Morse potential-based model for contacting composite rough surfaces: Application to self-assembled monolayer junctions

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This work formulates a rough surface contact model that accounts for adhesion through a Morse potential and plasticity through the Kogut-Etsion finite element-based approximation. Compared to the commonly used Lennard-Jones (LJ) potential, the Morse potential provides a more accurate and generalized description for modeling covalent materials and surface interactions. An extension of this contact model to describe composite layered surfaces is presented and implemented to study a self-assembled monolayer (SAM) grown on a gold substrate placed in contact with a second gold substrate. Based on a comparison with prior experimental measurements of the thermal conductance of this SAM junction [Majumdar et al., Nano Lett. 15, 2985–2991 (2015)], the more general Morse potential-based contact model provides a better prediction of the percentage contact area than an equivalent LJ potential-based model. © 2016 AIP Publishing LLC.

I. INTRODUCTION

The ability to accurately model the interaction of two bodies in contact is of great importance in the field of tribology, which is the study of interacting surfaces and their associated friction, lubrication, and/or wear behavior. In actuality, even surfaces that appear very smooth are relatively rough, since they are microscopically comprised of protuberances called asperities. Consequently, surfaces that appear to be in significant contact are actually in contact over an area known as the real area of contact. Situations where partial contact of surfaces occurs include micro/nano-scale systems, relatively hard surfaces where interfacial asperities undergo minimal deformation, and mixed lubrication, where the asperities partially support the loads at liquid-mediated interfaces. In all of these cases, the real area of contact must be resolved, usually as a function of the contact load, mechanical properties, surface topography, and adhesive and repulsive surface forces.

The seminal work on the contact of real surfaces is the Greenwood-Williamson (GW) model. It was developed to model the contact mechanics between two real surfaces by treating asperities as individual Hertzian hemispherical contacts of equal radii and varying heights. The GW model can be used to predict the elastic contact stresses on the asperities from the two contacting bodies. While this model continues to be the foundation of most statistical rough surface models, it makes two key assumptions of neglecting both plasticity and adhesion, which can cause errors while evaluating contact of smooth surfaces under large loads.

Asperities on real surfaces usually enter the plastic regime even when light loads are applied. Adhesion, which generally plays a smaller role in conventional macro-scale applications, becomes a stronger contributor to the resulting contact stress and surface deformation the smoother the surfaces are. While some surface contact models have added plasticity or adhesion separately to the GW modeling framework, Chang, Etsion, and Bogy (CEB) developed a series of models to introduce both adhesion and the full spectrum of surface deformation regimes—elastic, elastic-plastic, and purely plastic. They introduced plasticity effects through the concept of a critical interference, which is the inter-penetration length (or maximum deformation) of an asperity into a surface at which plasticity first begins. Volume conservation and a uniform applied pressure were then assumed at each of the asperities in order to account for plasticity. They incorporated adhesion with the elastic-plastic deformation using their deformed asperity profiles in conjunction with the Derjaguin-Muller-Toporov (DMT) model.

The two primary models for adhesion are the Johnson-Kendall-Roberts (JKR) model and the DMT model. The JKR model allows the adhesive force to affect the surface profile (i.e., shape) of a hemispherical contact, and the forces outside of the contact area are neglected. The DMT model, on the other hand, does not allow the adhesive force to affect the profile of a hemispherical contact. Its profile follows a Hertzian profile instead and all adhesive forces, even those outside the contact area, are included. Tabor first postulated that these two models were limiting cases of the same

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general adhesive theory. In other words, the DMT model is well-suited for hard materials with a small asperity radius such as metals, while the JKR model is better suited for soft materials with a large asperity radius. The adhesive force depends on the chosen surface interaction potential employed in the adhesive model, the most common being the Lennard Jones (LJ) potential. Muller et al. developed a complete model accounting for Tabor’s findings using the LJ potential. The Maugis-Dugdale model was the first to develop a closed form solution for the JKR-DMT transition. A comprehensive chart for determining which adhesion model to use for elastic contact was presented by Johnson and Greenwood.

The CEB models, due to their generality and simplicity, have been widely adopted and extended by other authors. The assumptions used, however, do not capture the correct asperity behavior in the elastic-plastic regime. Kogut and Etsion (KE) presented a thorough comparison of the CEB models to finite element analysis (FEA) of an asperity under deformation and found significant deviation. They went on to present a new set of models to capture rough surface contact in the elastic-plastic regime, also including the effects of adhesion. Their adhesion model incorporated the DMT model in conjunction with the LJ potential. While the LJ potential is most often used as a first approximation for a given material system due to its simplicity, for many materials it can lead to poor predictions of physical properties.

The Morse potential is more general than the LJ potential as it has three free parameters as compared to two free parameters in the LJ potential. It is suitable for many systems, including molecules and metals. It has been essential for representing complex material interactions, such as adhesion of thin films on metal substrates [e.g., self-assembled monolayers (SAMs) on gold], and has been parameterized for both covalent and van der Waals interactions. Herein, we develop an adhesion-based contact model for interfaces by incorporating the Morse potential into the KE (and as a consequence the DMT) modeling framework. The resulting contact model can be employed for a wide variety of surface materials, from hard-soft interfaces to organic-inorganic heterojunctions.

We first derive expressions for the adhesive pressure and interaction energy per unit area between two macroscopic bodies where atomic interactions are described using the Morse potential in Secs. II A–II C. We then incorporate these expressions into the KE model and calculate the total adhesive pressure between the rough bodies in Sec. II D. In Sec. II E, we present a method to calculate adhesive pressures where one or both bodies in contact are composed of layers of different materials. In Sec. II F, we describe the analytical model used to characterize the roughness parameters of a body. Lastly, we predict the percentage contact area (i.e., the ratio of the real area of contact to total surface area which appears to be in contact) between two rough gold surfaces where one is coated with a SAM in Sec. III. These predictions are validated using interface thermal conductance measurements performed by the authors.

II. THEORY

A. Derivation of surface pressure using the Morse potential

The Morse (subscript M) potential between two point particles (atoms), separated by a distance \( r \), is

\[
E_{M,pp} = D_e \left[ e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)} \right],
\]

where \( \alpha \) is the depth of the potential well, \( \alpha \) describes the inverse of the width of the well, and \( r_0 \) is the position of the minimum of the well. The \( 2D_e e^{-\alpha(r-r_0)} \) term represents London dispersion (i.e., van der Waals) interactions, which are attractive, and the \( D_e e^{-2\alpha(r-r_0)} \) term represents exchange repulsion. Repulsive energy is defined as positive and attractive energy as negative. The difference in behavior between the Morse potential and the LJ potential, given by

\[
E_{LJ,pp} = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^{6}],
\]

where \( \epsilon \) is the depth of the well and \( \sigma \) is interatomic distance at which \( E_{LJ,pp} = 0 \), is shown in Fig. 1(a). The parameters used in plotting the Morse potential describe the interaction between a thiol group (-SH group) and a gold atom. The LJ potential is constructed to have the same position and depth of the well as the Morse potential, but ultimately exhibits a different energy landscape at other positions due to its mathematical formulation. All parameters for the potentials used in Fig. 1(a) are listed in Table I.

