

Appendix A The Force Laws for Bodies of Different Geometries: the Hamaker Constant

A.1 Molecule-Surface Interaction

The Hamaker constant H is defined by $H = p^2 C r_1 r_2$, where r_1 and r_2 is the number of atoms per unit volume in the two bodies and C is the coefficient in the atom-atom pair potential. Let us assume that pair potential between two atoms or small molecules is purely attractive and of the form $U(r) = -C/r^n$. Then, with the further assumption of additivity, the net interaction energy of a molecule and the planar surface of a solid made up of like molecules (Fig. A.1 (a)) will be the sum of its interactions with all the molecules in the body. For molecules in a circular ring of cross-sectional area $dx dz$ and radius x , the ring volume is $2\pi x dx dz$, and the number of molecules in the ring will be $2\pi r x dx dz$, where r is the number density of molecules in the solid. The net interaction energy for a molecule at a distance D away from the surface will therefore be

$$U(D) = -2\pi C r \int_{z=0}^{z=\infty} dz \int_{x=0}^{x=\infty} \frac{x dx}{(z^2 + x^2)^{n/2}} = -\frac{2\pi C r}{(n-2)} \int_D^{\infty} \frac{dz}{z^{n-2}} \quad (\text{A.1})$$

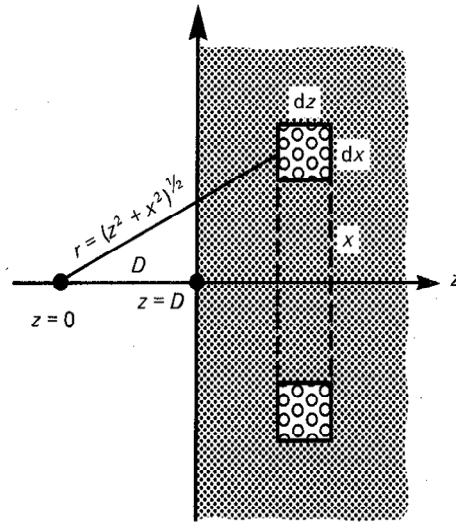
$$= -2\pi C r / (n-2)(n-3) D^{n-3} \quad \text{for } n > 3, \quad (\text{A.2})$$

Which for $n=6$ (van der Waals forces) becomes

$$U(D) = -\pi C r / 6 D^3. \quad (\text{A.3})$$

The corresponding force, $F = -\partial w(D) / \partial D = -\pi C r / 2 D^4$, could of course have been derived in a similar way by summing (integrating) all the pair forces resolved along the z axis.

(a)



(b)

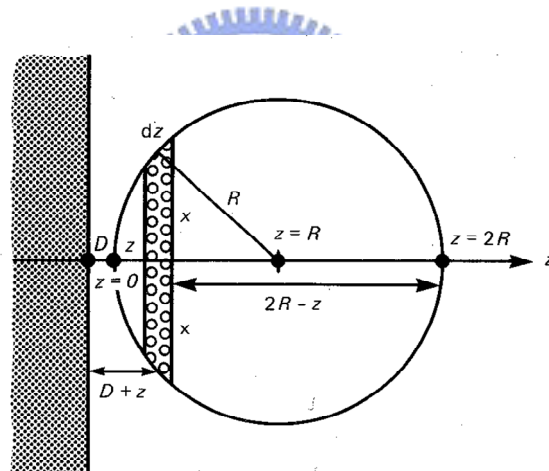


Fig. A.1 (a) The model is Molecule near a wall. (b) The model is a spherical particle near a wall ($R \gg D$)

We can now calculate the interaction energy of a large sphere of radius R and a flat surface (Fig. A.1(b)). First, from elementary geometry we know that for a circle

$$x^2 = (2R - z)z. \quad (\text{A.4})$$

The volume of a thin circular section of area πx^2 and thickness dz is therefore $\pi x^2 dz = \pi(2R - z)z dz$, so that the number of molecules contained within this section is $\pi r(2R - z)z dz$, where r the number density of molecules in the sphere is. Since all these molecules are at a distance $(D + z)$ from the planar surface, the net interaction energy is, using Eq. (A.1),

$$w(D) = -\frac{2\pi^2 C r^2}{(n-2)(n-3)} \int_{z=0}^{z=2R} \frac{(2R-z)z dz}{(D+z)^{n-3}}. \quad (\text{A.5})$$

