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"A New Method for Determining the Hamaker Constant with Atomic Force Microscopy"

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Prior to the start of this grant, we developed a new method for estimating Hamaker constants, A, from the non-contact approach regime of an atomic force microscope (AFM) experiment (Fronczak et al., 2017, *Langmuir* **33**, 714-725). The method, which accounts for the inertial effects of the cantilever's tip motion, was demonstrated to yield estimates of A for silica, alumina and polystyrene substrates that were in very good agreement with previously published Lifshitz calculations. A subsequent update of this method was also proposed, in which the difficult to quantify geometric effects of the AFM cantilever are still fully captured via the description of the tip as an 'effective' perfect sphere (Fronczak et al., 2018, *JCIS* **517**, 213-220). First, a tip is 'calibrated', whereby the deflection at first contact between the cantilever tip and a smooth surface of known properties is determined and an effective radius, R_{eff}, of the tip is calculated. The tip's approach to contact toward other similarly smooth surfaces can then be well-described by using only this single geometric parameter. We demonstrated the practicality and accuracy of this updated method by comparing the results with the Lifshitz predictions (when available) for various flat substrates.

Since the start of this grant, we have focused on developing important improvements to this method. In particular, the effects of surface roughness on the estimated Hamaker constants must be accounted for, an issue that has not been adequately addressed in the literature. The previous method is based on the use of the attractive force expression between a sphere and a flat plate. This expression, invoked in nearly all other AFM analyses, is chosen for convenience, and leads to a simple connection between A and the deflection of the cantilever when its tip first comes into contact with the surface, d_c. Yet, such perfectly smooth surfaces cannot be created, and a surface with a roughness of only a few nm still yields a broad distribution of d_c-values. Although the average d_c-value yields a good estimate of A, the obtained A nonetheless has a large uncertainty. A proper handling of surface roughness should significantly decrease the associated error in the estimated A. Furthermore, explicitly accounting for surface roughness will greatly extend the applicability of the method, as it is not practical to minimize the roughness of all surfaces of interest. So, in the first year of the grant, we have been 1) determining how to incorporate the effects of surface roughness into the method and 2) investigating how surface roughness affects the estimated values of A.

To begin, the cantilever tip is modeled as a sphere of radius R attached to a platform via a Hookean spring (Figure 1). The attractive force between the sphere and surface, F_{surf}, arises from dispersion interactions that are quantified by the Hamaker constant, A. The deflection, d, of the spring corresponds to the deflection of the cantilever tip that is measured during an AFM experiment. To determine F_{surf}, the surface is described by a collection of semi-infinite piles. The attractive force in the z-direction between the sphere and a given strip is then evaluated, and next summed over the entire substrate. Consequently, we have generated, for the first time, a formally exact expression for F_{surf} arising from any arbitrary surface.

With an expression for F_{surf} now obtained, the new method requires identifying the location of the sphere and platform at the critical point, beyond which the sphere can no longer be maintained in mechanical equilibrium. At this critical point, the sphere immediately jumps into contact with the surface, allowing one to obtain the deflection of the tip at first contact with the surface, or d_c. Using our exact expression for F_{surf}, we have obtained, again for the first time, the critical point conditions for any surface described by a well-behaved function.

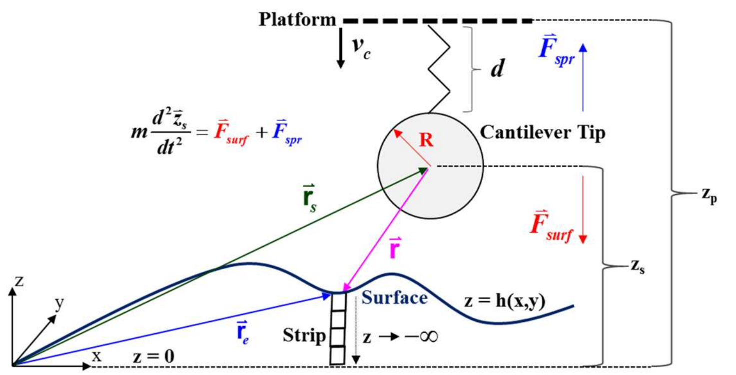

Figure 1: Surface of height function $h(x,y)$ interacting with a sphere of radius R and mass m attached to a moving platform, with speed v_c, via a Hookean spring with a deflection d and upward force F_{spr}. The attractive force between the sphere and the surface, F_{surf}, arises from the dispersion interactions between the sphere and all the semi-infinite strips comprising the surface. The platform is at a height z_p and the center of the sphere is at a height z_s at the vector position $\mathbf{r}_s$.

