AFM system. The adverse effects include vibrational dynamics, hysteresis, and creep effects [18,30] of the AFM system (consisting of the piezo-tube actuator and the cantilever along with the mechanical linkage in between). For force-curve measurements, the desired output (i.e., the applied force profile) is pre-defined, and the push-in/retraction operation is repetitive, making it possible to account for the above adverse effects on the output tracking through iterative updates of the control input with the measured output errors. Therefore, the iterative control strategy is intuitively appealing for force-curve measurements. It has been demonstrated that the IIC-type of control algorithms can adequately “cancel” the dynamics-induced vibrations [31] and the hysteresis-caused nonlinear measurement errors [28] during high-speed repetitive motion. However, in the IIC algorithm, the iteration of the input magnitude is coupled (in the frequency domain) with the iteration of the input phase. Such coupling is removed in the proposed EIIC technique. Therefore, the EIIC algorithm extends the IIC algorithm and can achieve convergence over a larger frequency range with a faster convergence rate [1]. We illustrate the use of the proposed EIIC technique in material characterization by applying it to quantitatively study the time-dependent elastic modulus of poly(dimethylsiloxane) (PDMS). The measured values of the elastic modulus are compared with the results obtained from the commonly used dynamic mechanical analysis (DMA) of the PDMS.

2. Methods

2.1. Force-curve measurement using AFM

Various materials properties can be interrogated at submicro to nano-scale by using AFM through the force-curve measurement [32]. To do so, the cantilever/tip is driven by a piezoelectric actuator to push against the sample until the bending of the cantilever (i.e., the force applied onto the sample surface) reaches a pre-specified value, then the AFM-tip will retrace to a pre-specified distance—the tip can be either in continuous or intermittent contact with the sample surface during the process [5] (see Fig. 1(a)). The force-distance curve, as schematically depicted in Fig. 1(b), is obtained by measuring the tip-sample interaction force along with the vertical displacement of the cantilever during the push-in/retraction process. The tip-sample force is derived by using the measurement of the cantilever deflection and the knowledge of the effective spring constant. The cantilever displacement is equivalent to the vertical displacement of the piezoelectric actuator if the indentation of the tip into the sample is negligible, i.e., when the sample is hard enough. In the case of soft samples, however, indentation will occur [5,33,34] and must be accounted for. In such cases, the indentation depth is obtained as the difference between the cantilever displacement on a reference hard sample and on the soft sample [32]. Then the sample mechanical properties such as elastic modulus [5] can be obtained from plots of the tip-sample interaction force vs. the indentation depth.

2.2. Enhanced inversion-based iterative-control (EIIC) technique

In this article, high-speed force-curve measurement is tackled as a control problem: The precise positioning of the cantilever must be maintained during high-speed force-curve measurements (as in the low-speed case), which is achieved by finding the control input (to drive the piezo-tube actuator) such that the cantilever will track a pre-specified trajectory precisely. Next, we describe the EIIC technique to obtain such a control input.

2.2.1. EIIC technique [1]

The EIIC control law can be described in frequency domain as follows: At the first iteration, $k = 0$, the initial input (e.g., the voltage applied to the piezo-tube actuator) is chosen as the scaled desired output trajectory $z_d(j\omega)$, where the scale factor is selected as the inverse of the system dynamics model, $G^{-1}_m(j\omega)$,$$
 u_0(j\omega) = G^{-1}_m(j\omega)z_d(j\omega), \quad k = 0,
$$where $f(j\omega)$ is the Fourier transform of a time-signal $f(t)$, and the frequency response model of the system dynamics, $G_m(j\omega)$, is measured experimentally [35]. Then for all other iterations, $k \geq 1$, the control input is computed by updating it with the positioning errors from the previous iteration, $z_d(j\omega) - z_{k-1}(j\omega)$,$$
 [u_k(j\omega)] = [u_{k-1}(j\omega)] + \rho(j\omega)G^{-1}_m(j\omega)[z_d(j\omega) - z_{k-1}(j\omega)],
$$where $\rho(j\omega)$ denotes the output obtained by applying the iterative input $u_k(j\omega)$ to the system during the $k$th iteration, and $\rho(j\omega) > 0$ is the iteration coefficient. It has been shown that to guarantee the convergence of the iteration, the choice of the iteration coefficient depends on the size of the uncertainty of the system dynamics [1].
More specifically, the above EIIC algorithm (2) will converge to the desired input \(u_d(j\omega)\) which leads to the exact tracking of the desired trajectory at frequency \(\omega\), i.e.,