![FIG. 1. (a) Comparison of Morse and LJ potentials for the same energy well depth and equilibrium separation for a thiol-gold interaction. (b) Schematic diagrams representing interactions between two point particles, one point particle and a flat, semi-infinite substrate, and two flat, semi-infinite substrates.](image-url)
To study the asperities that describe rough surfaces, this point-point potential must be extended to describe interactions between macroscopic bodies. Let us first consider the attractive part of the pair potential given by Eq. (2), \( E_{at} = -2D_e e^{-r/r_0} \). We assume additivity of these interactions, such that the net interaction between a single atom and a monatomic substrate is the sum of its interactions with all the atoms in the substrate.\(^{43}\) If we consider a substrate (semi-infinite solid) with a flat surface having a volumetric density of atoms \( \rho_1 \) at a distance \( D \) from an atom (the point particle), the attractive interaction energy will be

\[
E_{at}^{ps}(D) = -4\pi \rho_1 D_e \frac{D^2}{2} (2D + 2) e^{-r/r_0},
\]

where the subscript “ps” denotes a particle-substrate interaction. A schematic diagram of this geometry is shown in Fig. 1(b). Following a similar procedure, the attractive interaction energy per unit area between two substrates, whose surfaces are separated by a distance \( D \), is

\[
E_{at}^{ss}(D) = -4\pi \rho_1 \rho_2 D_e \frac{D^2}{2} (2D + 3) e^{-r/r_0}.
\]

Here, \( \rho_2 \) is the volumetric density of atoms in the second substrate. If the second structure is instead a single layer of atoms (i.e., a surface, such as in a two-dimensional material) with an areal atomic density \( \sigma_2 \), the attractive interaction energy per unit area is

\[
E_{at}^{sa}(D) = -\frac{4\pi \rho_1 \sigma_2 D_e}{2} (2D + 2) e^{-r/r_0},
\]

where the subscript “sa” denotes substrate-atoms. Derivations of Eqs. (2)–(4) are provided in Sec. S1 of the supplementary material.\(^{44}\) The corresponding attractive forces per unit area are

\[
P_{at}^{sa}(D) = -\frac{dE_{at}^{sa}(D)}{dD} = \frac{4\pi \rho_1 \sigma_2 D_e}{2} (2D + 2) e^{-r/r_0},
\]

where \( P_{at}^{sa} \) and \( P_{at}^{ss} \) are the attractive pressures.

Until now, we have only considered the attractive interaction. To realize a potential with an equilibrium separation, we need to add the repulsive interaction. Following the procedure of Eqs. (2)–(6), we obtain the general form of the repulsive interaction for either the substrate-substrate or surface-substrate configurations to be

\[
P_{rep}^{ss}(D) = \frac{4\pi \rho_1 \sigma_2 D_e}{2} (2D + 3) e^{-r/r_0},
\]

where \( P_{rep} \) is the repulsive pressure.

The physical constraint of \( P_M(D \to \infty) = 0 \) is naturally satisfied by the form of the Morse potential. There are no more physical constraints that can be imposed to specify the coefficient \( A_2 \).

We generalize the expression for \( P_M \) by grouping parameters into the coefficients \( B_1 \), \( B_2 \), and \( B_3 \) (defined in Table II), leading to

\[
P_M(D) = B_1 P_M \times \left[ B_2 P_M e^{2D/r_0} e^{-2D/r_0} - B_3 P_M e^{-2D/r_0} \right],
\]

where the corresponding interaction energy per unit area is
TABLE II. Coefficients in the expressions for pressure [Eq. (9)], energy per unit area [Eq. (10)], and work of adhesion [Eq. (11)] derived for the interaction between two substrates (ss) and a surface with a substrate (surf-ss) described by a Morse potential.

<table>
<thead>
<tr>
<th>$P_M(D)$</th>
<th>$P_{M,ss}$</th>
<th>$P_{M,surf-ss}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_1$</td>
<td>$B_2$</td>
<td>$B_3$</td>
</tr>
<tr>
<td>$\frac{\sigma^2}{z}$</td>
<td>$\frac{(2D + A_{ss})(2D + 2A_{ss})}{(2D + A_{surf-ss})(2D + 2A_{surf-ss})}$</td>
<td>$\frac{2D + 2}{2D + 2A_{surf-ss}}$</td>
</tr>
</tbody>
</table>

We note that evaluation of Eqs. (9) (A1)–(A4). For hemispherical asperities, a common form for expressing the energy and pressure equations is through the work of adhesion $\Delta \gamma$, which represents the magnitude of $E_M^\prime$ at its minimum value (i.e., at $D = r_e$) and is

$$\Delta \gamma_M = [E_M^\prime (D = r_e)] = \left( \frac{4 \pi D_0}{x^3} \right) B_1, A_{surf} e^{-z(r_e - r_0)} (B_2, A_{surf} - B_3, N_{NN}).$$

We note that evaluation of Eqs. (9) (A1)–(A4). We evaluate $r_e$ and $A_2$ using single-point energy calculations. We first place a single layer of atoms above a substrate of another kind of atom. A schematic diagram of this structure is shown in Fig. 2(a). The substrate is an fcc solid having a (111) surface with a lattice constant of 4.08 Å (i.e., that of gold). The surface is a close-packed structure having a nearest neighbor distance of 4.997 Å (i.e., that of a thiol-based SAM). Our calculations correspond to the case where the atoms of the single-layer surface are directly above the three-fold hollow sites of the surface of the substrate. Only the interaction potential (Morse or LJ) between the layer and the substrate is considered while calculating the energy of the system at different separations (details provided in Sec. S2).

