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

David S. Corti, Davidson School of Chemical Engineering, Purdue University

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. Specifically, 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 perfectly 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 eliminate, let alone even minimize, the roughness of all surfaces of interest.

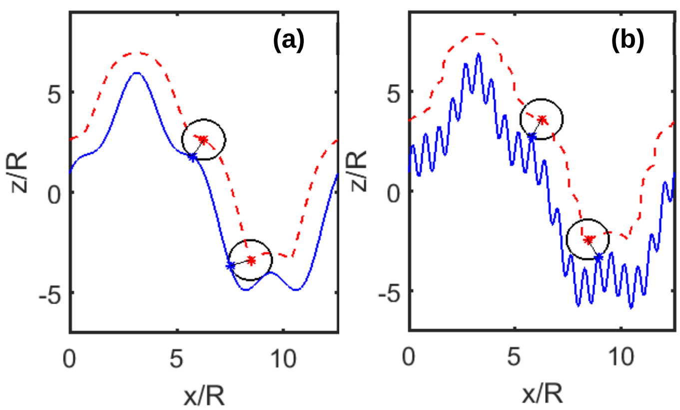

Figure 1: The contact locus (red) for two surfaces (blue) with different surface roughness, which traces the location of a sphere of radius *R* (black) when in contact with the surface.

In the second year of the grant, we have completed the key first phase of our extension of the previous method, which is discussed in detail in a paper recently submitted to the *Journal of Physical Chemistry C*. In this paper, we derive a general expression for the van der Waals (vdW) attractive force between a sphere and a surface of arbitrary surface roughness. We also derive the expressions needed for determining d_c along any point on the surface, thereby yielding the needed connection between *A* of the substrate and the resulting distribution of d_c-values (or the d_c-distribution). As the d_c-distribution is also a signature of the underlying inherent,

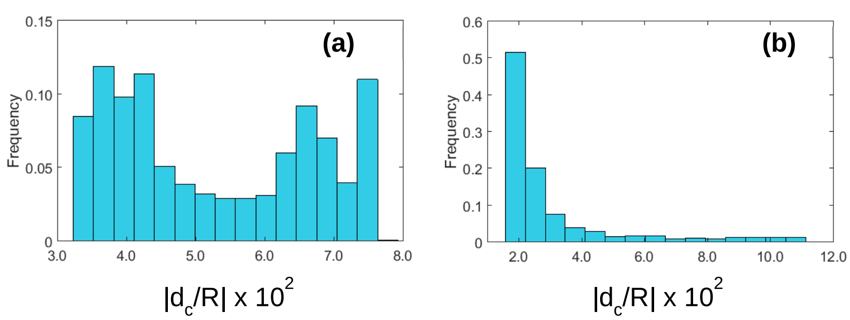

Figure 2: The d_c-distributions for the two surfaces in Figure 1. Despite similar contact loci, the surface roughness greatly impacts the obtained values of d_c.

and unavoidable, roughness of the surface, we also investigate the effects of surface topography on the predicted distribution of d_c-values (see Figures 1 and 2). This analysis has clearly shown that, unlike some previous approaches, the effects of surface roughness must be explicitly accounted for in determining the correct vdW attractive interactions. We also discuss a preliminary experimental test of our vdW force expression. Using a simplified version of the surface topography that is obtained directly from the AFM imaging of an amorphous silica surface, the predicted d_c-distribution was found to be in good agreement with the d_c-distribution also obtained directly from AFM experiments (see Figure 3).

