Implications of the Contact Radius to Line Step (CRLS) Ratio in AFM for Nanotribology Measurements

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Investigating the mechanisms of defect generation and growth at surfaces on the nanometer scale typically requires high-resolution tools such as the atomic force microscope (AFM). To accurately assess the kinetics and activation parameters of defect production over a wide range of loads ($F_L$), the AFM data should be properly conditioned. Generally, AFM wear trials are performed over an area defined by the length of the slow ($L_{slow}$) and fast scan axes. The ratio of $L_{scan}$ to image resolution ($res$, lines per image) becomes an important experimental parameter in AFM wear trials because it defines the magnitude of the line step ($LS = L_{slow}/res$), the distance the AFM tip steps along the slow scan axis. Comparing the contact radius ($a$) to the line step ($LS$) indicates that the overlap of successive scans will result unless the contact radius—line step ratio (CRLS) is $\leq 1/2$. If this relationship is not considered, then the scan history (e.g., contact frequency) associated with a single scan is not equivalent at different loads owing to the scaling of contact radius with load ($a \propto F_L^{1/3}$). Here, we present a model in conjunction with empirical wear tests on muscovite mica to evaluate the effects of scan overlap on surface wear. Using the Hertz contact mechanics definition of $a$, the CRLS model shows that scan overlap pervades AFM wear trials even under low loads. Such findings indicate that simply counting the number of scans ($N_{scan}$) in an experiment underestimates the full history conveyed to the surface by the tip and translates into an error in the actual extent to which a region on the surface is contacted. Utilizing the CRLS method described here provides an approach to account for image scan history accurately and to predict the extent of surface wear. This general model also has implications for any AFM measurement where one wishes to correlate scan-dependent history to image properties as well as feature resolution in scanned probe lithographies.

Introduction

Tribological phenomena on the nanoscale are inherently complex and difficult to probe owing to the vanishingly small population of species of interest such as atomic defects. For instance, the population of defects within a typical AFM tip—surface contact under load is often estimated to be on the order of one per contact and amounts to requiring the sensitivity to detect a single ruptured bond within a matrix of ca. 100 bonds.1-5 Surface wear phenomena are further complicated by chemical- and history-dependent dynamics, which continuously alters the dominant energy-dissipating mechanisms.1,2,6-7 The activation and coexistence of various energy-relieving pathways, such as abrasion, becomes more problematic once the wear threshold is breached, which further convolutes the various mechanisms at work. The direct evidence needed to unravel the mechanistic details of the tribological processes germane to wearing contacts can be probed with the various imaging modes of the atomic force microscope (AFM).8-10 AFM is well suited for probing tribocorrode wear, especially with the advent of force distance (FD) spectroscopy and frictional force ($F_F$) imaging.1,2,5,10-26 Quantitative interfacial energies, charge distributions, and interfacial tip-mediated reaction kinetics for phenomenally small wear areas (<10 nm²) can be measured, capturing surface modification and degradation from an atomic point of view.

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Figure 1. (A) Pictorial representation of the mica (001) cleavage plane showing the 0.52 nm lattice periodicity. (B) Repeating layered structure of mica along the c axis, orthogonal to the (001) plane, with interlayer distances referenced to the basal plane. The surface of the octahedral-coordinated aluminate layer is 0.22 nm from the surface of the (001) basal plane. Adapted with permission of Routledge/Taylor & Francis Group, LLC from ref 2.

Muscovite mica, a layered aluminosilicate in the form of KAl_2(Si_3AlO_10)(OH)_2, has been a standard for atomic-scale investigations because of the ability to readily generate large domains of an atomically smooth surface.^{1,2,5,10,34} Mica’s (001) crystal plane displays a 5.2 Å lattice, whereas the aluminosilicate sheets normal to the (001) plane have a periodicity of ≈10 Å.^{3,4,35} Mica also possesses an octahedral-coordinated alumina layer that is 2.2 Å from the surface of the (001) basal plane (Figure 1). The facile cleavage and chemical uniqueness of each mica layer in solution makes mica a model substrate for tribological investigations of oxides.^{27,28,36}

In this article, mica is employed to examine the impact of scan overlap on the wear of the surface using a contact radius—line step (CRLS) relationship developed with Hertz contact mechanics theory. We have previously reported the basics of this formulation^{2} and here present a complete comparison of experimental data to the analysis model. The CRLS analysis was tested by attempting to predict the requisite number of image scans required for experiments devoid of scan overlap (along the slow scan axis) to achieve an equivalent degree of surface wear found with “parent” trials possessing a predicted degree of scan overlap. Therefore, by design, to test the surface wear predictions of this model under a given set of conditions, experiments were conducted in pairs: one trial with scan overlap and one without. This approach allowed the nonoverlapping, CRLS-derived trial to be internally referenced to the parent trial (with overlap), fostering comparison and evaluation of the role that scan overlap plays in defect generation and wear as investigated by AFM.