The variation of the interaction energy between the surface and the substrate (non-dimensionalized by $\Delta \gamma_{ss}$) as a function of the separation distance between them is plotted in Fig. 2(b) for both Morse (blue circles) and LJ (red squares) potentials, corresponding to a thiol-gold interaction whose parameters are listed in Table I. The magnitude of the interaction energy at its minimum value is $\Delta \gamma$, and the corresponding separation distance is $r_e$. We can thus find the ratio $\Delta \gamma_M/\Delta \gamma_{ss}$ from this calculation, as shown in Fig. 2(b). We take this approach because exact analytical expressions for $\Delta \gamma$ exist for an LJ potential and are

$$\Delta \gamma_{ss} = \frac{\pi \rho_1 \rho_2 (4D_e \sigma_0^4)}{16 \sqrt{\pi}} \frac{1}{9 \sigma_0^2}.$$

Once $\Delta \gamma_M$ is calculated using the results of the single-point energy calculations and Eq. (12), we can analytically determine $A_2$ from Eq. (11). We note, however, that these calculations are specific to our system, with $A_2$ equal to $-4.9138$ and $\Delta \gamma_M$ equal to 0.66 J/m$^2$. To allow the implementation of this model to other surface-substrate systems, we provide generalized expressions describing the variation of $r_s/r_{NN}$ and $\Delta \gamma_M/\Delta \gamma_{ss}$ as a function of the parameters $r_s/r_{NN}$ and $r_0/r_{NN}$ (where $r_{NN}$ is the nearest neighbor distance between atoms in the substrate) in Appendix A [Eqs. (A1)–(A4)].

The expressions for adhesive pressure and energy per unit area based on the Morse potential, represented by Eqs. (9)–(11), can now be used with the DMT and KE models to estimate the total adhesive force for hemispherical asperities contacting a flat substrate.

B. Single asperity deformation

The DMT model provides a method to calculate the adhesive force for a deformed hemisphere contacting a flat, undeformable surface. The method to calculate the deformed hemispherical profile is summarized in this section. The hemisphere is assumed to obey Hertzian theory and to deform elastically. The height $Z$ of any point on the surface of the hemisphere at a radial distance $x$ from the asperity center, following the DMT convention, is

$$Z(a, x, R) = \frac{1}{\pi R} \left[ a(x^2 - a^2)^{1/2} - (2a^2 - x^2) \tan^{-1} \left( \frac{\sqrt{x^2 - a^2}}{a} \right) \right],$$

where $R$ is the radius of the hemisphere, and $a$ is the radius of the contact region. A schematic diagram of this setup is shown in Fig. 3(a).

The expression for $Z$ can also be written in terms of the interference $\omega$, which is the centerline deflection of the asperity, i.e., the maximum deformation of the compressed asperity. It can be seen that $Z = 0$ when $x = a$. Eq. (13) was, however, developed for macro-scale deformations. When molecular potentials are taken into account, it is physically impossible for two atoms, or in this case two bodies, to have a separation distance of zero. Thus, Eq. (13) is adjusted such that the minimum value of $Z$ equals the equilibrium separation between the surfaces $r_e$ (derived in Sec. II A) and is further simplified by substituting the Hertzian relation for the contact radius

$$a = (\omega R)^{1/2},$$

thus arriving at
use the FEA derived dimensionless separations found by Kogut and Etsion\textsuperscript{25,26}.

\[
\frac{Z(\omega, \bar{x})}{\omega_c} = \frac{0.951}{\pi} \left( \frac{\omega}{\omega_c} \right)^{1.153} f(\bar{x}) + \frac{r_e}{\omega_c} \quad \text{for} \quad 1 \leq \omega/\omega_c \leq 6,
\]

and

\[
\frac{Z(\omega, \bar{x})}{\omega_c} = \frac{0.457}{\pi} \left( \frac{\omega}{\omega_c} \right)^{1.578} f(\bar{x}) + \frac{r_e}{\omega_c} \quad \text{for} \quad 6 \leq \omega/\omega_c \leq 110.
\]

Kogut and Etsion validated Eqs. (17) and (18) for a range of values of the plasticity index $\psi$, which Greenwood and Williamson showed to be directly related to the critical interference as $\psi \propto \omega_c^{-0.5}$\textsuperscript{6}. We specifically note that the interference $\omega$ of the contacting asperities must fall within the range of 0 to 110 $\omega_c$ in order for the FEA data used to be accurate. The various deformation regimes used in this study are listed in Table III.

C. Morse potential-based adhesion model based on asperity deformation

We now derive expressions for the adhesive pressure between a single hemispherical asperity and a substrate interacting through a Morse potential. The asperity may be a solid structure (having a volumetric density of atoms $\rho_1$) or hollow and composed of a single layer of atoms on its surface (having an areal density of atoms $\sigma_2$). Derjaguin et al. found the adhesive force between atoms in a slice along the surface of the hemisphere (i.e., a ring with radius $x$ and thickness $dx$) and the flat surface to be\textsuperscript{16}

\[
dF_c^{ad} = 2\pi x P_M(Z) dx.
\]

It is important to note that the pressure $P_M(Z)$ contains the effect of all the atoms behind the exposed surface (if any). Thus, if we integrate Eq. (19) for all $x$, we get the total adhesive force between a deformed hemispherical asperity and a substrate to be

\[
F_c^{ad} = 2\pi \int_a^\infty x P_M(Z) dx.
\]

Strictly speaking, the upper limit of the integral should be the hemispherical radius $R$, but it can be approximated as infinity without significant error if $P_{M,ss}(Z) \to 0$ at separations much smaller than $R$, as is the case here.\textsuperscript{16}  Now, from Eq. (20), we define $F_c^{ad}(a = 0) = F_0^{ad} = 2\pi R A_Y$ as the point contact adhesive force. We use $F_0^{ad}$ to normalize the total contact adhesive force in the same manner as Kogut and Etsion by changing the integrating variable to $\bar{x} = x/a$ and then dividing throughout by $F_0^{ad}$.\textsuperscript{26}  The variables $\omega_c$, $a$, $r_0$, and $r_e$ are also non-dimensionalized using $\omega_c$. The normalized force of adhesion for an asperity in contact (in any deformation regime), with respect to the point contact adhesive

\[
F_c^{ad} = 2\pi \int_a^\infty x P_M(Z) dx.
\]
force, is found from Eq. (20) using the expression for \( P_M \) from Eq. (9). A general form of this expression is

\[
\frac{F^\text{ad} (\alpha)}{F_0^\text{ad}} = G_1 P_M \int_0^\infty \left[ G_2^\text{ad} e^{2(r \cos \alpha - r_e)} e^{-2(z_0/r_e)} \left( \frac{d}{C_0} \right)^2 \right] \cdot d \bar{r} \frac{d \bar{z}}{d \bar{r}}
\]

(21)

where the coefficients \( G_1 \), \( G_2 \), and \( G_3 \) for the substrate-substrate and surface-substrate cases are listed in Table IV. For any deformation regime, the corresponding separation \( Z \) [Eqs. (16)–(18)] can be used in Eq. (21).