For $R \gg D$, only small values of z ($z \approx D$) contribute to the integral, and we obtain

$$\begin{aligned} w(D) &= -\frac{2\pi^2 C r^2}{(n-2)(n-3)} \int_0^\infty \frac{2Rz dz}{(D+z)^{n-3}} \\ &= -\frac{4\pi^2 C r^2 R}{(n-2)(n-3)(n-4)n - (n-5)D^{n-5}}, \end{aligned} \quad (\text{A.6})$$

Which for $n=6$ (van der Waals forces) becomes

$$w(D) = -\pi^2 C r^2 R / 6D. \quad (\text{A.7})$$

However, for $D \gg R$, we may replace $(D + z)$ in the denominator of Eq. (4) by D , and we then obtain

$$w(D) = -\frac{2p^2 C r^2}{(n-2)(n-3)} \int_0^{2R} \frac{(2R-z)z dz}{D^{n-3}} = -\frac{2p C r (4p R^3 r/3)}{(n-2)(n-3) D^{n-3}}, \quad (\text{A.8})$$

Which, since $4p R^3 r/3$ is simply the number of molecules in the sphere, is the same as Eq. (A.1) for the interaction of a molecule (or small sphere) with a surface. It is left as an exercise for the interested reader to show that for two spheres of equal radii R whose surfaces are at a small distance D apart ($D \gg R$), their interaction energy is one half that given by Eq. (A.5) or (A.6), while for two spheres far apart ($D \gg R$) the energy varies as $-1/D^n$ as for two molecules. At intermediate separation ($D \approx R$) the expression for the interaction potential is more complicated but remains analytic (Hamaker, 1937).

The Hamaker constant of the Si cantilever and Pt coating cantilever, they had been researched by people to measure the vdW force term in the experiments, and the Hamaker constant (H) was determinate 4×10^{-19} [32].



Appendix B Constant Force Gradient

B.1 For Small Tip Oscillation Amplitude

In early NC-AFM papers, the observed frequency shift Δf of the oscillating cantilever was related to the gradient of the force k_{ts} between the tip and sample [64]. Forces between tip and sample cause a change in $f = f_0 + \Delta f$. The eigenfrequency of a harmonic oscillator is given by $(k^*/m^*)^{0.5}/2\pi$, where k^* is the effective spring constant and m^* is the effective mass. If the second derivate of the tip-sample potential $k_{ts} = \partial^2 V_{ts} / \partial z^2$ is constant for whole range covered by the oscillating cantilever, $k^* = k + k_{ts}$. If $k_{ts} \ll k$, the square root can be expanded as a Taylor series and the shift in eigenfrequency is approximately given by,

$$\Delta f = -\frac{f_0}{2k} \frac{\partial F_{ts}}{\partial z} = -\frac{f_0}{2k} k_{ts} \quad (\text{B.1})$$

where f_0 is the unperturbed resonance frequency, k_{ts} is the force gradient, and k is the spring constant of the force sensor. Unfortunately, this approximated equation is only valid for small tip oscillation amplitudes A , compared to the separation between probing tip and sample.

B.2 Analytical Expressions for the Force and Force Gradient Using Different Models

Model	F	F'	$d _{F'=const.}$
Electrostatic: Sphere Only $d \ll R$	$F_{sphere} = -\frac{pe_0RU^2}{D}$	$F'_{sphere2} = \frac{pe_0RU^2}{D^2}$	$\left(\frac{pe_0R}{F'}\right)U$
Charged line (~cone)	$F_{cone}(D) = -\frac{a^2}{4pe_0} \ln\left(\frac{L}{4D}\right)U^2$	$F'_{cone} = \frac{a^2U^2}{4pe_0D}$	$\left(\frac{a^2}{4pe_0F'}\right)U^2$
Plane surface (circle area)	$F_{vdW} = -\frac{pe_0R^2U^2}{2d^2}$	$F'_{plane} = \frac{pe_0RU^2}{D^3}$	$\left(\frac{pe_0R^2}{F'}\right)^{1/3}U^{2/3}$
Ven der Waals: Sphere	$F = -\frac{HR}{6d^2}$	$F'_{vdW} = \frac{HR}{3D^3}$...

$$a = 2pe_0 / \text{Arcsinh}[1 / \tan(q_{tip} / 2)] \quad [65]$$

Table I. Analytical expressions for the force and force gradient using different models for the tip shape. The formulas are valid for $D < R$ and zero contact potential. The right-hand column gives the variation in tip-sample separation with U for fixed force gradient. F : force, F' : force gradient, D : tip-to-sample separation, R : tip radius, q_{tip} : the tip open-cone angle, L : length of the tip, U : tip bias subtract contact potential, H : Hamaker constant, and ϵ_0 : vacuum permittivity.