CRLS Analysis Model

Development of the CRLS analysis first requires a functional form describing the geometry of the tip–surface contact. Although there are several models available, to maintain simplicity, the

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most general form defined by Hertz continuum contact mechanics is implemented. On the basis of the Hertz model, the contact radius \( a \) of a spherical AFM tip on a flat elastic body is defined as:

\[
a = \left( \frac{3RF_z}{4\epsilon} \right)^{1/3}
\] (1)

where, \( R \), \( F_z \), and \( \epsilon \) are the tip radius of curvature, the applied normal force, and the combined elastic modulus, respectively, with \( \epsilon \) given in terms of the individual Poisson ratio \( (\nu_1) \) and Young's modulus \( (E_i) \) of the tip and sample.

The second component of this analysis considers the general AFM image acquisition parameters (i.e., the image resolution \( \text{res} \) (lines scanned per image) and scan length \( L_{\text{scan}} \) in the slow scan direction). Although the settings have brought little attention as experimental parameters, as one may expect, they can predictably impact the tip–surface contact history and can therefore be employed advantageously in nanotribology studies. Specifically, the CRLS analysis uses the ratio of \( L_{\text{scan}} \) to \( \text{res} \), eq 3, to define the line step (\( L_S \)) or pitch of successive line traces along the slow scan axis.

\[
L_S = \frac{\text{length}_{\text{slowscan}}}{\text{resolution}} = \frac{L_{\text{scan}}}{\text{res}}
\] (3)

For a typical image resolution of 256, the line step is \( \sim 3.90 \) nm for an \( L_{\text{scan}} \) of 1000 nm, indicating that unless \( a \leq 1.95 \) nm, overlap of successive lines traces will occur. Furthermore, the contribution of scan overlap, postulated to introduce unaccounted scan history to the surface, becomes more significant for the smaller scan areas common to nanotribology studies (e.g., \( L_S \approx 1.56 \) nm for an \( L_{\text{scan}} \) of 400 nm with a \( \text{res} \) of 256). To assess the impact of scan overlap on surface degradation, a comparison of overlapping and nonoverlapping trials conducted under identical load conditions is required. Comparison is accessible by establishing criteria that effectively eliminate line-scan overlap from AFM experiments. The CRLS ratio, eq 4, intuitively provides this bridge for comparison. Within the nonoverlapping limit, eq 4 states that the ratio of the contact radius to line step is required to be less than or equal to \( 1/2 \).

\[
\text{CRLS} = \frac{a}{L_S} \leq \frac{1}{2}
\] (4)

This relationship further indicates that when the line step equals the contact diameter (\( L_S = 2a \)) all areas of the imaged substrate are contacted with the AFM tip while still avoiding overlap of successive line scans. This specific solution to eq 4 is taken as the ideal condition for an AFM wear trial and therefore is employed to establish the ideal length of the slow scan axis (\( L_{\text{scan}}^{\text{CRLS}} \)), which is simply the product of the contact diameter and image resolution (eq 5). Within the Hertz model, substitution then provides a general form of \( F_z^{\text{CRLS}} \), which can be determined a priori provided the tip radius of curvature is known and the applied load and image resolution are predefined. The relationship expressed in eq 5 is especially useful for the realization of self-consistent load-dependent wear studies because an \( L_{\text{scan}} \) versus \( F_z \) plot enables experiments to be designed and conducted in the absence of scan overlap and the unaccounted scan history it imparts to the surface.

\[
L_{\text{scan}}^{\text{CRLS}} = \text{res} \times \left( \frac{6RF_z}{\epsilon} \right)^{1/3}
\] (5)

The proposed analysis provides an approach to condition AFM data sets so that a single image scan for a given applied load systematically applies a single scan’s worth of load-dependent contact history to the surface. Here, line scan overlap and the contribution of additional defect-generating scanning is explicitly avoided and therefore conditions the data set for more intensive analysis, such as relating the number of image scans to the kinetics of defect nucleation and propagation.\(^5,12,13,20,30,37,38\) In this regard, if it is assumed that the Hertz pressure distribution adequately describes the tip–surface contact over a range of applied loads, then the contact frequency by the defect-initiating body (i.e., the AFM tip) is well defined within a single scan limit.