In the case of a hemispherical asperity not in contact with the surface, the adhesive force from the DMT model is

\[
F^\text{ad} \bigg| _{\text{nc}} = 2\pi R \int_{D_a} P_M(h)dh,
\]

(22)

where \( h \) is the separation between a slice of thickness \( dh \) within the asperity and the flat surface, and \( D_a \) is the minimum separation between the asperity and flat surface, as shown in Fig. 3(b). Using the expression for \( P_M \) from Eq. (9) and normalizing with \( F_0^\text{ad} \), we derive the non-contact adhesive force to be

\[
\frac{F^\text{ad} \bigg| _{\text{nc}} (D_a)}{F_0^\text{ad}} = G_1 P_M \left[ G_2^\text{ad} e^{2(r \cos \alpha - r_e)} e^{-2(z_0/r_e)} \left( \frac{d}{C_0} \right)^2 \right] - G_3 P_M \left[ e^{-2(z_0/r_e)} \left( \frac{d}{C_0} \right)^2 \right],
\]

(23)

where the coefficients \( G_1 \), \( G_2 \), and \( G_3 \) for the substrate-substrate and surface-substrate cases are listed in Table IV.

### D. Extension to two-body contact problem

Until now, we have derived expressions for the adhesive interaction of a single asperity with a substrate. To model the interaction between two real bodies, we analyze the interaction of a number of asperities (representing the rough surface of one body) with a substrate. The two-body contact problem can be visualized as shown in Fig. 4. A balance between any externally applied force, the adhesive force, and the contact force must exist for the bodies to be in equilibrium. In this section, we present the equations necessary to calculate each of these forces and the percentage contact area for the two-body system. In order to simplify the problem, the two bodies with rough surfaces are transformed into an equivalent system of one rough body (Body I) in contact with a smooth, rigid body (Body II). The geometrical properties of Body I are equal to the sum of the geometrical properties of the original two rough bodies. The elastic modulus of Body I

### TABLE IV. Range of contact regimes.

<table>
<thead>
<tr>
<th>Regime</th>
<th>Dimensionless separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-contact</td>
<td>( \alpha_0/\alpha_e \leq 0 )</td>
</tr>
<tr>
<td>Elastic</td>
<td>( 0 \leq \alpha_0/\alpha_e \leq 1 )</td>
</tr>
<tr>
<td>Elastic-plastic I</td>
<td>( 1 \leq \alpha_0/\alpha_e \leq 6 )</td>
</tr>
<tr>
<td>Elastic-plastic II</td>
<td>( 6 \leq \alpha_0/\alpha_e \leq 110 )</td>
</tr>
<tr>
<td>Plastic</td>
<td>( \alpha_0/\alpha_e \geq 110 )</td>
</tr>
</tbody>
</table>

### TABLE III. Coefficients in the expressions for contact [Eq. (9)] and non-contact [Eq. (23)] adhesive pressures derived for the interaction between two substrates (ss) and a surface with a substrate (surf-s) described by a Morse potential. The coefficients \( B_2 \) and \( B_3 \) are listed in Table II.

<table>
<thead>
<tr>
<th>( \frac{F^\text{ad} (\alpha)}{F_0^\text{ad}} )</th>
<th>( \frac{F^\text{ad} (\alpha)}{F_0^\text{ad}} )</th>
<th>( \frac{F^\text{ad} (\rho)}{F_0^\text{ad}} )</th>
<th>( \frac{F^\text{ad} (\rho)}{F_0^\text{ad}} )</th>
<th>( \frac{F^\text{ad} (\rho)}{F_0^\text{ad}} )</th>
<th>( \frac{F^\text{ad} (\rho)}{F_0^\text{ad}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (z_0) e^{2(r \cos \alpha - r_e)} )</td>
<td>( B_2 \lambda_M ) – ( B_3 \lambda_M )</td>
<td>( (z_0) e^{2(r \cos \alpha - r_e)} )</td>
<td>( B_2 \lambda_{M,ss} ) – ( B_3 \lambda_{M,ss} )</td>
<td>( (z_0) e^{2(r \cos \alpha - r_e)} )</td>
<td>( B_2 \lambda_{M,ss} ) – ( B_3 \lambda_{M,ss} )</td>
</tr>
<tr>
<td>( \frac{(z_0) e^{2(r \cos \alpha - r_e)}}{B_2 \lambda_{M,ss} - B_3 \lambda_{M,ss}} )</td>
<td>( (z_0) e^{2(r \cos \alpha - r_e)} )</td>
<td>( \frac{(z_0) e^{2(r \cos \alpha - r_e)}}{B_2 \lambda_{M,ss} - B_3 \lambda_{M,ss}} )</td>
<td>( (z_0) e^{2(r \cos \alpha - r_e)} )</td>
<td>( \frac{(z_0) e^{2(r \cos \alpha - r_e)}}{B_2 \lambda_{M,ss} - B_3 \lambda_{M,ss}} )</td>
<td>( (z_0) e^{2(r \cos \alpha - r_e)} )</td>
</tr>
<tr>
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<td>( (z_0) e^{2(r \cos \alpha - r_e)} )</td>
<td>( \frac{(z_0) e^{2(r \cos \alpha - r_e)}}{B_2 \lambda_{M,ss} - B_3 \lambda_{M,ss}} )</td>
<td>( (z_0) e^{2(r \cos \alpha - r_e)} )</td>
<td>( \frac{(z_0) e^{2(r \cos \alpha - r_e)}}{B_2 \lambda_{M,ss} - B_3 \lambda_{M,ss}} )</td>
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<td>( \frac{(z_0) e^{2(r \cos \alpha - r_e)}}{B_2 \lambda_{M,ss} - B_3 \lambda_{M,ss}} )</td>
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<td>( (z_0) e^{2(r \cos \alpha - r_e)} )</td>
<td>( \frac{(z_0) e^{2(r \cos \alpha - r_e)}}{B_2 \lambda_{M,ss} - B_3 \lambda_{M,ss}} )</td>
<td>( (z_0) e^{2(r \cos \alpha - r_e)} )</td>
</tr>
</tbody>
</table>