Appendix C Do STM Mode Using Cantilever for Atomic Resolution

We can use un-vibrating cantilever to do STM mode for obtaining height resolution image as shown in Fig. C.1. Scanning the surface using cantilever is as same as W tip. However, the cantilever has some vibration when it scans across surface, so we must set the lower scan-speed than the W tip to reduce the vibration noise. Figure C.1 shows the STM image that is acquired by using the parameters for $V_{sample} = 2.1$ V, feedback set = 0.18 nA, scanning-speed = 1000 nm/s, and scanning size = 100×100 nm².

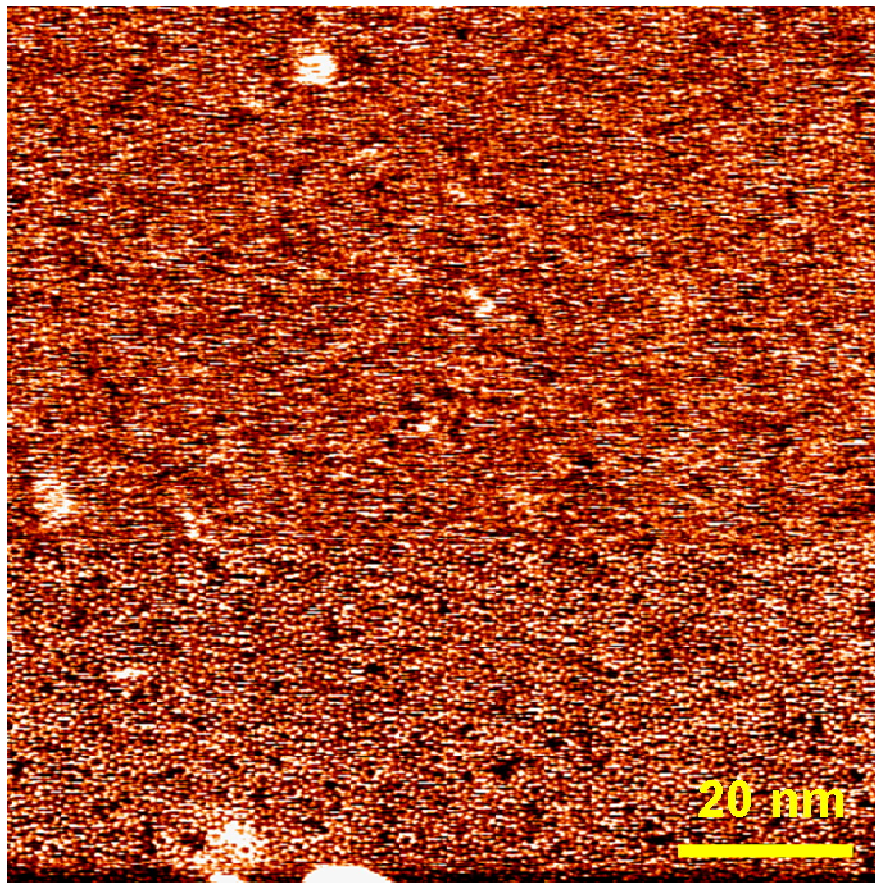


Fig. C.1. The STM image is obtained by using AFM Si-cantilever, and the scanning parameters are $V_{sample} = 2.1$ V, feedback set = 0.18 nA, and scanning size = 100×100 nm².