Although this analysis bears all of the caveats of the elastic contacts described by the Hertz model (e.g., isotropic materials, spherical contacts, no adhesion, etc.), the framework presented can be expanded to include the chemical interactions, material anisotropy, and inelastic processes excluded here for simplicity. Contact mechanics models that include the anisotropy of the materials have been previously described in the literature\(^{39–41} \) and can be readily incorporated into our model. For example, the contact area of an orthotropic material in contact with a spherical indenter would yield an elliptical contact. In such a case, the CRLS condition would then depend on the dimensions of the axes of the contact projected onto the slow scan direction. Ultimately by not considering scan overlap in AFM nanotribology studies, the scan history is invariably convoluted with the nonlinear load dependencies of the contact (vide infra). Although avoiding these secondary influences is desirable, a comparison of wear trials with and without scan overlap can provide further insight into wear processes.\(^{32,33} \)

The cumulative nature of line scan overlap and how it can add additional complexity to scanning probe investigations can be visualized in simulated AFM wear trials. The images of Figure 2 are representative contact history simulations of a silicon AFM tip (\( R = 30 \) nm) on a mica surface under a variety of applied loads. The AFM scanning parameters were held constant for these examples (i.e., a (400 \( \times \) 400) nm\(^2 \) scan area and an image resolution of 256 (\( L_S \) of 1.5625 nm)). The values of these parameters are consistent with those typically employed in experimentation as well as those used throughout the course of our work in developing this analysis. The images of Figure 2 are high-resolution views, (12.5 \( \times \) 12.5) nm\(^2 \), of a portion of the trial area. Here, the image contrast represents the cumulative (additive) pressure history, \( p_{\text{history}} \) (arbitrary scale units) experienced by the surface at specific locations in the scanned image area for a given applied area. The gray arrows represent the line step’s fast scan direction where the center of the AFM tip is rastered during imaging. Importantly, it is here at the center of the tip–surface contact where the Hertz pressure distribution is at its maximum (\( p_{\text{max}} \)), equal to 1.5 times the mean contact pressure (\( p_s \)), and corresponds to the peak in the pressure history for trials conducted in the absence of line scan overlap. However, when line scan overlap exists, the cumulative pressure history (\( p_{\text{history}} \))
may not coincide with $p_{\text{max}}$. Because of the additive accounting employed in the simulations, this peak radial stress is redefined as the nondimensional maximum pressure history, $p_{\text{max}}^{\text{history}}$, and is given in the upper right-hand corner of each image for reference. There are several interesting features appearing in Figure 2b–d that are direct consequences of line scan overlap. As implied, Figure 2a represents the ideal CRLS scan, where under an applied load of 1 nN scan overlap does not occur. Here, as would be expected from the Hertz model, the peak pressure history ($p_{\text{max}}^{\text{history}} \approx 0.89$) is found at the contact center as indicated by the intensity scale bar. However, as the load is increased so does the contact diameter, ($F_z \propto a^3$), which leads to the cumulative pressure images found in Figure 2b–d. The most striking feature of these simulations is the movement of the cumulative pressure history peak from the contact center to the midpoint between successive line traces. Even under low loads, for example, 2 nN in Figure 2b, this progressive translation leads to a maximum cumulative pressure ($p_{\text{max}}^{\text{history}} \approx 1.19$) at the midpoint between line traces and not at the contact center ($p_{\text{history}} \approx 1.12$). Furthermore, the movement is periodic, a direct consequence of the contact radius–load–LS interdependency. The profiles in Figure 2e clearly illustrate this periodic variation in the cumulative pressure intensity for a range of applied loads, noting that arrows at the bottom of the plot indicate the position of the contact center during each line trace.

The additional scan history evident in the simulated AFM
scans of Figure 2 can be estimated in terms of a scan correction (scan\textsubscript{cor}), defined as the number of nonoverlapping scans required to achieve, under identical experimental conditions, the same contact history (e.g., degree of wear) in an overlapping trial. The scan\textsubscript{cor} can be derived from the integrated Hertz pressure within the overlapping area of successive line traces and therefore can be estimated numerically. We have previously described the basis of this formulation,\textsuperscript{2} and the derivation of the complete expressions employed for numerical evaluation can be found in the Supporting Information.

\[
F_z = \int_0^{2\pi} \int_0^{\alpha} \rho(r) r dr d\theta = \frac{1.5F_z}{\pi a^2} \int_0^{2\pi} \int_0^a \left(1 - \frac{r^2}{a^2}\right)^{3/2} r dr d\theta = \frac{2p_{max} \pi a^2}{3} \tag{6}
\]

Here, \(p_{max}\) is the maximum pressure within the contact and is equal to 1.5 times the Hertz mean pressure \((p_{hm})\). In our calculations, we employed the following (eq 7) Cartesian coordinate form of \(p(r)\).

\[
p(x, y) = \left[1 - \frac{(x^2 + y^2)}{a^2}\right]^{1/2} \tag{7}\]

In practice, scan\textsubscript{cor} is calculated in terms of \(F^\text{total}_\text{ovlp}\) (eq 8a), the total force within all successive overlapping line traces. \(F^\text{total}_\text{ovlp}\) is formulated from a geometric breakdown of sequential overlapping circular contacts of radii \(a\). Normalizing \(F^\text{total}_\text{ovlp}\) with \((F_z \times \text{res})\) approximates the additional dimensionless scan history per experimental scan imparted to the surface from line scan overlap. The hemispherical symmetry of the pressure distributions \(p(x, y)\) is accounted for by the two terms preceding the summation, and the functions \(\alpha, \beta, \chi\) are given in eqs 9–11 and are also noted in Figure 3.