### FIG. 3. (a) Schematic diagram of a hemispherical asperity in contact with a flat surface and undergoing deformation. The flat surface is assumed to be rigid. (b) Schematic diagram of a hemispherical asperity at a height \( D_a \) above a flat surface.
is calculated using Eq. (B3). The surface of Body I is represented in a statistical manner as a distribution of hemispherical asperities of uniform radii $R$ with heights varying based on a specified probability distribution $\phi(z)$. The total non-dimensional adhesive force $F_{\text{ad}}$ between the asperities and the surface is calculated as the sum of all the adhesive forces (i.e., contact and non-contact) weighted by the distribution of asperity heights for all of the deformation regimes. Thus, using Eqs. (21) and (23), we arrive at

$$
F_{\text{ad}} = \frac{F_{\text{ad}}}{A_h H} = \frac{2\eta R A_g}{H} \left( \int_{-\infty}^{d^*} - \int_{d^*}^{d^* + 110a}\right. 
+ \int_{d^*}^{d^* + 110a} \frac{F_{\text{ad}}(z^*)}{F_{\text{ad}}(z^*)} \phi^*(z^*)dz^*ight),
$$

where $\eta$ is the areal density of asperities. Here, any variable with the superscript $*$, except for $F_{\text{ad}}$, is dimensionless and is normalized using the standard deviation of surface heights, $\sigma_h$, $F_{\text{ad}}$ is normalized by the nominal contact area $A_h$ and the hardness $H$. $d^*$ represents the non-dimensional separation between the flat surface and the mean-line of asperity heights. The distribution $\phi$ has each of its variables normalized by $\sigma_h$. For a normal distribution of asperity heights, 25

$$
\phi^*(z^*) = \frac{\sigma_h}{\sqrt{2\pi\sigma_s}} e^{-\left(\frac{\eta_1 s^*}{\sigma_s}\right)^2}.
$$

Alternatively, a deterministic approach could be used to calculate the contact area and the mean separation between our two surfaces. In addition to the complexity of numerically solving the elastic and plastic constitutive equations for deformation, such an approach would require an iterative optimization method in order to calculate the balance between the adhesive and contact stresses. While such a deterministic approach may shed additional insight, we believe that a statistical model better represents our system due to its isotropic nature and Angstrom-scale RMS roughness of the surface (Table I). The measurements of Majumdar et al. were also statistically averaged representations of the thermal conductance values. The potential difference between statistical and deterministic models is thus left for future study.

E. Composite asperity model for modeling layered structures

We now extend our formulation to model adhesion between two surfaces where one of them has a thin film grown on it. The thin film is treated as an incompressible coating that follows the deformation behavior of the underlying substrate, such as in the case of an organic SAM grown on a metal or dielectric substrate. Modeling the surface topography of such a system requires the asperities to be composed of multiple materials in a layered configuration, thus creating a composite asperity. Assuming substrate effects dominate, all materials of the composite asperity are assumed to have the same elastic modulus, Poisson ratio, and hardness, while having independent Morse (or LJ) parameters, layer thicknesses, and distances from the flat surface.

The contribution of each layer in the composite asperity to the adhesive pressure is incorporated by adjusting its distance from the flat surface. For example, considering only elastic deformations, each slice within the asperity will now have a height $Z$ from the surface [derived from Eq. (16)] given by

$$
\frac{Z(\omega_1)}{\omega_c} = \frac{1}{\omega_1} f(r) + \frac{t}{\omega_c} \omega_1 \text{ for } 0 \leq \omega_1 \leq 1,
$$

where $t$ is the minimum separation of a hemisphere composed of one kind of atoms within the composite asperity and the surface of the asperity. Similar adjustments are made for the elastic-plastic deformation regimes [Eqs. (C1) and (C2)]. The remaining calculations are the same as given by Eqs. (19)–(25). The contribution of each material layer to the adhesive pressure is modeled by subtracting the adhesive pressure of a smaller hemisphere from the adhesive pressure of the larger hemisphere, thus creating the hemispherical layer.

F. Characterization of an experimental surface

A rough surface can be geometrically modeled as being composed of multiple hemispherical asperities arranged with an areal density $\eta$. The asperities have a mean radius $R$ with a standard deviation of asperity heights $\sigma_s$, which is mathematically correlated to the standard deviation of surface heights $\sigma_h$. How these quantities can be obtained from atomic force microscopy (AFM) measurements has been studied in detail by Bush et al., 56 Gibson, 57 and McCool. 58 The quantities $\eta$, $R$, and $\sigma_s$ were originally derived by Nayak, 55 who built upon the work of Longuet-Higgins. 60 Nayak found that for random and isotropic surfaces having a Gaussian distribution of surface heights, a surface could be completely characterized by its spectral moments corresponding to height, slope, and curvature. Kotwal and Bhushan 61 studied non-Gaussian surfaces with kurtosis and
skew but such an analysis is extremely complex and beyond the scope of this study. More recent work has focused on the fractal-like behavior of surfaces and addressed variations with AFM scan parameters.\textsuperscript{30,62,63}

As opposed to surfaces explored in multi-scale studies,\textsuperscript{64} the sputtered thin-film surface discussed in Sec. III does not exhibit any trend in the roughness parameters between different AFM scans (see Sec. S3). Instead, random variations in \( \sigma_h, R \), and \( \eta \) are found between scans. Poon and Bhushan\textsuperscript{65} also found that AFM surfaces do not follow a trend in roughness properties with scan size. We speculate that the dominant cause of our variations is related to the surface manufacturing process. Furthermore, given the Angstrom-scale roughness of our surfaces, we do not believe that it is meaningful to consider them from a fractal perspective. We thus follow McCool’s approach to characterize the surface topography.\textsuperscript{58} From metrology data (i.e., AFM images) of a given surface, the parameters \( \eta, R, \sigma_h \), and \( \sigma_s \) can be calculated from

\[
\eta = \frac{(d\xi/dz)^2}{6\pi/3},
\]

\[
R = \frac{3\sqrt{R}}{8((d^2\xi/dz)^2)^{1/2}},
\]

\[
\sigma_h = \langle \xi^2 \rangle^{1/2},
\]

and

\[
\sigma_s = \sigma_h \left( 1 - \frac{0.0003717}{(\eta R \sigma_s)^2} \right)^{1/2},
\]

where \( \xi \) is the measured height (above the mean-line), and the operator \( \langle \rangle \) denotes a spatial arithmetic average. The derivatives are calculated along a set of straight lines parallel to the horizontal axis of an AFM scan. The derivatives are numerically calculated using central difference schemes (providing second-order error with respect to grid spacing). The derivatives are only calculated for the interior points, i.e., the edge points are not considered.

