Electronic Supplementary Material (ESI) for ChemComm.

Supplemental information to

The power laws of nanoscale forces in ambient conditions

Chia-Yun Lai, Tuza Olukan, Sergio Santos, Amal Al Ghaferi, Matteo Chiesa*

Laboratory for Energy and NanoScience (LENS), Institute Center for Future Energy (iFES),

Masdar Institute of Science and Technology, Abu Dhabi, UAE

Contents

Atomic force microscope AFM force spectroscopy

The AFM has been operated in amplitude modulation (AM) and the observables are the oscillation amplitude (A) and the phase shift (Φ). By recording these observables via standard amplitude and phase distance APD curves we can recover the interactions (conservative and dissipative) between the tip and the sample. We exploited the Sader-Jarvis-Katan (SJK) formalism (Eq.S1)[1] to reconstruct the conservative part of the force:

$$F(d) = 2k\int_{u=d}^{u=\infty}\left[\left(1+\frac{A^{1/2}(u)}{8\sqrt{\pi(u-d)}}\right)\Omega(u) - \frac{A^{3/2}(u)}{\sqrt{2(u-d)}}\frac{d\Omega(u)}{du}\right]du \qquad \text{(S1)}$$

where Ω is the normalized frequency shift expressed by:

$$\Omega(d) = \left[1+\frac{A_0}{QA}\cos(\Phi(d))\right]^{\frac{1}{2}} - 1 \qquad \text{(S2)}$$

Q is the quality factor and A_0 is the free amplitude. All the experiments have been carried out with a Cypher AFM from Asylum Research and standard OLYMPUS cantilevers (AC160TS). Since it is well-known that the tip radius R significantly affects the interaction force between the tip and the surface[2], R was constantly monitored *in situ* during the experiments.

The experimental steps to take AFM-APD curves are:

1) A graphite sample was mounted for standard AFM (Cypher AFM from Asylum Research) data acquisition.

2) A new AFM cantilever (OLYMPUS AC160TS with k=40N/m and Q factor≈ 500) was mounted on the AFM cantilever holder.

3) The value of R was monitored[2] by acquiring standard[3] APD curves and these were used to compute the critical amplitude A_c value in raw Volt units[2]. The A_c value was then converted into meter units and employed to compute R with the use of the expression $R=4.75(A_c)^{1.1}$.

4) Approximately 100-200 APDs were acquired immediately after computing the value of R.

5) The tip was then gently blunted to an arbitrary size as done elsewhere[2,4] by imaging in the repulsive regime while monitoring the A_c value.

6) A new data set of 100-200 APDs was collected for the new value of R.

7) Steps 3 to 6 were carried out until a range of values for R were collected with a given cantilever.