\[
\text{scan}_{\text{cor}} = 1 + \frac{F^\text{I}_\text{ovlp}}{\text{res} \times F_z} + \frac{F^\text{II}_\text{ovlp}}{\text{res} \times F_z} = 1 + \frac{F^\text{total}_\text{ovlp}}{\text{res} \times F_z} \tag{8a}
\]

\[
\begin{align*}
(x, y) \ dy \ dx - \int_0^a \rho(x, y) \ dy \ dx + \int_0^\alpha \int_0^\beta \left[\frac{\pi a^2}{\pi a^2} \int_0^{\alpha \sin(\theta)} \int_0^{\sqrt{a^2 - y^2}} p(x, y) \ dy \ dx + \int_0^\chi \int_0^{\sqrt{a^2 - y^2}} p(x, y) \ dy \ dx\right] \text{res} \times F_z \tag{8b}
\end{align*}
\]

\[
\begin{align*}
\alpha &= 0 \text{ for } \left(\theta \leq \frac{\pi}{3}\right) \\
\chi &= \text{for } \left(\theta > \frac{\pi}{3}\right) \tag{9}
\end{align*}
\]

\[
\begin{align*}
\beta &= -\sqrt{a^2 - x^2} + 2a \cos(\theta) \tag{10} \\
\chi &= \sqrt{a^2 - (2\alpha \cos(\theta))^2} \tag{11}
\end{align*}
\]

The Hertz half-space and the associated overlap are undefined for negative \(y\) values and therefore necessitate the third integral in eq 8b whose first integration limit is the negative of eq 10. This situation arises when \(\theta > 60^\circ\) or equally when \(\Delta_y > a\). Here, \(\Delta_y\) is the center-to-center distance along the slow scan axis for successive line traces as referenced to the first scan line \((n_0 = 0)\).

\[
\Delta_y = n \times LS = 2a \cos(\theta) \tag{12}
\]

The positive integer increment \(n\) corresponds to the \(n\)th line step from \(n_0\) as shown in Figure 4. Again the steps are along the slow scan axis, which is arbitrarily assigned to the \(y\) axis in Figures 3 and 4. Because scan overlap does not occur for the \(n\)th successive scan, where \(\Delta_y \geq 2a\), the series is then truncated on the line scan prior to the \(n_i (n_i = 2a/LS)\) line trace. For convenience, the summation is redefined in terms of \(m\), which encompasses the integer range \([m_1, m_2]\), because the last overlapping line trace is \(m_i = n_{i-1}\) and the 1 in eqs 8a and 8b accounts for \(n_0\). These relationships defined in eqs 1 and 12 indicate that \(n_i \propto F_z^{1/3}\), which enables scan\textsubscript{cor} to be evaluated a priori for a given material pair. The merit of eq 12 and the value of the \(\theta - a\) relationship it establishes is further exemplified by its ability to simplify scan\textsubscript{cor} calculations. This \(\theta - a\) relationship provides a general geometric-based form of the correction to be established, and it is proposed that this form, established with the tenets of Hertz continuum elasticity, is applicable to “all” tip–substrate material pairs. The general form of this relationship is detailed in the Supporting Information.

According to CRLS analysis, the calculated scan\textsubscript{cor} provides an estimate of the additional scan history applied to the surface by scan overlap. For example, if scan\textsubscript{cor} has been evaluated to be unity, then there is no additional history applied to the surface from scan overlap. However, if scan\textsubscript{cor} is found to be greater than unity, then the surface has experienced additional scan history due to scan overlap. In this situation, scan\textsubscript{cor} can be used to predict the number of nonoverlapping scans (i.e., with a trial area defined by eq 5) required to impart to the surface the identical scan history achieved when scan overlap is present. The product of scan\textsubscript{cor} and the experimental number of scans possessing line scan overlap, \(N^\text{correct}_\text{ovlp}\), yields the corrected number of scans \((N^\text{correct}_\text{ovlp})\) within the nonoverlap limit as defined by eq 13. In this manner, the experimental AFM trial with line scan overlap is the parent upon which the CRLS prediction, \(N^\text{correct}_\text{ovlp}\), and future
nonoverlapping experiments are based. For instance, nonoverlapping trials with $L_{\text{scan}}$ defined by eq 5 can then be conducted at a Hertz mean pressure ($p_m$) equivalent to that of the parent overlapping study. After the evaluation of $\text{scan}_{\text{cor}}$ for the parent trial, the paired nonoverlapping wear experiment is then performed for a number of scans equal to $N_{\text{scans}}$. The extent of surface degradation may then be evaluated for both trials with force of adhesion ($F_{\text{adh}}$) measurements, topography, and frictional force microscopy. Again, within the Hertzian development, the two wear experiments are coupled, and the elastic scan histories in both trials are equivalent. Deviations from CRLS predictions are to be expected because the tenets of continuum elasticity do not include inelastic energy dissipation pathways natural to a wearing contact.