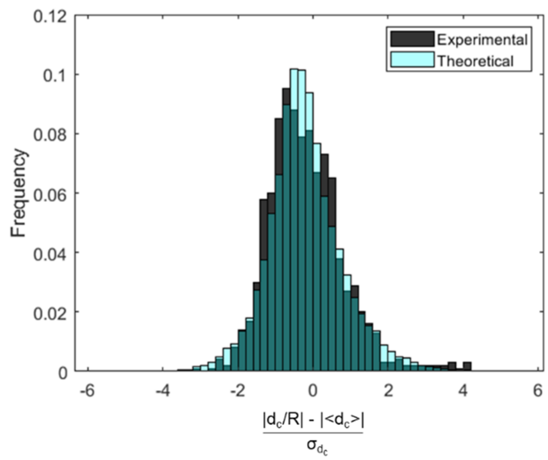

Figure 3: Comparison of the d_c-distribution obtained from AFM experiments for an amorphous silica substrate and the predicted d_c-distribution obtained with our new method and using a modified version of the same surface imaged with an AFM.

We have also started the second phase of our proposed extension of the new approach-to-contact method. We are investigating the impact of the inertial effects of the cantilever on the resulting d_c-distributions (see Figure 4). The impact of these inertial effects become negligible as the approach speed decreases to very low values. We are also developing methods for extracting the actual underlying surface from the AFM topographical imaging, given that the cantilever tip has a non-zero radius of curvature (and thus cannot image surface features with length scales smaller than this radius). We are investigating various methods to reconstruct the surface from these images, including ongoing work in which a discrete Fourier transform, and the corresponding power spectrum, are analyzed to provide signatures of the true underlying surface features. The last aspect of this second phase involves a full computational test of the extended method, for which a known surface with a given value of A is then used to generate a surface image and a given d_c-distribution. In turn, the d_c-distribution is used within an iterative procedure in which the surface, the effective radius of the cantilever tip, and the effective Hamaker constant of the substrate are all extracted, and shown to match up with the known, or initially inputted, values. (Details of this phase will appear shortly in a forthcoming publication.) We are also carrying out additional experimental tests of our method. We have purchased a surface with a prescribed shape (e.g., saw tooth profile with known dimensions), along with AFM cantilevers for which a colloidal probe of known radius has been attached. The predicted d_c-distributions for this sphere-surface system will be compared to the d_c-distributions obtained within AFM experiments (and represents a proper comparison between experiments and various theoretical aspects of our current work.)

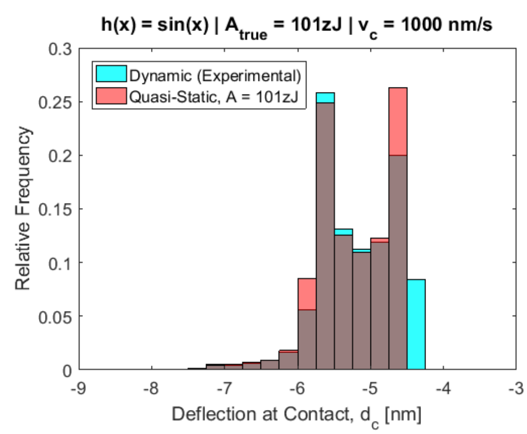

Figure 4: Comparison of the d_c-distributions obtained for the quasi-static limit and for a cantilever with an approach speed of v_c = 1000 nm/s. The surface is the same in both cases (and described by the same sine wave).

In the final third phase of the project, which will begin in the no-cost extension year of the project, our analyses from the first two phases will be extended to the experimental determination of A for various surfaces (with known Hamaker constants). For example, the same substrate material will be modified to have different surface roughness. If our updated method is correct, all AFM measurements on these surfaces will yield the same value of A (independent of the roughness). If time permits, our analysis will also be extended to a range of materials in which the values of A are not known *a priori*, the results of which will again be compared to the Lifshitz predictions. We will also provide a detailed statistical analysis of the method, in which a given d_c-distribution is mapped onto a single, unique value of A, thereby decreasing the statistical uncertainty in the estimated values of A. Such a statistical analysis is needed for determining the appropriate error when mapping an obtained distribution, which itself has some inherent degree of uncertainty, to a given value of A (which should be reported with its own appropriate error). Finally, and again if time permits, we will begin extending our approach to deformable surfaces, and for AFM experiments performed in an aqueous environment, such that our method can be ultimately applied to, for example, important biological systems (and not just solid materials).