Now, for a perfectly smooth surface, the value of d_c will be the same for any location on the surface, and occurs when the bottom of the sphere first touches the surface. But for any other surface, the bottom of the sphere may no longer be the part of the sphere that makes first contact with the surface. Thus, we have developed two equivalent approaches for finding the initial sphere-surface contact point, either through the use of the unit normal to the surface

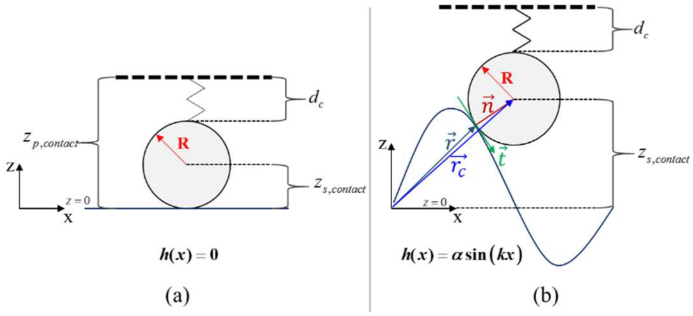

Figure 2: a) The bottom of the sphere is the first point of contact with a flat surface. b) For another surface, chosen to be a sine wave of amplitude α and wavelength $2\pi/k$, the first point of contact can be obtained via the unit normal, **n**, to the surface. The center of the sphere is located at the vector position $\mathbf{r}_c$ with a vertical height of $z_{s,contact}$. The deflection of the spring at first contact is d_c. The unit vector tangent to the surface is **t**.

(see Figure 2), or by finding the minimum vertical distance between the lower portion of the sphere and the surface. Both methods are valid for any surface of interest, though we have first tested them for a "simple" rough surface generated from a sine wave with a given amplitude and wavelength. Interestingly, even this "simple" surface exhibits complicated and relevant behavior to the analyses of AFM deflection data. As seen in Figure 3, when the amplitude of the surface is large enough, the sphere can no longer reach the bottom of the local minimum of the sine wave, and the curve tracing the height of the sphere when it is in contact with the sphere develops a discontinuity, or cusp. This result has interesting implications for the reconstruction of surfaces from AFM height maps, suggesting that some information about these high-curvature valleys may be lost despite their possible importance to F_{surf}. These cusp points also have an effect on the obtained distribution of d_c-values for a given surface. In general, the sphere experiences the smallest attractive force as it approaches the top (local maximum) of the sine wave, which corresponds to the smallest d_c-value. In contrast, the sphere experiences the largest attractive force when it approaches the bottom (local minimum) of the sine wave, which corresponds to the largest d_c-value. But when the sphere is too big to fit inside the valley, the sphere no longer experiences this maximum possible attractive interaction. Hence, the d_c-distribution exhibits a complicated "geometry"-dependence, and is strongly affected by the amplitude and wavelength of the surface (Figure 4).

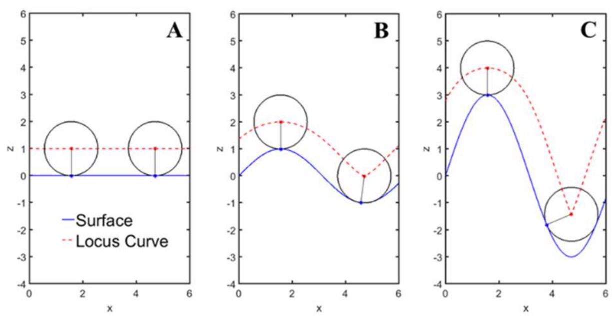

Figure 3: The locus curve of $z_{s,contact}$ (red) for three surfaces (blue): A) flat plate; B) and C) sine waves of k = 1 (in units of R) and α = 1 and 3, respectively.

In the next twelve months, we will be considering more complicated surfaces: 1) a sum of sine waves of different amplitudes and wavelengths, and 2) a sine wave with local "ripples" (i.e., two different length scales of surface roughness). We will also investigate the dynamic behavior of the cantilever tip as it approaches a given surface for different approach speeds of the platform. We will investigate how the d_c-distributions change with approach speed, and how the d_c-distribution can be used to extract (with as minimal error as feasible) the estimated Hamaker constant of a surface with arbitrary roughness. In addition, we will expand the method in order to analyze fully two-dimensional surfaces. Then, we will begin experimental validation of the updated approach. Utilizing a solid with a known Hamaker constant (e.g., amorphous silica), we will generate various surfaces comprised of the same material but with very different scales of roughness. For each of these surfaces, the surface function will be generated via the AFM height mapping technique, and then introduced into our method. For surfaces of the same material but different shapes (i.e., degrees of roughness), the method should recover the same value of the Hamaker constant, at least within statistical error.

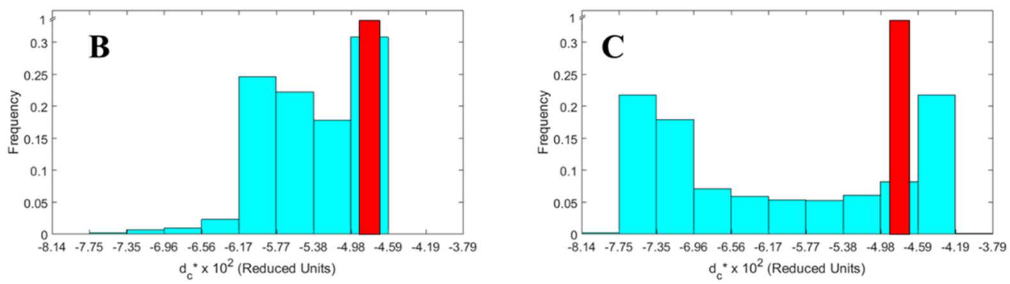

Figure 4: The d_c-distributions for the three surfaces in Figure 3, in which the vertical red bar is the single value of d_c for the flat plate (Figure 3A).