Appendix D Additional Calculation

D.1 Apparent z -Height Deviation versus Tip Bias for Constant Force Gradient

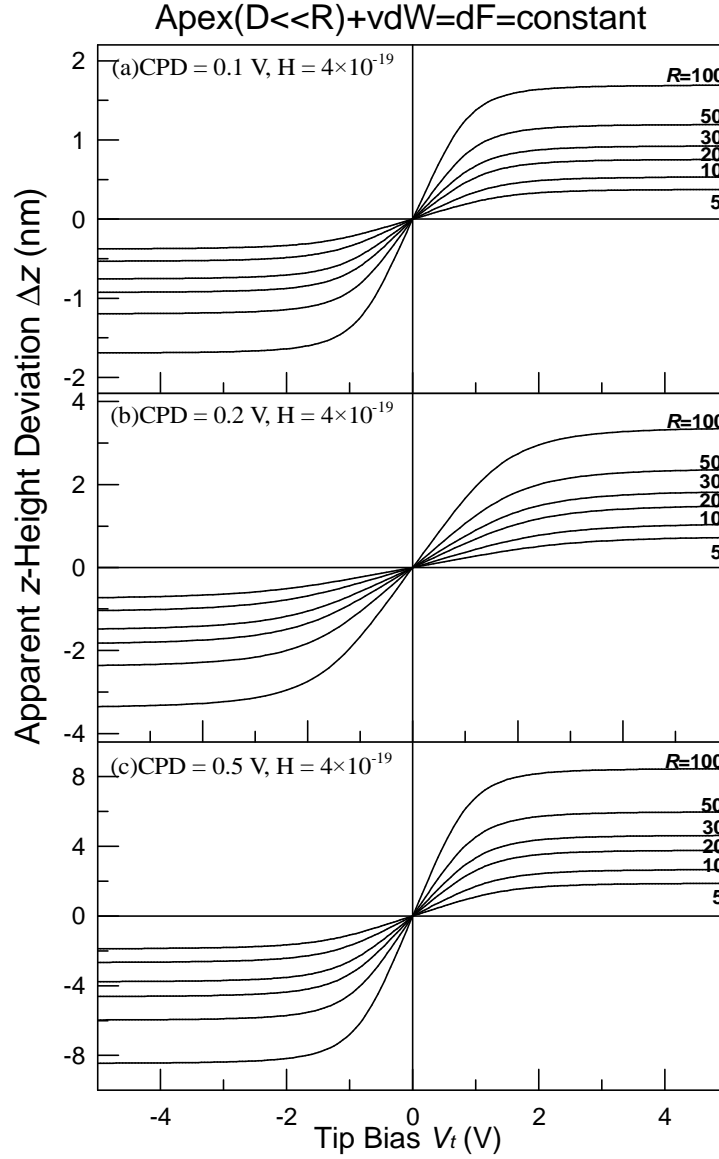


Fig. D.1 The apparent topographic height deviation Δz is as a function of V_t with various R when the $F'_{ts} = (F'_{s_sphere} + F'_{vdW}) = const.$ The different contact potential (a) 0.1 V (b) 0.2 V, and (c) 0.5 V show the different variation heights. The Hamaker constant is set as 4×10^{-19} J.

D.2 Apparent z -Height Deviation versus Tip Bias for Non-Constant Force Gradient

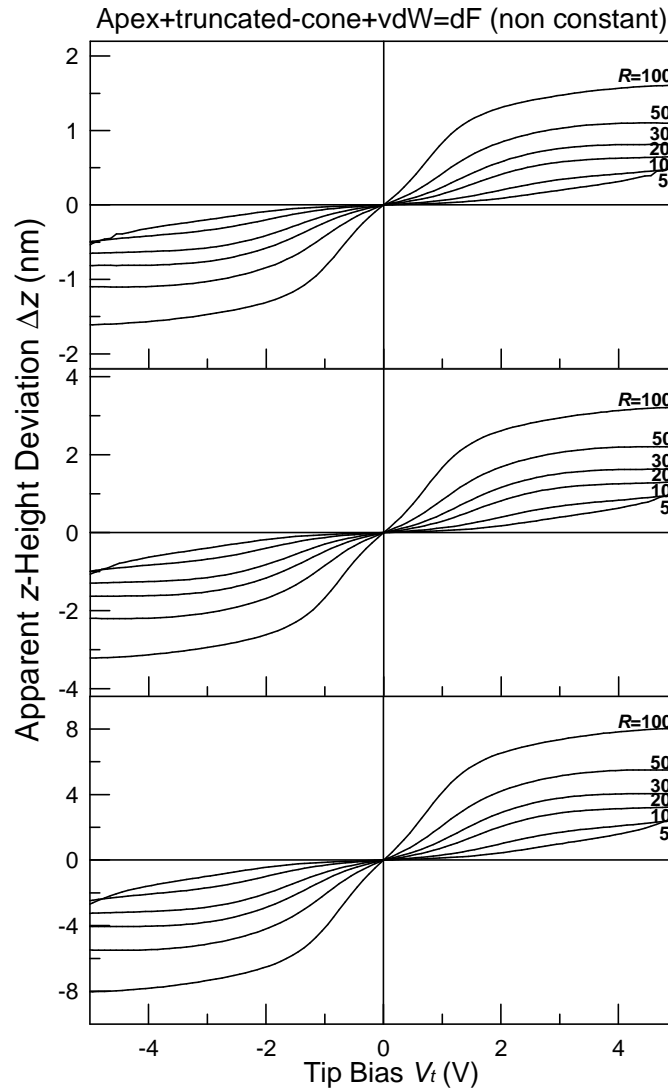


Fig. D.2 The apparent topographic height deviation Δz is as a function of V_t with various R when the $F'_{ts} = (F'_{apex} + F'_{tr_cone} + F'_{vdW}) = nonconst.$ The different contact potential (a) 0.1 V (b) 0.2 V, and (c) 0.5 V show the different variation heights. The Hamaker constant is set as 4×10^{-19} J.