\[
\lim_{k \to \infty} u_k(j\omega) = u_d(j\omega) \quad \text{and} \quad \lim_{k \to \infty} \angle u_k(j\omega) = \angle u_d(j\omega)
\]

provided that the iterative coefficient \(\rho(\omega)\) is chosen within the following range:

\[
0 < \rho(\omega) < \frac{2}{\|G(j\omega)\|_2}.
\] (3)

In Eq. (3), \(\Delta G(j\omega)\) denotes the the dynamics uncertainty that is defined as the ratio of the actual AFM dynamics \(G(j\omega)\) over the measured dynamics model \(\hat{G}(j\omega)\):

\[
\Delta G(j\omega) = \frac{G(j\omega)}{\hat{G}(j\omega)} = \frac{|G(j\omega)|e^{j\angle G(j\omega)}}{|\hat{G}(j\omega)|e^{j\angle \hat{G}(j\omega)}}
\] (4)

Therefore, the converged control input will remove the system dynamics effect on the output (e.g., the AFM-cantilever deflection).

Note that in the above convergence analysis, the effect of noise is ignored. However, it can be shown that the noise effect is small provided that the noise level is low. Specifically, let the noise level be bounded by a constant proportional to the noise level as given below,

\[
\|u_k(j\omega) - u_d(j\omega)\| \leq \|\hat{G}(j\omega)\|_2 |\Delta u_k(j\omega)|
\] (5)

\[
|\angle u_k(j\omega) - \angle u_d(j\omega)| \leq \tan^{-1} \frac{|\Delta u_k(j\omega)|}{|\hat{u}_k(j\omega)|} \quad \text{for} \ k \geq 1
\] (6)

2.2.2. Implementation Scheme of the EIIC Algorithm

Eq. (3) implies that to determine the iteration coefficient \(\rho(\omega)\) in the EIIC algorithm (2), the dynamics uncertainty \(\Delta G(\omega)\) must be quantified. Although in many applications, the exact dynamics uncertainty may not be quantifiable as the actual dynamics \(G(\omega)\) is unknown, an estimation of the dynamics uncertainty can be obtained through experiments—the exact dynamics uncertainty \(\Delta G(\omega)\) is bounded above by the estimated dynamics uncertainty \(\hat{G}(\omega)\), i.e., \(|\Delta G(\omega)| \leq |\hat{\Delta G}(\omega)|\). Therefore, the iterative coefficient \(\rho(\omega)\) computed by using the estimated dynamics uncertainty in Eq. (3) will guarantee the convergence of the EIIC algorithm. Experimentally, the dynamics uncertainty can be estimated by measuring frequency responses of the system multiple times (with, for example, different input amplitudes) and then finding the maximum difference among the measured frequency responses at each frequency [1].

We further note that as the iterative control methodology is intended for repetitive applications where the desired trajectory \(z_d(t)\) is usually known a priori, the comparison between the desired output trajectory and the measured output, and thereby the computation of the EIIC algorithm can be proceeded offline, instead of online. The obtained iterative control input is then applied as a feedforward, open-loop control input to the system. This implies that the proposed EIIC algorithm can be implemented in frequency domain directly using the fast Fourier transform (FFT) algorithm (and inverse Fourier transform), i.e., the time-domain iterative control input is obtained as

\[
u_k(t) = \mathcal{F}^{-1}[u_k(j\omega)]
\] (7)

where \(\mathcal{F}^{-1}\) denotes the inverse Fourier transform. Such a frequency domain realization also implies that the experimentally measured frequency response data can be used directly in the EIIC algorithm. Therefore, the explicit transfer function model obtained via, for example, curve fitting method, is not needed. Not only is the implementation simplified, but modeling errors generated during the curve fitting to obtain the transfer function model are removed—as usually a lower-order transfer function model is preferred over high-order ones for computational efficiency in time-domain realization.