$$\text{scan}_{\text{cor}} \times N_{\text{scans}}^{\text{overlap}} = N_{\text{scans}}^{\text{correct}}$$

(13)

The work presented herein focuses on testing the appropriateness of the CRLS analysis in this context by directly comparing the wear of a test surface (mica) for the overlapping and nonoverlapping cases. Although the rationale behind avoiding the overlap of successive line scans is logical, one may dismiss its utility because single, repeated line traces accomplish this without complication. However, most commonly used AFM tips have parabolic profiles that invariably yield position-dependent stresses relative to the contact center (Figure 2). This latter point is addressable in a several ways: (1) the radial stress variation can be included in models of the tip–surface contact for studies probing the dynamics of tip-mediated defect generation, and (2) one can employ intentionally blunted probes with a flattened, punchlike contact area. One of the principal justifications of the proposed analysis relates to measurement accuracy within the active trial area and the favorable statistics achieved when working over nanoscale areas greater than the contact diameter (i.e., a single line trace). The sensitivity to the typically small population of defects nucleated within the wear trial area has been found to be readily monitored by at least one of the scanning probe observables (e.g., friction, adhesion, or surface topology). Our previous work on mica wear succinctly demonstrated this aspect, where during the early stages of defect nucleation discernible changes in topography and friction were not readily apparent but significant changes in the mean $F_{\text{adh}}$ between the native and defective mica surfaces were observable. The ability to accurately probe adhesive interactions within a large scan area (e.g., $(400 \times 400)$ nm$^2$) proved beneficial. Conversely, generating a statistically relevant $F_{\text{adh}}$ data set from only repeated, single-line trace studies would encompass several experimental challenges considering that the critical dimension (contact diameter) of the test area would have been less than 10 nm.

In conjunction with the experimental guidelines outlined by this method, the calculated excess contact history is then implemented as a correction factor for overlapping wear trial data, which further enables the wear behavior to be predicted for a range of applied loads. Although the analysis presented here accounts only for the elastic component of the tip–surface contact, the estimated systematic errors in recorded scan history are nonetheless representative of the minimum contribution of scan overlap effects. Therefore, these approximations can be immediately applied to correct earlier $F_{\text{adh}}$ versus $N_{\text{scans}}$ studies and present a foundation for continued improvement. The CRLS methodology thereby provides a unique experimental framework for conducting comparative scanning probe nanoscale investigations of defect propagation with and without the influence of line scan overlap. In addition to the investigation of wear phenomena, other scanned probe methods that rely on the controlled, reproducible scanning of surface features, such as in instances where a scanned probe is employed as a scribe for nanolithography, can be improved by the presented methodology and thereby enhance control over nanoscale pattern feature fidelity. The scaling of the mean pressure used in this analysis to the critical stresses for failure (i.e., wear) is dependent upon whether the material is brittle or ductile and requires a complete understanding of the impact of the local stress fields on the wear of the material. As we have previously described, a purely mechanical description of the wear of the mica surface under aqueous environments is not possible. In the presence of water, defects initiate at the edges of the contact where the radial stress induces bond strain, lowering the activation barrier to OH$^-$ insertion, initiating bond scission (defect nucleation).

**Experimental Section**

**CRLS Model Parameters.** A silicon (Si) AFM microcantilever with a tip possessing a radius of curvature ($R$) of 30 nm was used for numerical Scan$_{\text{cor}}$ analysis on a muscovite mica substrate. Scan$_{\text{cor}}$ was evaluated for a range of applied loads with the length of the fast scan axis ($L_{\text{scan}}$) and $r_{\text{ex}}$ fixed at 400 nm and 256 lines per image, respectively. The physical constants $v_i$ and $E_i$ for mica and silicon are 0.1, 56.5 GPa and 0.3, 155 GPa, respectively. Mathcad 8 (MathSoft, Inc.), Graphmatica version 1.6c (kSoft, Inc.), and WSXM 4.0 develop 7.4 (Nanolect Electronica S. L., Spain) were used for numerical calculations (Supporting Information) and graphical analysis.

