Supplementary to

Spatial horizons in amplitude and frequency modulation atomic force microscopy

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Discretising the tip-sample forces

In this Appendix a detailed description of how the continuum forces in (2) and (3) in the main text have been discretized is given. Discretization has allowed perfect control of each atom on the surface, i.e. these can be added and/or removed one by one if required. This is the key concept behind the generation of the figures (Figs. 2 and 3) in the main text.

1) GENERAL CONSIDERATIONS

The tip has been modeled as a sphere of radius R (5nm or 20nm) and atomic density ρ_t. Here d is the instantaneous-vertical distance between the tip and the sample as typically described in the literature[1]. We further use an intermolecular distance, i.e. a_0=0.165 nm as in other studies (Ref. 1). It is assumed that 'non-contact' occurs when $d>a_0$, and that the 'contact' situation occurs otherwise.

The atoms of the sample are located on the vertices of a cubical lattice with an atomic distance of s=0.2 nm and an atomic density $\rho_s = 1.25 \times 10^{29}$ atoms/m^3. This is a standard intermolecular distance in a solid[2]. The tip moves along the z axis just above a central atom. This motion characterizes the oscillation amplitude of the cantilever. The value of the Hamaker constant for a given atom has been calculated as $H=\pi^2 C \rho_s \rho_t$. The Hamaker for the tip-sample

2) THE van der Waals (vDW) SINGLE ATOM-TIP FORCE

The van der Waals (VdW) interaction-energy between an atom and an sphere of radius R is given by[3]

$$W_{vdW}(d) = \frac{C.\rho_T.\pi}{12.(d+R)} \cdot \left(\frac{3}{d^2} - \frac{2.(d+R)}{d^3} - \frac{3}{(d+2.R)^2} + \frac{2.(d+R)}{(d+2.R)^3} \right) \quad \text{(S1)}$$

Then the force (VdW for the atom-sphere interaction) is obtained as

$$F_{vdW}(d) = -\frac{\partial W(d)}{\partial d} \qquad \text{(S2)}$$

Giving

$$F_{vdW}(d) = -\frac{H}{2.\rho_s.\pi}\left(\frac{-(3.d+2.R)}{2.d^3.(R+d)^2} + \frac{1}{d^4} + +\frac{3.d^2+10.R.d+8.R^2}{2.(d+2.R)^4.(d+R)^2} - \frac{1}{(2.R+d)^4}\right) \qquad \text{(S3)}$$

The expression above (S3) has been used to calculate the single atom-sphere interactions where the sphere is the tip of the AFM.

3) FORCE BETWEEN A CYLINDRICAL SAMPLE AND THE TIP

A cylindrical, infinitely thick, sample composed of a lattice of atoms with an intermolecular distance s forms the main concept behind the definition of Spatial Horizon (SH). In particular, the SH is the cylinder (sample)-sphere (tip) interaction which produces the minimum detectable interaction as compared to an infinite plane (sample)-sphere (tip). Cylindrical samples have recently been discussed in the literature and the reader can refer to our recent work[4].

For the non contact case (d> a_0) the force between the tip and a cylindrical sample of radius r has been calculated with the use of (S3) by using M values of r within the range from 0 nm to XX nm (radial axis for the cylinder) and N values of d within the range from a_0 to 100nm (y axis). Take into account that for all the atoms which are not directly under the tip, i.e. other than the central

atom, only the vertical component of (3) is used for all the atoms that lie inside the cylinder. Finally the individual contributions are summed.

The final result can be written as $F_z(r,d)$. This force expresses the vertical value of the long range attractive interaction for an MxN matrix containing the values of the vertical force that is used in the simulation models to calculate the force (AM and FM)

4) FORCE BETWEEN A CYLINDRICAL SAMPLE AND THE TIP
Contact case ($d< a_0$)

The force is obtained using the DMT model as detailed in the main text.

We use $\delta = d-a_0$ as the indentation; $\delta<0$ if $d< a_0$ as usual[1].

The contact radius $a = \sqrt{R.\delta}$ is the radius of the circle drawn by the intersection of the tip and the free surface of the sample[5].

Then ($d<a_0$)

$$F_{DMT}(d) = F_{VdW}(a_0) + \frac{4}{3}.E.\sqrt{\frac{a^2}{R^3}} \qquad \text{(S4)}$$

Where the first term on the right stands for the adhesion force which is calculated with the use of (S3) when $d<a_0$ by simply putting $d=a_0$ in (S3).

5) DISCRETIZATION: Contact case $d<a_0$

For the F_{DMT} expression (S4) is used only if the contact surface (circle drawn over the sample with radius a) is completely filled with sample atoms. Otherwise the contact force is smaller. This is done in order to establish the interaction due to less atoms than those that would otherwise be involved in the ntact and has a

similar significance to the cylinder described in point 3 above. The method to solve this case is what we have termed 'Discretization: contact case'.

N is the number of atoms of the sample surface that lie inside a circle of radius a. This radius is found using the atomic distance parameter, s. M is the number of atoms that actually lie inside the circle and that depends on the sample size. Obviously M≤N. N and M have been found by taking into account the distance between each atom of the surface of the sample and the 'central atom' (the one that is just below the tip-apex). It is assumed that the actual force is proportional to the relative number of contact atoms.

We write

$$n_R = M/N \qquad \text{(S5)}$$

Then, we get

$$F_{DMT}(d) = F_{VdW}(a_0) + n_R \cdot \frac{4}{3} \cdot E \cdot \sqrt{\frac{a^2}{R^3}} \qquad \text{(S6)}$$

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