Finally, the EIIC algorithm (2) is applied at those frequency components of the desired output trajectory \(z_d(j\omega)\) where the gain of the system dynamics is large enough—relative to the noise level of the system, and the control input is set to zero at all other frequencies (readers are referred to Ref. [1] for details). The iteration process should be stopped if the tracking error, \(z_d(t) - z_k(t)\), measured by using some chosen signal norm (e.g., 2-norm and/or infinity norm), cannot be further reduced.

2.2.3. Experimental instrumentation

In this article, a commercial AFM system (Dimension 3100, Veeco Inc.) was used in all experiments along with a standard V-shaped Silicon Nitride cantilever. The nominal spring constant and the nominal curvature radius of the cantilever were 0.12 N/m and 20 nm, respectively. The effective spring constant of the cantilever, 0.07 N/m, was measured by using the thermal noise method [36] at room temperature. To minimize the effect of the tip shape variation during the experiment, the tip had been used to image a silicon calibration sample for over 5000 scan lines at the scan size of over 50 μm before the tip was used to measure the force-curve in the following experiments, thus containing a “steady-state” radius. Kanaga Karuppiah and co-workers found negligible wear on the probe as a result of sliding friction and force curve experiments on ultra-high molecular weight polyethylene [37]. Indentation on a soft material like PDMS is therefore not expected to result in wear of probe tip during the force displacement experiments. Hence a constant tip radius is used for calculation of modulus in Hertzian analysis. In our previous work [37,38], we consistently obtained a tip radius between 42 and 50 nm after imaging a hard sample for similar number of scan lines. The tip radius was measured through inverse imaging the probe over a calibration grating that has silicon spikes with radii of curvature less than 10 nm. Hence, in the following, a tip radius of 50 nm was assumed for modulus computation during Hertzian analysis.

The experimental system to implement the EIIC control law to achieve high-speed force-curve measurement is depicted in Fig. 2. All the control inputs to the piezoelectric actuator were generated by using MATLAB xPC-target (Mathworks Inc.), and sent out through a data acquisition card (DAQ_PCI-DAS1602/16, Measurement Computing Inc.) to the high-voltage amplifier of the AFM-controller—The AFM-controller was modified so that the PID (proportional-Integral-Derivative) control circuit is bypassed when the external control input is applied. The corresponding cantilever deflection signal was sampled at 50 KHz by using the DAQ system. The environment humidity was controlled under 20% by feeding Nitrogen gas into a home-made sealed plastic box that covered the AFM head for over 40 min before the experiments were conducted (We note that PDMS is a hydrophobic material, and residual humidity is not expected to significantly influence the experimental measurements). All the experiments, including the iterations of the control inputs using the EIIC law on the hard surface, and the application of the obtained control inputs to measure the force-curves on the PDMS sample, were conducted with the box sealed (A flash light and a webcam were placed...
inside the box to aid the operation). The force-curve at different push-in rates were measured in sequence with a separation time of ~15 s in between. The iteration was stopped when neither the relative RMS-tracking error $E_2(\%)$ nor the relative maximum-tracking error $E_{\infty}(\%)$ decreased further, where $E_2(\%)$ and $E_{\infty}(\%)$ are defined as

$$
E_2(\%) = \frac{\|z_d(\cdot) - z(\cdot)\|_2}{\|z_d(\cdot)\|_2} \times 100\% ,
$$

$$
E_{\infty}(\%) = \frac{\|z_d(\cdot) - z(\cdot)\|_{\infty}}{\|z_d(\cdot)\|_{\infty}} \times 100\% .
$$