### III. RESULTS

#### A. Comparison of Morse and LJ adhesive pressures

We now use the example of a thiol-gold interaction to highlight the difference in adhesive behavior predicted by a Morse potential and an equivalent LJ potential [Fig. 1(a)]. The non-dimensional adhesive (\( F_{\text{ad}} = F_{\text{ad}} / \lambda_c H \)) force between a flat gold substrate and a rough thiol surface (i.e., a single layer of thiol groups) is plotted in Fig. 5(a) as a function of \( d^* \) using Eq. (24) (Morse potential-based, solid blue line) and using the KE model\textsuperscript{25} (LJ potential-based, solid red line) with appropriate values of \( \Delta V \) (calculated separately for the Morse and LJ cases), \( r_0 \), and \( \sigma \). Details of the formulation involving surface-substrate adhesion based on the LJ potential are described in Appendix D and were derived as an extension to the KE model. The roughness parameters \( \eta, R, \sigma_h \), and \( \sigma_s \) are obtained from AFM measurements of a gold surface, as outlined in Sec. II F, and are listed in Table I for one particular AFM measurement from a set of separate measurements (details in Sec. S3). It must be noted that the roughness parameters listed in Table I are for the new, effective rough surface for which the AFM measurements of the surface heights were doubled before using Eqs. (27)–(30). Expressions for the total non-dimensional contact pressure \( P_{cs}^* \) and the percentage contact area \( A^* \) between deforming asperities and the substrate are provided in Appendix E [Eqs. (E1) and (E2)]. The contact reaction pressure using Eq. (E1) is also plotted in Fig. 5(a) (dashed line).

The equilibrium separation between the bodies under contact is achieved when \( P_{\text{ad}} = F_{\text{ad}} / \lambda_c = P_{cs}^* \) (i.e., a balance between the adhesive and contact pressures). This separation is found by identifying the point of intersection between the adhesive and contact pressure curves, as shown in Fig. 5(a). If an external load is applied to the top surface, then it is added to \( P_{\text{ad}}^* \). This equilibrium separation is then used to find the percentage contact area \( A^* \), whose behavior as a function of \( d^* \) [using Eq. (E2)] is shown in the inset of Fig. 5(a). The Morse potential-based adhesion model predicts 1.74 times the percentage contact area than the LJ based model, wherein emphasizing the importance of the specialized framework based on the Morse potential.

#### B. Application to thin films: Self-assembled monolayer on gold

Thin films of SAMs provide a convenient and simple system to tailor interfacial properties of surfaces.\textsuperscript{46} They have gained widespread use in nanoscience with applications in surface functionalization,\textsuperscript{66–67} electrochemistry,\textsuperscript{68–69} electronics,\textsuperscript{70–71} and thermoelectrics.\textsuperscript{72–74} A thiol-based SAM on a gold substrate is the most widely studied configuration with detailed studies performed on its preparation,\textsuperscript{46} structure,\textsuperscript{75–76} and transport properties.\textsuperscript{39,77–79}

Many experiments for probing the transport properties of SAMs require the formation of a SAM junction.\textsuperscript{80} Here, a SAM grown on one substrate has another substrate (usually a metal) brought in contact with it either through high-energy deposition techniques such as sputtering or evaporation\textsuperscript{82} or through transfer printing.\textsuperscript{83} The latter technique is widely used, as it does not damage the underlying SAM layer during the formation of the junction.\textsuperscript{83–85} This technique has recently been used to create SAM junctions comprised of metal-dielectric\textsuperscript{77,78} and metal-metal substrates\textsuperscript{39} to study the junction thermal conductance. Experimental measurements of the junction thermal conductance,\textsuperscript{39,78} however, do not agree with predictions from molecular dynamics simulations.\textsuperscript{39,86,87} We hypothesize that a major source of this discrepancy is incomplete contact between the two surfaces—one being the SAM grown on a metal/dielectric and the other being the bare transfer-printed metal.

Using our Morse potential-based contact model in conjunction with the composite asperity model, we can predict the percentage contact area between two rough metal substrates where one has a SAM grown on its surface. We choose a system composed of a 1,10-decanedithiol SAM grown on a gold substrate brought in contact with another gold substrate, which
is identical to the system recently studied by Majumdar et al.\textsuperscript{39} The asperities are composed of three materials—thiol (denoted by S), carbon (denoted by C), and gold (denoted by Au; we also neglect the contribution of hydrogen atoms) as shown in Fig. 5(b). The planar substrate is gold. The thiol layers are single-atom thick and are treated as surfaces. The thickness of the carbon layer is assumed to be 12 Å, given that the SAM layer has an average thickness of 16 Å,\textsuperscript{39} which is commensurate to that measured in other experiments.\textsuperscript{46,75} The asperities defining the carbon shell are assumed to be shifted 1.5 Å \( (t_1) \) and 13.5 Å \( (t_2) \) from the asperity surface. The inner thiol layer is shifted by 15 Å \( (t_3) \), which is also where the Au section of the asperity is assumed to begin. The thiol-gold interaction is modeled using a Morse potential, while the carbon-gold and gold-gold interactions are modeled using LJ potentials (and the KE model for their adhesion). We calculate a plasticity index of 12\textsuperscript{6}3 for our gold samples [using Eq. (B4)], which is consistent with those reported in literature for sputtered gold.\textsuperscript{41}

The adhesive pressure between the flat gold substrate and each of the three components in the asperities and the contact pressure are plotted in Fig. 5(c) as a function of the mean separation between the two surfaces. The contribution from the two different thiol layers is added together into a single thiol adhesion curve. The material properties used to plot the curves in Fig. 5(c) are listed in Table I. The total adhesive pressure is the sum of the individual contributions from each material within the asperity and is dominated (>99%) by the thiol-gold adhesion involving the thiol layer.
closest to the asperity surface. Materials deeper in the asperity and thus further away from the flat substrate exhibit a lower adhesion. The equilibrium separation between the surfaces is found from the intersection of the total adhesive pressure and contact pressure, which is then used to find the percentage contact area using Eq. (E2). Using surface topography data obtained from our AFM scans of the gold substrate used to create the SAM junction in Ref. 39, we predict a percentage contact area \( A'_{\text{M}} \) of 56\( \pm \)25\% (Ref. 88) between the two surfaces. The percentage contact area is strongly correlated to the RMS surface roughness, as shown in the sensitivity analysis (details in Sec. S4). The uncertainty value of 25\% is obtained by averaging the uncertainty for each AFM scan, details of which are provided in the supplementary material of Ref. 39.

To demonstrate the importance of using the Morse potential-based contact model within the composite asperity model, we also predict the percentage contact area by using an equivalent LJ potential to describe the thiol-gold adhesion (as described in Sec. III A). Keeping all other parameters the same (as listed in Table I), we predict a percentage contact area \( A'_{\text{LJ}} \) of 31\% \( \pm \)17\%.