Full figures corresponding to Fig. 2a and 2b in the main text

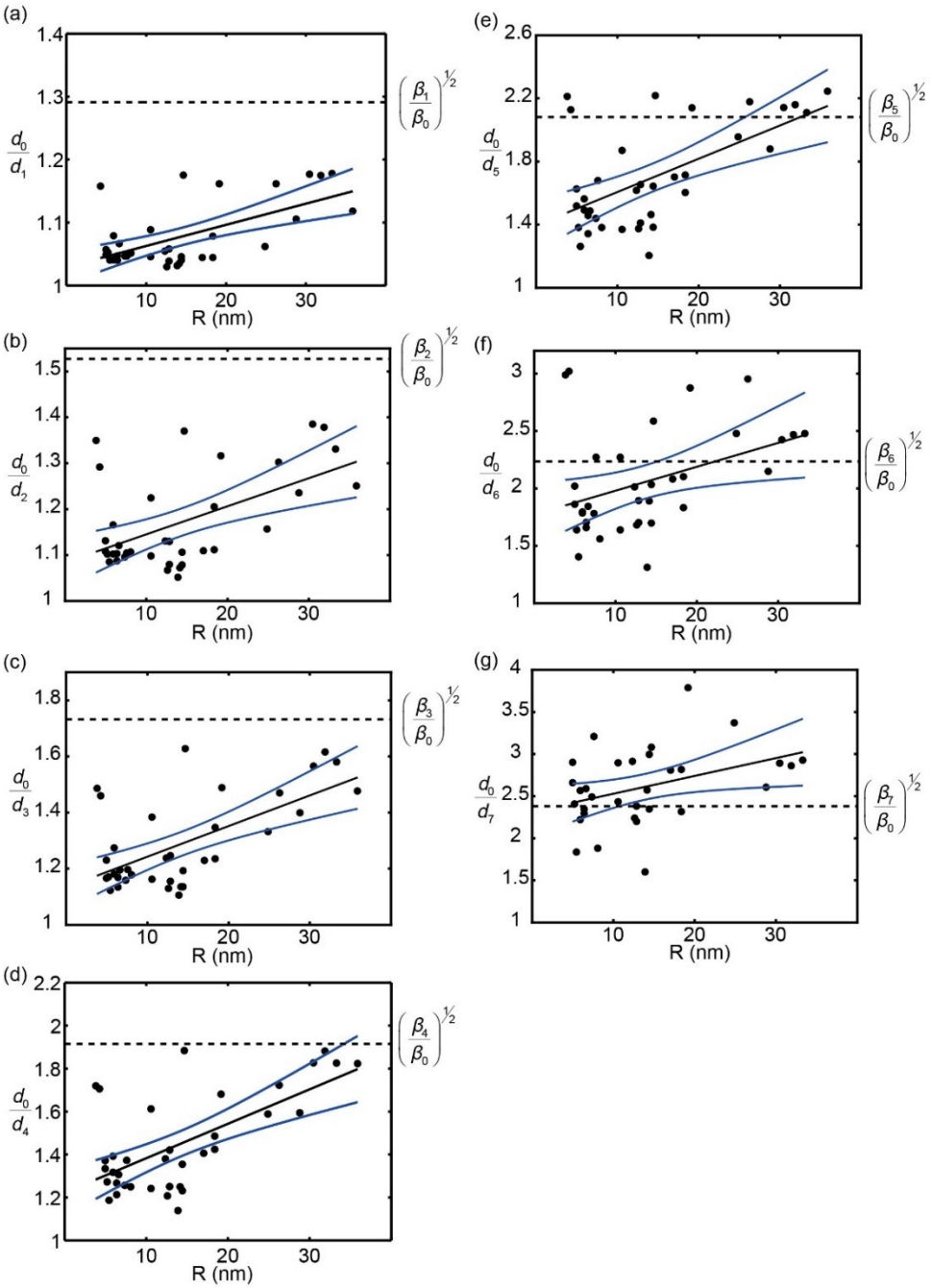

Figure S1. Values of d0/d1 (a), d0/d2 (b), d0/d3 (c), d0/d4 (d), d0/d5 (e), d0/d6 (f), d0/d7 (g) versus tip radius R with the fit (black line) and 95% of CI (blue lines). Black dashed lines indicate the value of $(\beta1/\beta0)^{1/2}$ (a), $(\beta2/\beta0)^{1/2}$ (b), $(\beta3/\beta0)^{1/2}$ (c), $(\beta4/\beta0)^{1/2}$ (d), $(\beta5/\beta0)^{1/2}$ (e), $(\beta6/\beta0)^{1/2}$ (f) and $(\beta7/\beta0)^{1/2}$ (g).