2.3. Application of EIIC technique to elastic modulus measurements of PDMS

2.3.1. Desired trajectory design

One exemplary application of high-speed force measurement is to interrogate the time-dependent elastic modulus of soft materials like PDMS. To that end (by using the above EIIC algorithm), the desired trajectory ($z_d$ in Eq. (2)), e.g., the desired AFM-tip vertical displacement vs. time during the push-in/retraction process, needs to be pre-specified. The desired trajectory used in the experiments is schematically depicted in Fig. 3, where the push-in and the retraction sections are separated by two flat sections. Since the push-in section of the force-curve was chosen to measure and calculate the time-dependent elastic modulus of soft materials like PDMS. To that end (by using the above EIIC algorithm), the desired trajectory was designed by varying the push-in period, $[t_0, t_1]$ in Fig. 3, while maintaining the same push-in distance. The retraction time period, $[t_2, t_3]$, was chosen to be twice longer than the push-in period $[t_0, t_1]$ in the experiments to reduce the zero load plastic deformation. The constant flat period of a fixed duration at 5 ms, was added to help the tracking during the push-in section (at high speed), which can also be used to investigate material relaxation at different push-in rates.

It is noted that other shapes of user-defined trajectories can be used in the EIIC algorithm, provided that the trajectory is continuous with its main frequency components within the bandwidth of the piezo actuator. The desired cantilever displacement trajectory can be designed by reversing the design of the above asymmetric trajectory to have a fixed push-in rate but different retraction rates. Therefore, the proposed EIIC algorithm allows the use of trajectory design [14] in high-speed force-curve measurements.

2.3.2. Force-curve measurements using EIIC technique

First, to obtain the control input that compensates for the dynamics effects of the AFM system (consisting of the piezo-tube actuator and the cantilever along with the mechanical linkage in between) during high-speed force-curve operations, the EIIC algorithm was applied to measure the force-curve on a hard sample (e.g., a silicon calibration sample). The use of a hard sample ensures that the control input results in force curve free of system dynamics effects as well as negligible sample indentation. As a result, the difference between the force-curve obtained on the hard sample and that obtained on the soft material should yield the mechanical property (e.g., elastic modulus) of the soft material.

2.3.3. Force and indentation computation

The force applied to the sample $F_2$ was computed according to

$$
F_2 = k \times C \times \theta_3 ,
$$

where $k$ is the stiffness constant of the cantilever, $C$ is the sensitivity constant of the deflection signal vs. the vertical displacement of the cantilever, and $\theta_3$ denote the deflection signal measured on the sample. Then the indentation depth $z_t$ was computed by

$$
z_t = C \times (\theta_4 - \theta_3) ,
$$

where $\theta_4$ denotes the deflection signal measured on the hard surface. Note both the stiffness constant $k$ and the sensitivity constant $C$ can be experimentally calibrated [36].

2.3.4. Theory: Hertzian contact model

Hertzian model [5,32] is widely used to estimate the elastic modulus of soft materials like PDMS by using the experimentally measured force-curve data. The time-dependence of the elastic modulus was examined by using the force-curves obtained at different push-in rates in the calculation. According to the Hertzian model [5,39], for two elastic materials (the sample and the tip) brought into contact, the contact area at zero load is zero ($a_0 = 0$) and the surface forces or adhesion force is negligible during the contact ($F_{adh} = 0$). Then the stiffness modulus of the sample ($E_3$) can be calculated by using the indentation depth $\delta$, and the reduced Elastic modulus $E_{tot}$ of the sample:

$$
\delta = \left( \frac{F^2}{R \times E_{tot}} \right)^{1/3} ,
$$
\[
\frac{1}{E_{\text{tot}}} = \frac{3}{4} \left( \frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_t^2}{E_t} \right),
\]
(11)

where \( F \), \( R \), and \( E_t \) are the applied force, the tip radius, and the tip elastic modulus, respectively, and \( \nu_s \) and \( \nu_t \) are the Poisson’s ratio of the sample and the tip, respectively. For soft samples like PDMS, its elastic modulus \( E_s \) (in several MPa range) is over seven orders smaller than that of the probe (silicon nitride) \( E_t \) at 160–290 GPa [5], therefore the above Eq. (11) can be simplified as

\[
\frac{1}{E_{\text{tot}}} \approx \frac{3}{4} \left( \frac{1 - \nu_t^2}{E_t} \right).
\]
(12)