**AFM Wear Studies.** AFM measurements were acquired at room temperature, 22 ± 3 $^\circ$C, with a Molecular Imaging Pico SPM.


tally, these details have been compared using paired wear tests of overlapping and nonoverlapping conditions. Wear trials were first performed over a \((400 \times 400)\) nm\(^2\) region under a \(p_{\text{m}}\) of 1.4 GPa for five scans. As can be seen in Figure 5b and f the \(F_{\text{t}}\) has decreased, relative to the native mica, in most of the worn region, yet there is little to no change in topography, Figure 5a and d, in the same low-friction areas. We have previously addressed the qualities of the pH-dependent wear of mica and attribute this to localized Si–O/Al–O surface bond rupture yielding negatively charged surface species.\(^{1,2}\) Because the oxidized, hydroxylated Si\(_3\)N\(_4\) tip primarily exhibits a SiO\(_2\) surface at pH 5 \(^{47}\) and the isoelectric point (IEP) of SiO\(_2\) falls between pH 2 and 3, the tip will therefore carry a net negative charge under these aqueous conditions.\(^{18–20}\) We can therefore conclude that the extra repulsive interactions acting between the negatively (−) charged defective surface and the negatively (−) charged tip lead to the observed decline in friction (Figure 5b and f). The broad distribution of \(F_{\text{adh}}\) measurements, Figure 5g, suggests that the worn surface and tip possess several types of defects (e.g., charges and pits). This is also evident in the topography (Figure 5c) and \(F_{\text{t}}\) (Figure 5e) profiles, which indicate the presence of 2.2 Å holes with a correspondingly higher friction. Working under solution conditions gives us the ability to qualify these observations chemically upon the basis of the unique IEP of the individual mica layers. Using Al\(_2\)O\(_3\) IEP (pH ~9) as a reference, it is anticipated that the surface of mica’s aluminate layers should retain a net positive charge under these pH 5 conditions and thereby introduce the additional attractive tip/surface potential. This is consistent with the increased fractional force, relative to the native mica surface, observed for the 2.2 Å deep holes.\(^{1,50}\)

The paired, nonoverlapping \(L_{\text{CRLS}}(400 \times 400)\) nm\(^2\) trial was conducted using CRLS analysis of the preceding experiment with line scan overlap. CRLS calculations indicate that the slow scan length \((L_{\text{CRLS}})\), under an equivalent load, should be 2.2 μm. \(L_{\text{CRLS}}\) was found to be 3.0, instructing us to perform the nonoverlapping wear trial for a total of 15 scans (eq 13). In practice, an \(L_{\text{CRLS}}\) of 2.0 μm was used because the spring constant of the AFM cantilever was calibrated after the trials were complete, and the nominal spring constants were used in the initial, experimentally applied \(L_{\text{CRLS}}\) Calculations. In all cases, the error between theoretical and experimental \(L_{\text{CRLS}}\) was ~10% and is not likely to substantially influence the results.

The topographic and \(F_{\text{t}}\) images, Figure 6a and b, show that surface charging, Figure 6d and f, and abstraction, Figure 6c and e, of materials from the mica surface also occurs for the nonoverlapping experiment.\(^1\) The extent of wear for this CRLS experiment is in near quantitative agreement with the previous \((400 \times 400)\) nm\(^2\) overlapping trial, as indicated by the relative area composed of ~0.22 nm pits (abstraction regime). In terms of a percentage, ca. 21% of the overlapping trial area is occupied by ~0.22 nm pits, whereas ca. 28% of the nonoverlapping CRLS trial area possesses ~0.22 nm pits. The agreement in the extent of surface degradation for the paired trials within the mild wear regime for mica is impressive, especially considering the simplicity of this analysis. There are, however, important distinctions between these two trials that are noteworthy. For instance, closer inspection with FD spectroscopy, comparing Figure 5g and Figure 6g, clearly indicates that the \(F_{\text{adh}}\) distributions within the wear trial area for the two studies are markedly different.

**(Results and Discussion)**

**Paired AFM Wear Studies.** The complete details of the CRLS model are presented in the Supporting Information. Experimentally, Cantilever spring constants were calibrated against levers of the reproducibility of the results. Si\(_3\)N\(_4\) cantilever-tip assemblies were acquired from Veeco (Santa Barbara, CA) and were cleaned prior to use in a 4:1:1 \((v/v/v)\) mixture of 18.2 Ω-cm H\(_2\)O, 30% reagent-grade H\(_2\)O\(_2\) (Fisher), and concentrated NH\(_4\)OH (Fisher) at 80°C. Imaging of a SrTiO\(_3\) (305) single crystal provides an estimate of the tip apex radius of curvature \((R_{\text{tip}})\).\(^{44}\) At least 10 topographic line traces across the SrTiO\(_3\) (100)/(001) steps were fit with a second-order polynomial, which was then used to extract \(R_{\text{tip}}\) by solving for the local asperities circle of curvature \((K_i)\), where \(K_i = [(f_k)/(1 + (f_k)^2)]^{1/2}\) and is the inverse of the (tips) radius of curvature \((K_i = 1/R_{\text{tip}})\). For the two paired sets of experiments used to illustrate the trends in the CRLS method, the radii of curvature \((R_t)\) were determined to be 76 and 68 nm. After each wear trial, \(R_t\) was determined again and consistently showed no change within ±15% of the original values. Cantilever spring constants were calibrated against levers of known spring constants yielding \(k_{\text{tip}}\), \(k_{6\text{nm}}\), \(k_{68\text{nm}}\) = 0.41 N/m.\(^{45}\) The values of \(v_r\) and \(E_{\text{as}}\) for the Si\(_3\)N\(_4\) cantilevers are 0.24 and 220 GPa, respectively.\(^{46}\) The SC2 cleaned tip and freshly cleaved native mica surface serves as an internal reference so that the degree within the native and worn mica regions.