We assess the accuracy of the predicted percentage contact areas from the Morse and LJ models by using them to compare experimental measurements of junction thermal conductance \( G_{\text{junc}} \), performed by Majumdar et al.,\(^{39}\) to area-corrected predictions \( G_{\text{junc}}^{\text{cor}} \) from MD simulations. For an Au-(1,10-decanedithiol)-Au junction, \( G_{\text{junc}}^{\text{cor}} \) was obtained using frequency domain thermoreflectance (FDTR) and represents the thermal conductance of the entire SAM junction.\(^{39}\) Assuming that the SAM itself has a negligible thermal resistance compared to the interfaces, \( G_{\text{junc}}^{\text{cor}} \) can be approximated as two interface thermal conductances in series (one at each gold substrate). Based on the fabrication technique described in Ref. 39, the interface on which the SAM is grown is assumed to be perfect. Its interface thermal conductance is represented by \( G_{\text{junc}}^{\text{int}} \). The first term inside the square brackets on the right-hand side of Eq. (32) represents the thermal conductance for the regime where the mean free path (MFP) of the heat carriers (in this case, atomic vibrations or phonons) is comparable to the size (represented by \( a_R \)) of the contact regions. The second term represents the regime where the MFPs are much smaller than \( a_R \). For the case where the MFPs are much smaller than \( a_R \), the interface thermal conductance is the Maxwell constriction conductance as described by Prasher and Phelan.\(^{89}\)

Using Eq. (32), we find \( G_{\text{M}}^{\text{junc}} \) to be 112\( \pm \)45 MW/m\(^2\) K and \( G_{\text{LJ}}^{\text{junc}} \) to be 61\( \pm \)26 MW/m\(^2\) K, based on averaging over all AFM measurements (details of the uncertainty calculation are provided in Sec. S5). We now use Eq. (31), finding \( G_{\text{M}}^{\text{int}} \) to be 73\( \pm \)20 MW/m\(^2\) K and \( G_{\text{LJ}}^{\text{int}} \) to be 47\( \pm \)17 MW/m\(^2\) K. From the FDTR measurements, the experimental value of the junction thermal conductance \( G_{\text{junc}}^{\text{exp}} \) is 65\( \pm \)7 MW/m\(^2\) K.\(^{39}\) We independently estimate the degree of agreement between the experiment and Morse or LJ predictions using an overlapping coefficient.\(^{90}\) Assuming that each prediction can be represented by a normal distribution, the overlapping coefficient is equal to the area of the overlapping region between the two distributions (details are provided in Sec. S6). When comparing with \( G_{\text{junc}}^{\text{exp}} \), we find the overlapping coefficient to be 0.50 with the Morse-based prediction and 0.38 with the LJ-based prediction.\(^{91}\)

The Morse potential is a physically accurate description of the thiol-gold bond present in our junctions (as shown in Ref. 32 and used by us in Ref. 39). Thus, an adhesion model derived using the Morse potential is a better representation of our system. It should also provide the more accurate prediction of contact area compared to using an equivalent LJ potential. Our finding of better agreement between the Morse prediction and the experimental measurements of the SAM junction thermal conductance supports these arguments. This study can also potentially explain the discrepancy between electronic conductance measurements of SAMs made by different research groups.\(^{92-96}\) The measurements using nano-transfer printed metal films, AFM tips, STM tips, and sputtered metal films as electrodes are also sensitive to the areal contact between the molecular layer and the surface of the metal film. Some of these works measured the surface roughness of their films and even attributed the observed variations of measured electronic conductance to it,\(^{92,94-96}\) especially for interfaces having strong, covalent bonds (e.g., the thiol-gold interface studied in this work). None, however, use rigorous mathematical analysis as we have done here to quantify the areal contact at the metal-molecular layer interface.

IV. SUMMARY

We formulated a rough surface contact model that accounts for plasticity through the FEA-derived model of Kogut and Etsion, and adhesion through the use of the DMT
model in conjunction with the Morse potential. Our Morse potential-based contact model is especially useful for covalently bonded materials whose interactions cannot be accurately described using an LJ potential. A composite asperity model was derived to extend this study to a layered substrate and applied to a system comprised of a thiol-based SAM on a gold substrate in contact with another rough gold substrate, as shown in Fig. 5(b). Generalized expressions for calculating the work of adhesion and equilibrium separations between a surface and a substrate interacting through a Morse potential were also presented, which only required knowledge of the Morse potential parameters and the substrate lattice constant. The percentage contact area between these rough bodies was found to be 56±25% when using the Morse-based adhesion model and 31±17% for the LJ-based model. Using the Morse prediction of percentage contact area provided better agreement between experimentally measured and MD predicted values of the thermal conductance of a thiol-based SAM junction than the LJ prediction. The Morse potential-based contact model will be an important tool for researchers to quantify how charge and energy transport through covalent interfaces are influenced by incomplete areal contact.

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APPENDIX A: GENERALIZED EXPRESSIONS TO CALCULATE \( r_e \) AND \( A_2 \)

Calculating \( r_e \): We find a numerical fit for the variation of the ratio \( r_e/r_{NN} \) obtained from the single-point energy calculations for a range of values of \( x_{NN} \) and \( r_0/r_{NN} \) to be

\[
\frac{r_e}{r_{NN}} = C_1(x_{NN})^2 + C_3 \quad \text{for } 3 \leq x_{NN} \leq 14, \quad (A1)
\]

where

\[
C_1 = -1.373 \times 10^5 e^{-11.88 \left( \frac{r_0}{r_{NN}} \right)} - 13.32 e^{-1.078 \left( \frac{r_0}{r_{NN}} \right)}
\]

\[
C_2 = 1.933 \left( \frac{r_0}{r_{NN}} \right)^5 - 9.226 \left( \frac{r_0}{r_{NN}} \right)^4 + 16.530 \left( \frac{r_0}{r_{NN}} \right)^3 - 15.850 \left( \frac{r_0}{r_{NN}} \right)^2 + 12.000 \left( \frac{r_0}{r_{NN}} \right) - 8.558
\]

\[
C_3 = 1.138 \left( \frac{r_0}{r_{NN}} \right) - 0.328
\]

For our case, \( r_{NN} = l_c/\sqrt{2} \), where \( l_c \) is the lattice constant. Eq. (A1) has a maximum error of 8% with respect to the energy calculations for our chosen ranges of \( x_{NN} \) and \( r_0/r_{NN} \), which are sufficient to describe both covalent and van der Waals bonding characteristics.