### 2.3.5. Materials: PDMS

As an illustrative example, the elastic modulus of PDMS was measured at different push-in (loading) rates by using the EIIC technique. The PDMS sample with an appropriate thickness was prepared as follows. The prepolymer (Sylgard 184 Silicon Elastomer base, Dow Corning) and curing agent were vigorously mixed at 1:10 ratio by weight. The prepolymer/curing agent mixture was then degassed in vacuum oven for 1 h to remove any trapped air inside the mixture. Subsequently, the mixture was deposited in a plastic Petri dish, and cured at room temperature for 2 days in vacuum oven. Finally, the resulting PDMS film was truncated into a desirable dimension for DMA and AFM measurements.

### 3. Experimental results and discussion

#### 3.1. Experimental implementation results of the EIIC algorithm

The frequency response of the AFM dynamics was measured by, first, positioning the AFM probe on a hard (silicon) sample with a small deflection force (tuned by using the AFM controller software), then driving the piezoelectric actuator with a sinusoidal input with frequency sweeping from 1 Hz to 6 KHz (i.e., the sweep sine method), and measuring the cantilever deflection signal. The frequency responses acquired with three different input levels (20, 40, and 50 mV) at three different locations of the sample, respectively, were shown in Fig. 4. The maximum magnitude variations among the three frequency responses \( |\Delta G(j\omega)| \) and the upper bound of the iteration coefficient \( \rho_{\text{sup}}(\omega) \) computed by (3) are shown in Fig. 5, from which the iterative coefficient \( \rho(\omega) \) used in the experiments were determined, as shown in Fig. 5. Finally, the nominal frequency response used in the EIIC algorithm was obtained as the average of the four measured frequency responses (see Fig. 4). Note Fig. 4, in the high frequency range (around 4–6 KHz), the gain of AFM system drops dramatically and large dynamics uncertainty occurs, therefore the EIIC algorithm was implemented for frequency \( \omega \leq 6 \text{KHz} \), i.e., the iterative control input \( u_0(j\omega) \) was set to zero for all frequency \( \omega > 6 \text{KHz} \).

#### 3.2. Tracking results on a silicon sample

The force-curves at 12 different push-in rates, spanning 400 times difference from 2.16 to 864 \( \mu\)m/s, were measured on a Silicon sample—every push-in rate is a multiple integer times of the base speed at 1.08 \( \mu\)m/s (or equivalently, 12 mV/ms—with the system sensitivity at 90 nm/V). The displacement range was fixed at 270 nm—thus the slowest push-in rate of 2.16 \( \mu\)m/s corresponds to a scan rate of 2.53 Hz (the scan rate is defined as the rate of one push-in/retraction operation). The RMS positioning error \( E_t(\%) \) and the relative maximum error \( E_{\text{max}}(\%) \) for the 12 different push-in rates are listed in Table 1, where the iteration numbers to achieve the convergence are also listed for each push-in rate. In addition, the cantilever vertical displacements vs. time at the push-in rate of 2.16 and 648 \( \mu\)m/s are plotted in Fig. 6. As can be seen from Table 1 and Fig. 6, precise positioning was maintained for all push-in rates—both the RMS error \( E_t(\%) \) and the maximum tracking error \( (E_{\text{max}}(\%) \leq 2.5\%) \) are small and close to the noise-level of the system. Particularly, we note that even at the high rate of 864 \( \mu\)m/s, the positioning error is still close to the error at the low rate of 2.16 \( \mu\)m/s. Therefore, our experiment results show that high-speed force curve measurement with no loss of spatial resolution can be obtained by using the proposed EIIC technique.
To ensure that later the force-curves of PDMS were measured within the elastic deformation range of PDMS, a relatively small cantilever displacement (indentation) range (~270 nm) was chosen in the experiments (see Fig. 6). As shown later in Fig. 12, such a displacement range resulted in a force load size at 14 nN, which is well-below the elastic deformation range of PDMS as reported elsewhere [40]. However, even if we quadrupled the displacement range but kept the same time duration of the push-in portion, precise output tracking can still be maintained. As shown in Fig. 7, at the push-in rate of 3.456 mm/s, the RMS error and the maximum error of the output tracking obtained by using the EIIC algorithm (after 12 iterations) are still small ($E_2(\%) = 0.6\%$ and $E_{\text{max}}(\%) = 6.9\%$). Thus, the experiment results show that high-speed force-curve measurements can be achieved by using the EIIC technique.