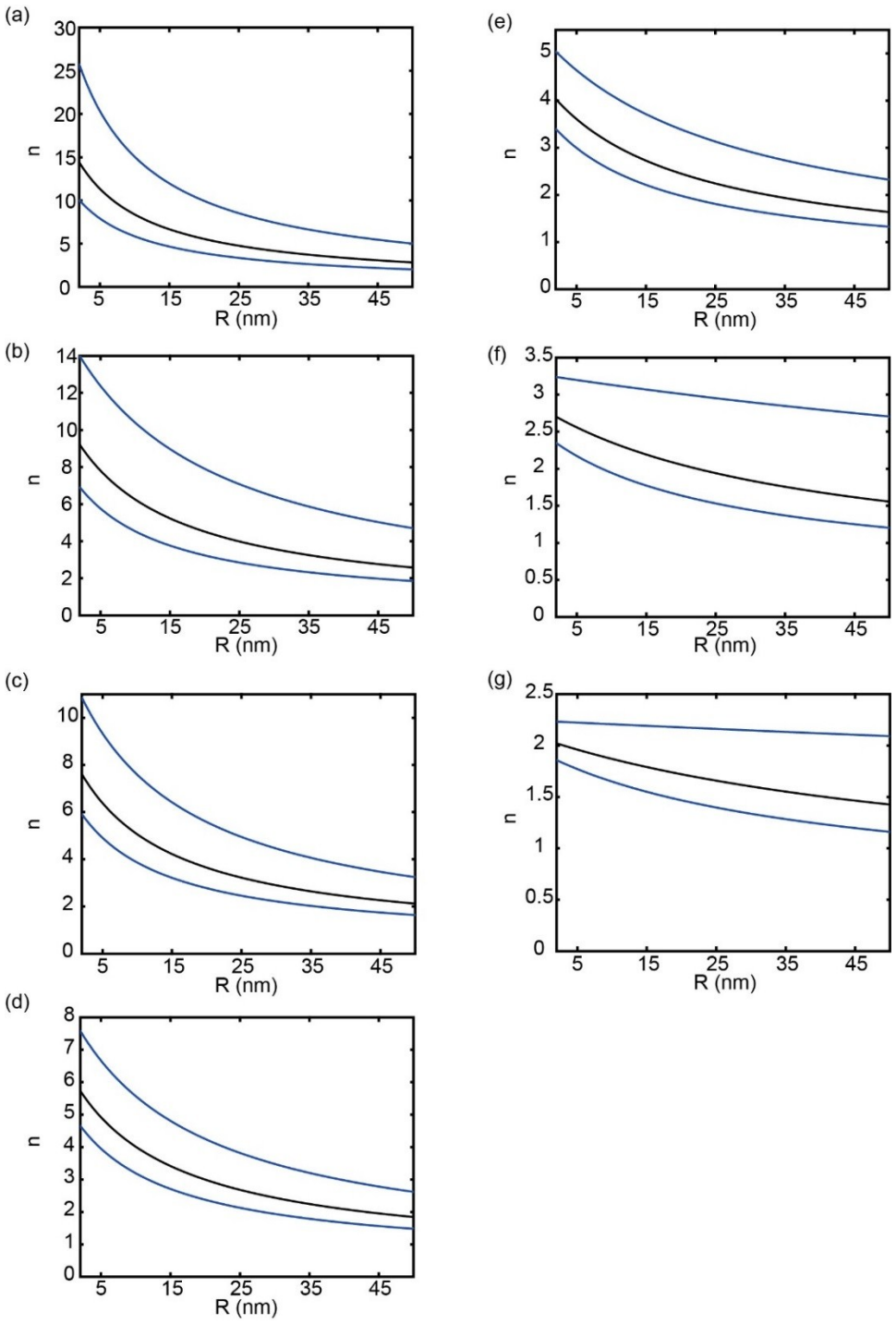

Figure S2. The powers n as a function of R decreases with R increase. Continuous black line in (a, β1/β0), (b, β2/β0), (c, β3/β0), (d, β4/β0), (e, β5/β0), (f, β6/β0), and (g, β7/β0) show the predicted n while the continuous blue line in (a, β1/β0), (b, β2/β0), (c, β3/β0), (d, β4/β0), (e, β5/β0), (f, β6/β0), and (g, β7/β0) show the 95% of CI

Variations in tip size prediction and possible induced errors

We have conducted the calculations for values of 1.08-1.12 and 1.16. In the original work we employed a power of 1.12 but we wrote 1.1, which is exact to one decimal place. In the original paper where the powers are given (Santos, S., L. Guang, et al. (2012). "A method to provide rapid in situ determination of tip radius in dynamic atomic force microscopy." Review of Scientific Instruments **83**: 043707-043717.) a value of 1.12 is given for the cantilever model we have employed here (OLYMPUS AC160TS).