Calculating \( A_2 \): We find a numerical fit for the variation of the ratio \( \Delta \gamma_M/\Delta \gamma_{LJ} \) obtained from the single-point energy calculations for a range of values of \( x_{NN} \) and \( r_0/r_{NN} \) to be

\[
\frac{\Delta \gamma_M}{\Delta \gamma_{LJ}} = E_1(x_{NN})^2 + E_3 \quad \text{for } 3 \leq x_{NN} \leq 14, \quad (A3)
\]

where

\[
E_1 = 204.10 e^{-2.172 \left( \frac{r_0}{r_{NN}} \right)} + 0.0504 e^{1.706 \left( \frac{r_0}{r_{NN}} \right)}
\]

\[
E_2 = -0.3229 \left( \frac{r_0}{r_{NN}} \right)^2 + 2.096 \left( \frac{r_0}{r_{NN}} \right) - 4.49 \quad \text{for } 0.79 \leq \frac{r_0}{r_{NN}} \leq 1.96. \quad (A4)
\]

\[
E_3 = 0.3135 \left( \frac{r_0}{r_{NN}} \right)^2 - 1.407 \left( \frac{r_0}{r_{NN}} \right) + 1.683
\]

Eq. (A3) has a maximum error of 12% with respect to the energy calculations for our chosen ranges of \( x_{NN} \) and \( r_0/r_{NN} \). Details regarding these fits are provided in Sec. S2.

APPENDIX B: EXPRESSION FOR CRITICAL INTERFERENCE AND PLASTICITY INDEX

The critical interference is...
where $K$ is the hardness coefficient,\textsuperscript{15}

\begin{equation}
K = 0.454 + 0.41\nu,
\end{equation}

$H$ is the Vickers hardness of the softer material, $\nu$ is the Poisson ratio of the softer material, $E$ is the Hertz elastic modulus,

\begin{equation}
\frac{1}{E} = \frac{1 - \nu^2}{E_1} + \frac{1 - \nu_2^2}{E_2},
\end{equation}

$E_1$ and $E_2$ are the Young’s moduli for the hemisphere and surface, and $\nu_1$ and $\nu_2$ are their Poisson ratios. The plasticity index $\Psi$ is calculated as follows:

\begin{equation}
\Psi = \frac{2E}{\pi KH} \left( \frac{\sigma_x}{R} \right)^{1/2}.
\end{equation}

**APPENDIX C: PLASTIC DEFORMATION REGIMES FOR COMPOSITE ASPERITIES**

For the deformation regimes where $\omega/\omega_c \geq 1$ (elastic-plastic regime), we adjust the FEA derived dimensionless separations found by Kogut and Etsion to be\textsuperscript{25,26}

\begin{equation}
\frac{Z(\omega, \tilde{x})}{\omega_c} = 0.951 \left( \frac{\omega}{\omega_c} \right)^{1.153} f(\tilde{x}) + \frac{r_c}{\omega_c} + \frac{t}{\omega_c} \quad \text{for} \quad 1 \leq \omega/\omega_c \leq 6,
\end{equation}

and

\begin{equation}
\frac{Z(\omega, \tilde{x})}{\omega_c} = 0.457 \left( \frac{\omega}{\omega_c} \right)^{1.578} f(\tilde{x}) + \frac{r_c}{\omega_c} + \frac{t}{\omega_c} \quad \text{for} \quad 6 \leq \omega/\omega_c \leq 110.
\end{equation}

**APPENDIX D: ADHESIVE PRESSURE AND ENERGY BETWEEN A SURFACE AND A SUBSTRATE FOR AN LJ POTENTIAL**

The analogous expressions of Eqs. (9)–(10), (21), and (23) for describing adhesive pressure, energy per unit area, and work of adhesion between a single layer of atoms (surface), and a substrate interacting through an LJ potential are

\begin{equation}
P_{\text{LJ,surf-s}}(D) = \frac{\pi \rho_1 \sigma_2 (4\pi \rho_0 a)^6}{2\pi^4} \left[ \left( \frac{r_c}{D} \right)^{10} - \left( \frac{r_c}{D} \right)^4 \right],
\end{equation}

\begin{equation}
P''_{\text{LJ,surf-s}}(D) = \frac{\pi \rho_1 \sigma_2 (4\pi \rho_0 a)^6}{6\pi^3} \left[ \frac{1}{3} \left( \frac{r_c}{D} \right)^9 - \left( \frac{r_c}{D} \right)^6 \right],
\end{equation}

\begin{equation}
\frac{F_{\text{ad}}(\omega)}{F_{\text{ad}}^{0}} = \frac{9(\omega/\omega_c)^\infty}{2(\epsilon/\omega_c)^4} \left[ \frac{r_c/\omega_c}{Z/\omega_c} \right]^4 \left( \frac{r_c/\omega_c}{Z/\omega_c} \right)^{10} \hat{x} d\tilde{x},
\end{equation}

\begin{equation}
\frac{F_{\text{ad}}^\text{out}(\omega)}{F_{\text{ad}}^{0}} = 3 \left[ \frac{(r_c/D)^3 - 1}{3} \left( \frac{r_c}{D} \right)^9 \right].
\end{equation}

**APPENDIX E: CONTACT STRESS AND CONTACT AREA**

The total non-dimensional contact stress $P_{cs}^*$ and the percentage contact area $A^*$ between deforming asperities and the surface are given by

\begin{equation}
P_{cs}^* = \frac{P_{cs}}{A_n \tilde{H}} = \frac{2\pi \eta R \sigma_5 K \alpha^*_c}{3} \left( \int_{d^*}^{d^*+6\alpha^*_c} t^{1.263} + \frac{3}{K} \int_{d^*}^{d^*+6\alpha^*_c} t^1 \right),
\end{equation}

\begin{equation}
A^* = \frac{A}{A_n} = \frac{\pi \eta R \sigma_5 \alpha^*_c}{3} \left( \int_{d^*}^{d^*+6\alpha^*_c} t^{1.146} + 2 \int_{d^*}^{d^*+6\alpha^*_c} t^1 \right),
\end{equation}

where

\begin{equation}
F^2 = \left( \frac{z^* - d^*}{\omega_c} \right)^z \phi^*(z^*) dz^*.
\end{equation}

Each of the four integrals represents the elastic and plastic deformation regimes listed in Table III.

F. Jensen, Introduction to Computational Chemistry (John Wiley and Sons, 2007).


F. Jensen,

Introduction to Computational Chemistry


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In Ref. 39, we used modified versions of Eqs. (31) and (32) to compare G_junc with G_0, where G_0 = \frac{\pi}{2} = 113.9 \text{ MW/m}^2. We found G_junc to be 102±26 \text{ MW/m}^2, which differs from the area-corrected junction thermal conductance reported in Ref. 39 due to further refinement of our model and averaging of more AFM measurements.