3.3. High-speed force-curve measurements on PDMS

The converged control inputs for the 12 different push-in rates, obtained in Section 3.2, were applied to measure the force-curves on the PDMS sample. We note that due to the difference of the tip-sample interaction on PDMS and on silicon, the obtained push-in rate and the cantilever vertical displacement range on the PDMS sample were different from those on the silicon sample, respectively. Particularly, non-constant push-in rate may occur due to the indentation of the AFM-tip into the soft sample. However, our experiment results show that the deviation of the push-in rate from the constant push-in rate was very small and thus negligible. We calculated the push-in rates obtained on the PDMS sample for the 12 different control inputs, and further quantified the deviations of the cantilever deflection from the nominal trajectory (specified by the computed push-in rates). The deviations were quantified by using both the relative RMS error $E_2(\%)$ and the relative maximum error $E_{\text{max}}(\%)$, and are shown in Table 1. By using the proposed EIIC technique, the variation of the push-in rates is still very small even when the push-in rate is as
high as 777.4 μm/s (corresponding to the push-in rate of 848 μm/s obtained on silicon sample). This can also be seen from Fig. 8, where the cantilever vertical displacements for push-in rate of 1.7 and 565.2 μm/s are compared to the corresponding cantilever displacements obtained on the Silicon sample for push-in rates of 2.16 and 648 μm/s, respectively. Table 1 and Fig. 8 also show that the differences in the push-in rate and the (cantilever vertical) displacement, between the silicon sample and the PDMS sample, decreased as the push-in rate increased. At the low push-in rate, PDMS exhibits a rubbery characteristic. As the push-in rate increases, however, the movements of PDMS molecules are significantly retarded since they cannot follow the external deformation fast enough, thereby behaving like a stiff material [41,42]. As a result, the tip-sample interaction on PDMS becomes similar to the interaction on silicon, which in turn, leads to a similar push-in rates on these two different materials (Fig. 8(b)) when the push-in rate is high.

The measured force-curves were analyzed using the Hertzian model to calculate the elastic modulus of PDMS at different push-in rates. First, the tip indentation was obtained as the difference of the cantilever vertical displacement on PDMS and on silicon, as shown in Fig. 8 for the push-in rates of 1.7 and 565.2 μm/s, respectively. We note that Si is not infinitely hard and might experience slight deformation during the force-curve measurements. However, since the elastic modulus of Si is much larger than that of PDMS, we can safely assume that the indentation on Si was negligible in the experiments—compared to the indentation on the PDMS. Consequently, the indentation vs. force curves were obtained for the 12 different push-in rates, and fitted using the Hertzian model (see Eqs. (10) and (12), Section 2.3) to find the elastic modulus of PDMS. The cantilever stiffness of 0.07 N/m was experimentally calibrated and a nominal tip radius of 50 nm was used in the calculation. Finally, the elastic modulus of the PDMS sample for the 12 different push-in rates were obtained, as plotted in Fig. 12. The variation of initial tip radius from 30 to 70 nm will cause a change of +29.1% to −15.5% in the computed modulus values. As an example, the force curves of PDMS for push-in rates of 1.7 and 565.4 μm/s are shown in Fig. 9, respectively.