D.3 Forces versus Tip-Sample Distance and Forces versus Degree

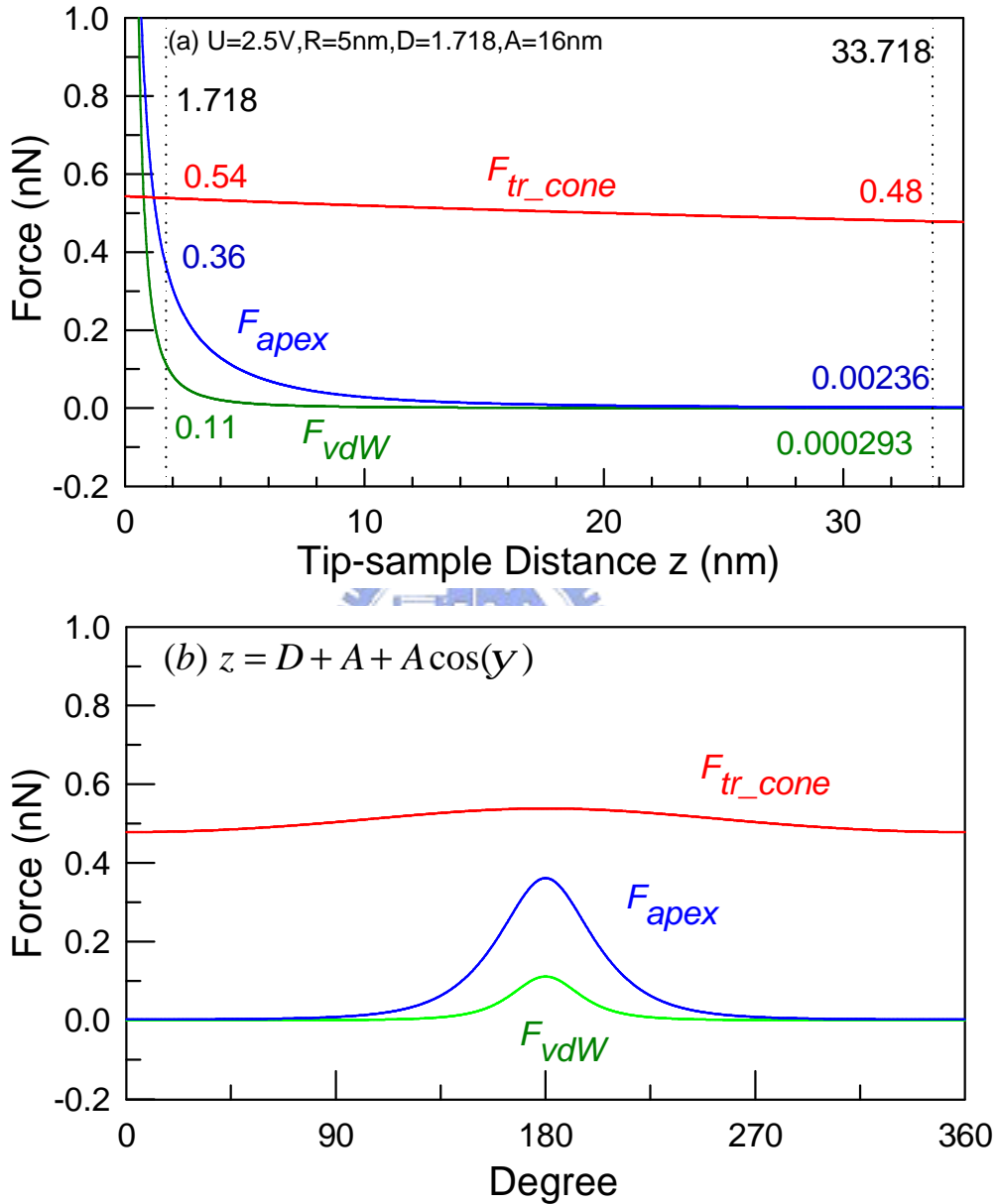


Fig. D.3 (a) The force as a function of tip-sample distance (z) calculated for $R = 2.5$ nm, $U = 2.5$ V, $A = 16$ nm and $D = 1.718$ nm. (b) The force as a function of degree is transformed from (a) by $z = D + A + A\cos(y)$, and the maximum Force occurs at the 180°; hence the tip-sample distance is the minimum at D . The truncated-cone force is larger than the other forces at D .