**(References)**


For the nonoverlapping wear trial, a narrow $F_{adh}$ distribution, Figure 6g, with two distinct peaks is evident, whereas a broad distribution is observed in the overlapping case Figure 5g. The discrete peaks in the CRLS trial likely represents the two fundamental defect species generated during mica surface damage; proceeding in a discrete progressive fashion (i.e., from the surface-charging (surface bond rupture) to the molecular abstraction ($\sim$0.22 nm pits) regime$^1$). There is, however, a

Figure 5. AFM analysis of wear trial area with scan overlap. The trial was conducted for five scans over a (400 x 400) nm$^2$ scan area under a $p_{nm}$ of 1.4 GPa. AFM (a) topography, (b) frictional force, $F_t$, and the respective topography profiles (c, d) and friction loops (e–f). (g) Local $F_{adh}$ distributions for the native and wear trial areas. Each distribution consists of at least 110 $F_{adh}$ measurements. According to eqs 5 and 13, $L_{scan}$ and $L_{scan}$ are 2.0 $\mu$m and 3.0, respectively. In practice, the paired trial was conducted with an $L_{scan}$ of 2.0 $\mu$m (Figure 6).
noticeable difference in the maximum $F_{adh}$ measured between these two trials that needs further inquiry because the origin of this difference is presently unclear. In a broader sense, the FD spectroscopy measurements may also be indicating that defect generation is more uniform in the nonoverlapping, $(L_{scan} \times 400)$ nm$^2$, trial region than in the paired overlapping, $(400 \times 400)$ nm$^2$, trial. Although more work is required to substantiate this hypothesis, it is not an unreasonable conjecture, considering that the sequence of defect-generating events for the CRLS-derived trials are geometrically more evenly distributed over the working area.

To test this hypothesis, CRLS analysis was also employed to investigate its predicative capabilities within the gross deformation regime, where elastic energy-dissipating pathways account for
only a small part of the total energy within the contact. Gross wear trials were similarly performed over a (400 x 400) nm$^2$ region under a $p_{nm}$ of 1.5 GPa for 10 scans. This resulted in the removal of the first mica repeat layer, leaving a 10 Å wear scar over ~85% of the scan area, Figure 7a and c. Frictional force imaging, Figure 7b, is unable to detect a difference between the native and worn SiO$_3$ planes, corroborating topography measurements in which a complete repeat layer was excavated. The residual area is defined by a 2.2 Å deep step, resulting from the removal of the outermost Si--O$_3$ surface units. Again, the 2.2 Å deep hole exposes the surface of the aluminate layer, and although much less distinct, an increase in friction is observed (profile not shown). The small $\Delta F_f$ in the aluminate area may be attributed to tip-size effects, variation in the imaging force, or local charge density (impacting Coulombic interactions) as well as a high population of defects present on this layer surface (indicated by the two 10 Å holes in the center of the ~2.2 Å deep step). The controlled generation of 2.2 and 10 Å holes has been previously demonstrated by Kopta et al.$^5$ as well as by Helt et al.$^1$ In the solution studies by Helt et al.,$^1$ the ease of ultimately generating the 10 Å holes far exceeds that of the 2.2 Å, as the apparent threshold pressure for the further breakdown of the aluminate layer, again under pH 5 conditions, appears to be less than the initial threshold pressure for the breakdown of the basal (001) crystal plane. There are inherent difficulties in establishing even a nominal value for the aluminate layers threshold pressure, as the apical SiO$_3$/AlO$_3$ units of the basal plane need to be removed without introducing defects into this layer. The lack of clear friction contrast on the 2.2 Å step, Figure 7b, suggests to us that this alumina layer is likely highly defective even though topographically it appears to be intact.