Note that the Hertzian model was used to obtain the optimal fit (in the least-square sense) of the later part of the experimental force curve, and the difference between the experimental and fitting curves at the beginning part of the curve represents the so-called zero-load plastic deformation (i.e., the residual plastic deformation, see Fig. 9) [5]. Such a zero-load plastic deformation, as schematically denoted in Fig. 10, is generated because the force was applied repetitively on the PDMS sample—At each push-in rate, the push-in/retraction operation was repeated by over 10 times, and the period was much shorter than the relaxation time of PDMS. Note that the zero-load plastic deformation depends on the kinetic energy applied to the PDMS sample during the operation [5]. Since the same force profile was applied during a longer time interval at low push-in rate than that at high push-in rate, a larger amount of kinetic energy was applied to the PDMS at low push-in rate than that at high push-in rate. Therefore, a larger zero-load plastic deformation was generated at low push-in rate than that at high push-in rate. This was verified by our experimental results. As shown in Fig. 11, the zero-load plastic deformation decreased as the push-in rate increased. Therefore, by using the EIIIC technique, force-curves of both hard and soft materials can be measured in a broad spectrum of push-in (and/or retraction) rates, spanning two order of differences.

Table 2
Tracking performance results ($E_1(\%)$ and $E_{max}(\%)$) during the push-in section of the force-curve, obtained by applying the converged EIIIC control input to the PDMS sample

<table>
<thead>
<tr>
<th>Push-in rate on Si (μm/s)</th>
<th>2.16</th>
<th>5.4</th>
<th>10.8</th>
<th>21.6</th>
<th>43.2</th>
<th>64.8</th>
<th>86.4</th>
<th>108</th>
<th>216</th>
<th>432</th>
<th>648</th>
<th>864</th>
</tr>
</thead>
<tbody>
<tr>
<td>Push-in rate on PDMS (μm/s)</td>
<td>1.7</td>
<td>4.4</td>
<td>9.0</td>
<td>18.5</td>
<td>36.9</td>
<td>56.4</td>
<td>75.3</td>
<td>95.2</td>
<td>193.5</td>
<td>384.9</td>
<td>565.2</td>
<td>777.6</td>
</tr>
<tr>
<td>$E_1(%)$</td>
<td>0.39</td>
<td>0.47</td>
<td>0.71</td>
<td>0.67</td>
<td>1.11</td>
<td>0.66</td>
<td>0.70</td>
<td>0.84</td>
<td>0.97</td>
<td>1.59</td>
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<td>2.86</td>
</tr>
<tr>
<td>$E_{max}(%)$</td>
<td>0.84</td>
<td>1.11</td>
<td>1.45</td>
<td>0.96</td>
<td>3.24</td>
<td>1.17</td>
<td>1.60</td>
<td>1.52</td>
<td>2.22</td>
<td>3.09</td>
<td>4.71</td>
<td>4.98</td>
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</table>

Fig. 8. The comparison of the cantilever vertical displacement obtained by using the same control input for the push-in rate of (a) 2.16 μm/s on the silicon sample and 1.7 μm/s on the PDMS sample, and (b) 648 μm/s on the silicon sample and 565.4 μm/s on the PDMS sample. The corresponding displacement difference between the silicon and the PDMS measurements are also shown, which equals to the indentation of the tip into the PDMS sample during the measurement. The inset in (a) is the zoomed-in view of the flat portion of the trajectories.
3.4. DMA result

The viscoelastic properties of PDMS in bulk were characterized by DMA measurement (TA instrument, Q800). The storage modulus ($E'$), loss modulus ($E''$), and $\tan\delta$ as a function of temperature (−133–60 °C) were obtained from a 20 × 2 × 7 mm$^3$ sample under the tension mode at a frequency of 1 Hz and a heating rate of 5 °C/min.