The rationale leading us to employ these numbers in this revised version is as follows.

1) The manufacturer of these OLYMPUS AFM cantilevers estimate tip radii, for new tips, of approximately 7-11 nm (http://www.asylumresearch.com/Probe/AC160TS,Olympus) Therefore our method of tip radii estimation for new tips should be in the range of these values when the tips are new.

2) When employing powers much lower than 1.1, i.e. 1, or larger, i.e. 1.2, we obtain tip radii that are very large, i.e. 40 nm or more, or very small, i.e. 1 nm or less, respectively for the new tips. This leads us to deducing the right power has to be in between these numbers, in agreement with (Santos, S., L. Guang, et al. (2012). "A method to provide rapid in situ determination of tip radius in dynamic atomic force microscopy." Review of Scientific Instruments **83**: 043707-043717)

RANGE OF POWERS FOR TIP PREDICTION

For powers of 1.08 the new tips employed here produced values of R ranging from 8-11 nm.

For powers of 1.12 the new tips employed here produced values of R ranging from 4-6 nm.

For powers of 1.16 the new tips employed here produced values of R ranging from 1.7-2.5 nm.

Reproducibility:

Note: The reviewer/s editors can see these values when entering the appropriate value of Ac in the file Dx_Main.m that can be found at https://github.com/nanoscalepowerlaws.

The name of the variable is (matlab code):

Power_CA=1.12; also 1.08 or 1.16 can be employed.

The resulting variable with the tip radii is ALL_Radius_Ac

Instructions on how to run the Dx_Main.m code can be found on the readme.md file at github.com

https://github.com/nanoscalepowerlaws

Account: https://github.com/nanoscalepowerlaws

Arguably, since the manufacturer claims a nominal size for new tips ranging from 7-11 nm the power law for the critical amplitude method should be closer to 1.08 than to 1.12, as we have employed in this work. Nevertheless we decided to employ 1.12 since this is the power reported in the Review of Scientific Instruments. Overall, we believe that the power is, on the other hand reasonable. For the benefit of the reviewer/s, editor/s and the readers we have now produced the results in Fig. 3 of the original manuscript for powers of 1.08 and 1.16 and added them to the supplementary. We are also reporting the statistics of Table II in the original manuscript in the supplementary for these values of the power. The details are below (as in supplementary):

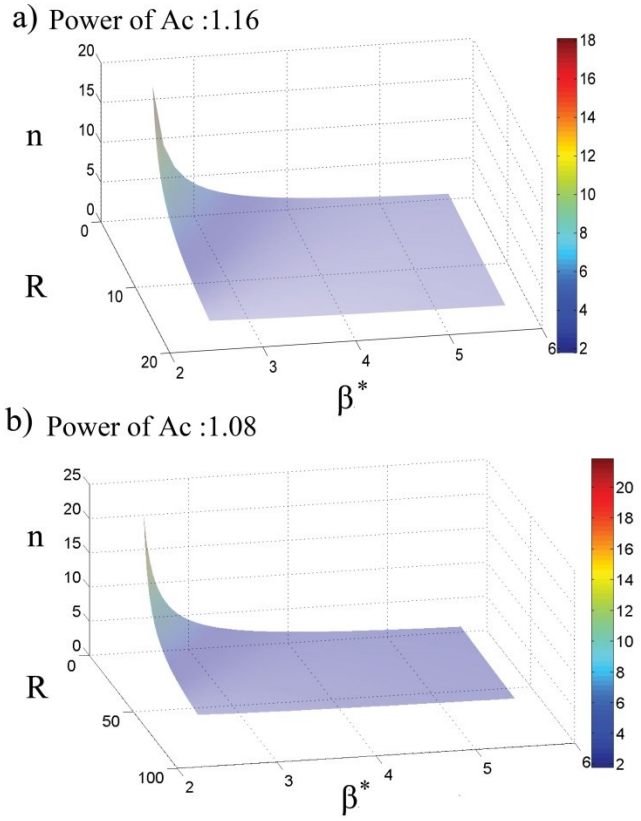

Fig. S3 a) Experimental prediction of n according to Eq. (13) for a power in the *A*c method of a) 1.16 and b) 1.08.