Again, a paired ($L_{scan} \times 400$) nm$^2$ trial was conducted using CRLS analysis of the preceding (400 x 400) nm$^2$ run. Contact radius--line step calculations within the nonoverlap limit led to a $L_{scan}$ of 2.3 μm and a scan$_{cor}$ of 3.2, indicating that this run would consist of 32 scans. An $L_{scan}$ of 2.11 μm was used for reasons explained earlier. As illustrated in Figure 8a and b, after 32 scans nearly exclusive removal of the basal planes’ apical SiO$_3$/AlO$_3$ molecular fragments resulted, yielding a 2.2 Å deep region. Here, the wear scars’ feature fidelity is impressive and supports our earlier hypothesis that the more uniform load distribution enabled by this analysis invariably increases the resulting wear scar uniformity. Clearly, the 2.2 Å hole has a larger $F_f$ (Figure 8c) and $F_{adh}$ (Figure 8e) relative to the native mica owing to the Coulombic attraction between the net negatively (−) charged tip and net positively (+) charged aluminate surface. A significant departure in the extent of wear, relative to the parent (400 x 400) nm$^2$ trial in Figure 7, is observed in both topographic and $F_f$ imaging. This clearly demonstrates the importance of scan overlap on defect growth, where rapid removal of the aluminate layer occurs as a direct consequence of the additional scan history applied within overlapping sequential line traces. The inability of the CRLS model to accurately predict
this gross wear behavior is a testament to the significance of line scan overlap in the generation and propagation of defects within inelastic contacts. Considering that the presented model is based entirely on elastic continuum mechanics, such deviations are expected and instructive. Here, the role of scan overlap on defect growth is substantial and results in the removal of a complete mica crystalline layer, which is equivalent to progressing to a completely distinct wear regime. This is compelling evidence that such effects can compromise AFM data sets. Our paired AFM wear experiments show that the presented approach can be used to establish a benchmark for probing the details of how defects proliferate, especially because a variety of derivative tests, such as varying $p_{nm}$ with a fixed scan size, may also be pursued.

CRLS analysis can be quite beneficial when conducting experiments to estimate the critical defect density leading to wear. The critical defect density ($\eta_{crit}$) can be extracted from examining the relationship between the load (normal force) and the number of scans required to initiate pit formation. In this model, $N_{scans} \propto \exp(-B_0)$, where $B_0$ is a collected physical constant ($B_0 = l^6 kTB_0 / \mu TR_0^{4/3}$) with $l$, $k$, $T$, and $n_0$ being the Si–O bond length, Boltzmann constant, temperature, and Si–O bond density per unit area, respectively. By not accounting for the actual scan history, an overestimate of the material constant ($B_0$) would most likely occur. This underestimate of the number of scans imparted by scan overlap may partly explain the overestimate of $B_0$ by at least a factor of 13 found in recent work investigating mica wear under vacuum and humid conditions.

In a similar case, our own recent work investigating muscovite mica wear in aqueous solution also did not account for this additional scan history and prevented kinetic analysis of the initiating stages of defect nucleation, which is readily followed as a reconstruction of the native mica lattice from 5.2 to 3 Å periodicity. In this work, the lattice reconstruction is observed to occur progressively within the first 20 experimental scans conducted over a $(7 \times 7)$ nm² area under an applied load of 9 nN (p$_{nm}$ $\approx$ 1.25 GPa). For such small scan areas where the tip–sample contact diameter is on the order of the dimensions of the image, significant overlap of scan lines is inevitable. As such, this convoluted contact history is unavoidable for in situ lattice-resolved AFM studies, which can therefore never be viewed in terms of a single scan worth of history. A considerable amount

Figure 8. AFM analysis of the wear trial area, without scan overlap, that is paired with the trial in Figure 7. The wear trial was conducted using 32 scans over a $(2100 \times 400)$ nm² scan area under a $p_{nm}$ of 1.5 GPa. AFM (a) topographic and (b) frictional force, $F_f$, images and the respective (c) friction loop and (d) topography profile. (e) Local $F_{adh}$ distributions for the native and wear trial areas. Each distribution consists of at least 100 $F_{adh}$ measurements.
of work is still required to assess the accuracy and predictive capabilities of the scan overlap model fully, yet there are several unique aspects that indicate that this approach will assist both fundamental and practical inquires into defect nucleation and growth.

Conclusions

The systematic error attributed to scan overlap can be avoided by the CRLS analysis described herein. Our analysis has also arrived at a general expression that can estimate the actual scan history for previous experiments possessing scan overlap allowing more accurate predictions of wear behavior. A comparison of wear predictions based on the CRLS analysis to experiments is encouraging, particularly within the mild wear regime limit for mica under aqueous solution conditions. Not unexpectedly, this model is incapable of following severe wear trends as the details of the chemical bonds made and broken under these conditions obviate such a simple Hertzian-based analysis. The empirical evidence presented here, however, validates the importance of scan overlap in AFM wear studies and holds promise as a new methodology for probing the earliest stages of defect growth. Although experiments containing line scan overlap can be beneficial for probing defect nucleation, comprehensive wear studies should include both overlapping and nonoverlapping trials because the comparison can provide valuable new insight into defect generation. This general method also affords a clear way of evaluating the influence of scan history on any AFM measurements that require delineation of the exact extent of tip–surface contact such as in dynamics experiments. Scanned probe lithography experiments that also depend on the finite volume swept out by the AFM tip can also benefit from this analysis to improve feature fidelity.

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Supporting Information Available: Derivation of the expressions used in the scan correction (scan_<sub>cor</sub>) calculations described in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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