3.5. Rate-dependent elastic modulus of PDMS

The results show that at low push in rates, the elastic modulus obtained from the force curve measurements match well with the values obtained from the DMA. This is because in case of PDMS, a viscoelastic material whose glass transition temperature is close to room temperature, when the push-in rate is low (e.g., 1.7 μm/s), the PDMS molecules are able to move (i.e., deform, and subsequently recover to their equilibrium conformation) in response to the applied deformation. So the modulus ($E'$) compares well to that obtained in the DMA measurement at room temperature. As shown in Fig. 12, the value of the PDMS elastic modulus at low push-in rate of 1.7 μm/s (equivalent to a push-in/retraction frequency of 2.53 Hz), estimated by using the AFM experimental data, is at ~2 MPa, while the elastic modulus value obtained from the DMA measurement at the frequency of 1 Hz and the same room temperature (25.5 °C) is at 1.56 MPa, as pointed out in Fig. 13. However, as the rate of external deformation increased by more than two orders of magnitude (e.g., 565.4 μm/s), the PDMS molecules cannot move fast enough to follow the imposed external deformation and thereby PDMS behaves as a polymeric material at temperatures well below the glass transition temperature, i.e., like a stiff material. This led to a dramatic increase in the elastic modulus $E'$, as evidenced in Fig. 12.

Time temperature superposition (TTS) principle is widely applied to characterize material response of viscoelastic polymeric materials [43]. According to TTS, material response at low (high) temperature (compared to its glass transition temperature) is similar to the response at high (low) frequency loadings. At low temperatures or under high frequency loadings, polymers behave as a stiff or glassy solid. While at high temperatures or low frequency loading, polymer molecules are mobile and as a result lower modulus values are measured. Following TTS principle, PDMS response determined using fits of high-speed force displacement curves (Fig. 12) can be qualitatively compared to storage modulus measured using DMA (Fig. 13). As the loading rate is increased, PDMS modulus increases from about 2 MPa to about 6 (Fig. 12). Similar magnitude of change in storage modulus...
is observed as the temperature is decreased from room temperature (Fig. 13). Note that results of the DMA test are used to demonstrate the viscoelastic nature of PDMS sample investigated in the study. Comparison of the force displacement and DMA test results indicates that force curves acquired using the EIIC technique may be utilized to measure the time dependent modulus. The magnitude of the modulus determined from force displacement relationship is higher than that measured using DMA because of the limitations in the analytical model of contact between tip and sample that was used. In previous work VanLandingham and co-workers [44] have noted that mechanics of contact between indenting tip and sample surface is not correctly captured by analytical Hertzian models. This limitation of contact mechanics models leads to consistent overestimation of modulus measured from indentation experiments in comparison to bulk measurements [44]. Since the focus of this paper is on development and demonstrate the iterative control algorithm for high-speed force measurement, a simple analytical (Hertzian) model was utilized to extract the modulus. The correlation between modulus determined from high speed force-displacement and DMA clearly indicates that the described technique can be used for characterization of material time dependent response.

4. Conclusions

In this article, we presented a novel enhanced inversion-based iterative control (EIIC) technique to achieve high-speed force-distance measurement using AFM, and utilized it to measure the time-dependent elastic modulus of poly(dimethylsiloxane) (PDMS). The experimental results showed that the proposed EIIC technique is efficient in removing the effect of the AFM dynamics (from the piezotube actuator to the cantilever along with the mechanical connection in between) during high-speed force-curve measurements. A push-in or retraction rate as high as 864 μm/s (over 80 times faster) was achieved with no loss of spatial resolution. The time-dependent elastic-modulus of PDMS was obtained by measuring the force-curve measurements with different push-in rates, and utilizing the measurements on a hard (silicon) sample and on the PDMS in the Hertzian contact model. The obtained values of the elastic modulus were compared with the results from the DMA test of the PDMS. As expected, the elastic (storage) modulus value obtained from the DMA test compared well with our experimental result at low push-in rate (~1.7 μm/s). The measured elastic modulus increased as the push-in rate increased, signifying that a faster external deformation rate transitions the viscoelastic response of PDMS from that of a rubbery material toward a glassy one. Compared with other approaches, the proposed EIIC technique and associated high-speed force curve measurements has advantages of being readily applicable to current commercial AFM systems with minor hardware modification/updates, robust to system/operation variations (because such variations can be compensated for via iterations), and possibly achieving measurement precision beyond the signal noise limit (the signal noise effect can be significantly reduced using averaging methods, as the control input is computed off-line iteratively, ). Therefore, we expect the high speed force measurements to be implemented in a variety of material characterization studies.

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References