λ_2	λ_2 at **CI 95%**	λ_1	λ_1 at CI 95%	λ_0	λ_0 at CI 95%	RR	Power A_c
0.027	0.018-0.035	0.361	0.332-0.390	0.104	-0.022-0.231	0.72	1.16
0.014	0.009-0.018	0.361	0.332-0.390	0.099	-0.029-0.227	0.72	1.12
0.07	0.05-0.09	0.361	0.0332-0.390	0.092	-0.037-0.222	0.72	1.08

Table SI. Results for the range of power in the *A*c method.

The tip radii variations (predictions) are:

1) For Power=1.08 from R=8 to 70 nm
2) For Power=1.12 from R=4 to 36 nm
3) For Power=1.16 from R=2 to 18 nm

The λ_2 parameter accounts for variations in power law with tip radius R.

The range of tip radii approximately halves from a power of 1.12 to a power of 1.16 and doubles with the 1.08. The λ_2 parameter follows a similar trend (see table S1).

There are two possible outcomes:

Outcome 1

If (assuming the power law should be larger than 1.12) the tip radii are underestimated in Fig. 3 and Table II due to the 1.12 power law, the real transition in power law should occur at smaller tip radii than those predicted in the main text.

Outcome 2

If (assuming the power law should be smaller than 1.12) the tip radii are overestimated in Fig. 3 and Table II due to the 1.12 power law, the real transition in power law should occur at larger tip radii than those predicted in the main text.

A transition would, on the other hand, be expected irrespective of the power law for the critical amplitude method for monitoring tip radii, i.e. from 1.08 to 1.16 which are reasonable powers in order to stay within the range predicted by the manufacturer.

RANGE OF intermolecular distances, i.e. a_0

An argument in relation to the range of intermolecular distances and possible variations in predictions in the main text is given next as follows.

Our data shows that forces are detectable, i.e. values in the order of 1-10pN or larger (in absolute terms) for a range of distances of 1-2 nm above the distance at which minima in force occurs, i.e. the force of adhesion. See for example data from Tip 1 (first data point or curve) for R=5 nm (critical amplitude of 0.24 Volts) and R=26 nm (critical amplitude 1.06 Volts) in Figure S4a (normalized forces with the absolute of the force of adhesion in Figure S4b).

This data has been taken by polotting the raw vectors in matlab, i.e. the matlab file

ALL_DATA_STATS_0_FC1.mat (Ac=0.24 Volts) and ALL_DATA_STATS_0_FC8.mat (Ac=1.06 Volts) and can be accessed in dropbox (https://www.dropbox.com/home/PowerLaw).

These distances, particularly for the smaller values of β, i.e. β_1/β_0=0.25/0.15=0.16 and β_2/β_0=0.35/0.15=2.3, as measured from minima in Fts, i.e. Force of adhesion F_{AD}, are in the range of 1-2 nm as observed in Figure S4 (we note that these distances held very well throughout the data acquired in the approximately 2500 force curves).

These smaller values of β are particularly interesting because they show that the data does not obey the inverse square law, i.e. $1/d_2$ in (1), particularly well throughout all the figures in the text when the tip radii are small. See for example β_1/β_0 (continuous lines) in Figure 2c and Fig. 3b in the main text for the smaller values of the β ratio. These values are also large compared to intermolecular distances, i.e. d_1 and d_2>> 0.18 nm since d_1 and d_2~ 1-2nm. These two conditions suffice for the approximation below regarding uncertainties in a0.

The parameters being tested by Eq. (6) in the main text can be written with a certain tolerance in a_0, i.e. accounting for uncertainties the intermolecular distance a_0, as follows:

$$\left[\frac{\beta_i}{\beta_0}\right]^{1/n} = \frac{d_0 + \varepsilon}{d_i + \varepsilon} \qquad \text{(S2)}$$

wher ε is the uncertainty in a_0. In the main text d_0 and d_i are the distances already corrected by adding a_0 to the distances measured from $F_{ts}=F_{AD}$, i.e. coinciding with minima in force and are of the order of 1-2 nm as stated above, in particular for i=1 or 2, i.e. β_1/β_0=0.25/0.15=0.16 and β_2/β_0=0.35/0.15=2.3.

Thus, since $a_0 \approx 0.18$ nm (as employed in the main text and Figures 2 and 3 and Tables I and II, the uncertainty should also be of similar magnitude) an uncertainty of the same order of magnitude would not dramatically alter (S2). This shows that the predictions of the main text should stand variations in the value of a_0 of 1-2 Å.

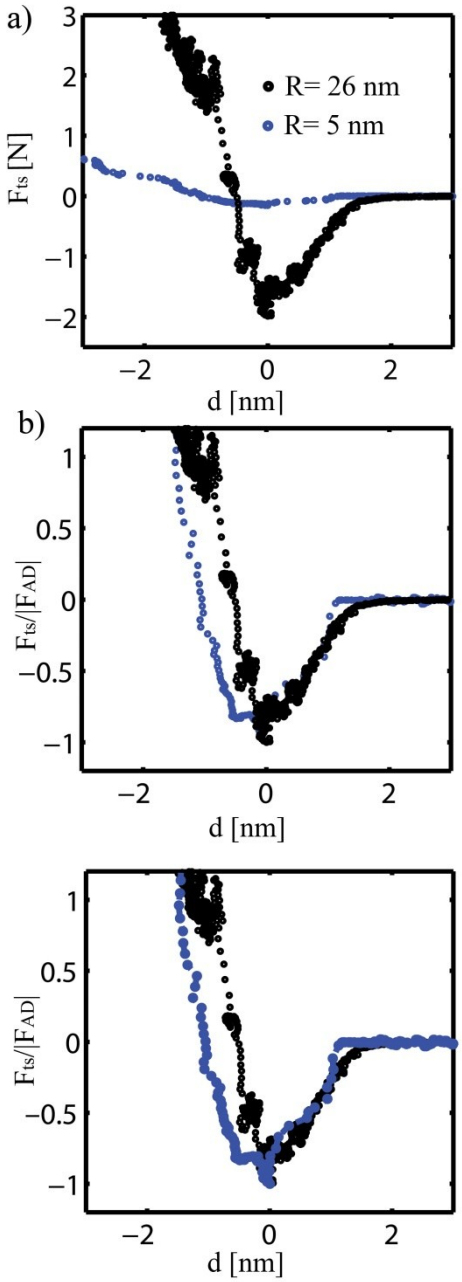

Figure S4. Force profiles for R=5 nm (blue) and R=26 (black) nm in a) standard units (Newtons and meters) and b) where the force has been normalized with the absolute of the adhesion force for comparison between the data for the two force profiles. c) Samer figure as b) but the data of the sharpest tip (blue) is placed on top in order to allow easy visual comparison. Reproduced here from the supplementary.

Raw data sets and codes for implementation

The raw data, detailed instructions and scripts employed to carry out this work can be found at:

https://github.com/nanoscalepowerlaws

https://github.com/FSDataAnalysis/PowerLawsNanoscaleForces

The repository is public and no username or password are necessary.

https://www.dropbox.com/home/PowerLaw

Dropbox username: nanoscalepowerlaws@gmail.com

Password: 123456

Reference

1 Katan, A. J., van Es, M. H. & Oosterkamp, T. H. Quantitative force versus distance measurements in amplitude modulation AFM: a novel force inversion technique. *Nanotechnology* **20**, 165703, (2009).

2 Santos, S. *et al.* A method to provide rapid in situ determination of tip radius in dynamic atomic force microscopy. *Review of Scientific Instruments* **83**, 043707, (2012).

3 Ziegler, K. J. *et al.* Bistable nanoelectromechanical devices. *Appl. Phys. Lett.* **84**, 4074, (2004).

4 Ramos, J. Tip radius preservation for high resolution imaging in amplitude modulation atomic force microscopy. *Appl. Phys. Lett.* **105**, 043111-043114, (2014).