

Non-additivity of molecule-surface van der Waals potentials from force measurements

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Van der Waals (vdW) forces act ubiquitously in condensed matter. Their description as an inherently quantum mechanical phenomenon was developed for single atoms and homogeneous macroscopic bodies by London¹, Casimir², and Lifshitz³. For intermediate-sized objects like organic molecules an atomistic description is required, but explicit first principles calculations are very difficult since correlations between many interacting electrons have to be considered⁴⁻⁷. Hence, semi-empirical correction schemes are often used that simplify the vdW interaction to a sum over atom-pair potentials⁸⁻¹⁰. A similar gap exists between successful measurements of vdW and Casimir forces for single atoms on the one hand¹¹⁻¹⁵ and macroscopic bodies on the other^{16,17}, as comparable experiments for molecules are absent.

Here we use the extremely sensitive force detection of an atomic force microscope¹⁸⁻²¹ in combination with its molecular manipulation capabilities^{22,23} to determine long-range vdW potentials between a series of related molecules and a metal surface in excellent agreement with theory. The results further allow us to confirm the asymptotic r^{-3} force law, to specify its validity range, and even to quantify the non-additive part of the vdW interaction which is particularly challenging for theory. In the present case experiments indicate that cooperative effects due to deconfinement of electrons²⁴ account for approximately 10% of the total interaction. This non-additivity is of general validity in molecules and thus relevant at the intersection of chemistry, physics, biology, and materials science²⁵⁻²⁷. As non-additive contributions (which can amount to several eV in bio-molecules) cannot, by construction, be accounted for in state-of-the-art density functional calculations, we suggest further development in that direction.

Even for two electrically neutral objects devoid of any static multipole moments, quantum mechanical fluctuations lead to the attractive dispersion or van der Waals interaction¹. The most accurate method available today to calculate electron correlations in general and the vdW interaction in particular, the coupled-cluster approach²⁸, is computationally so expensive that it can only serve as a "gold-standard" for small systems (up to ~ 100 light atoms). In contrast, the most widely used methods to calculate the vdW interaction for systems of practical relevance, namely the semi-empirical dispersion correction schemes^{8,9} for density functional theory (DFT), employ drastic simplifications: The vdW interaction is obtained by a pair-wise summation over atom-atom potentials and, related, the polarizability of complex objects such as multi-atomic molecules is

decomposed into a sum of atomic, possibly volume-scaled, polarizabilities. Moreover, the analytically derived asymptotic relation for the atom-atom potential $V_{a-a}^{\text{vdW}}(r) = -C_6 r^{-6}$ [8, 9] is attenuated by a purely empirical damping function and used at short distances.

Here we present quantitative measurements of the vdW interaction that enable us to scrutinize these simplifications and to reconstruct the asymptotic and short range vdW potentials in an approach that combines experiment and theory. In our experiments we measure the distance dependence of the molecule-surface interaction between a Au(111) surface and single molecules. The asymptotic atom-surface vdW potential $V_{a-s}^{\text{vdW}}(z) = -C_3(z - z_0)^{-3}$ is closely related to the $1/r^{-6}$ atom-atom law and can be obtained from the latter analytically by integrating over half space⁴. Atom-surface and atom-atom potentials have, up to now, only been measured directly for highly polarizable Rydberg atoms^{11,12}, or reconstructed from bound state resonances in elastic scattering experiments for noble gas atoms, H₂ and D₂ [13–15].

We have carried out our experiments on three π -conjugated poly-naphthalene derivatives, namely 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTCDA), and its perylene and terrylene counterparts PTCDA and TTCDA (Fig. 1). The investigation of this series of structurally related molecules allows us to gain insight into size-dependent cooperative effects in the vdW interaction that break its additivity. In contrast to previous force-distance measurements^{16,17} that were designed to determine van der Waals and Casimir interactions between macroscopic bodies, we perform *force gradient* (dF_z/dz) vs. distance (z) measurements, using a commercial qPlus quartz tuning fork sensor¹⁸ in a combined CREATEC scanning tunnelling / non-contact atomic force mi-

croscope (STM/nc-AFM)^{22,23}. It was recently demonstrated that qPlus sensors yield very precise force gradient spectra and images^{19–21}.

Experiments

In the experiment, the gold-covered tip of the qPlus sensor is approached at zero bias voltage to an isolated adsorbed molecule until a chemical bond between the tip and the molecule forms^{22,23,29–32}. Then, the tip is retracted again, such that the contacted molecule is gradually lifted into an upright position^{22,23}, detached from the surface and finally lifted by approximately 2 nm (Fig. 1). The molecule-surface attraction aligns the diagonal of the tip-suspended molecule with the surface normal. Throughout the lifting process, changes in the qPlus resonance frequency are recorded. Our qPlus sensor converts force gradients dF_z/dz into resonance frequency shifts Δf with a proportionality constant of $\xi = 8.4 \text{ Hz}/(\text{N/m})$. The high stiffness of the qPlus sensor of 1800 N/m and its small oscillation amplitude $A < 0.2 \text{ \AA}$ allow removing the molecules from the surface without abrupt rupture events. Thus, the manipulation is reversible and we perform up to 45 up-and-down cycles (90 $\Delta f(z)$ spectra) within one contacting experiment before the molecule is released from the tip by a voltage pulse. The contribution of tip-surface forces to the measured force gradient is removed by subtracting the bare-tip approach curve recorded at the beginning of each contacting experiment. The cleanliness and stability necessary for a straightforward data interpretation is achieved by working in ultra-high vacuum and at low temperature ($T = 5 \text{ K}$). Details on the sample preparation are contained in the Supplementary Information Section S1.

When determining a force gradient law $dF_z/dz(z)$, the accurate quantification of z is as important as the precise measurement of dF_z/dz . As the orientation of the molecule is stabilized by the molecule-surface attraction, only the absolute height remains to be determined. Here we use the following solution: We use the lifted molecule itself as a ruler, employing the model of the lifting process that was developed in Ref. 23. In short, the force gradients $dF_z/dz(z)$ measured when lifting the molecules from the flat into the upright configuration, together with molecular-mechanics simulations and the known lengths of the molecules, allow us to precisely link relative experimental tip heights (z-piezo voltages) to absolute heights of the molecules above the surface. In that way, the molecular geometries, i.e. individual atom heights z_i above the surface can be obtained for the entire lifting process. With a tip-molecule bond length of 2.2 Å we obtain tip-sample distances of $z_{\text{tip}} = 13.4 \text{ Å}$ (NTCDA), 17.5 Å (PTCDA), and 21.7 Å (TTCDA), for the upright molecules. The insets in Fig. 2a show the respective geometries.

Regarding the accuracy of the force gradient measurements, a peak-to-peak noise in Δf below 0.05 Hz is required, more than one order of magnitude lower than in the seminal experiment in Ref. 19. This is achieved by averaging over several hundred carefully aligned individual Δf curves (each with ~ 0.4 Hz noise level), obtained in 11 NTCDA, 7 PTCDA and 7 TTCDA contacting experiments (see Section S2 of the Supplementary Information). These global averages exhibit a noise level as low as 0.02 Hz and form the basis of our analysis. The averaged curves from each individual contacting experiment are shown in Fig. 2a. We note that while the curves scatter considerably as long as the molecules are under the influence of the surface corrugation, they become perfectly reproducible (exemplified for TTCDA in the inset of Fig. 2a) in the region

of interest where the molecules and the surface are well separated and the asymptotic vdW force law is expected to apply. It is this reproducibility that allows us to average over several contacting experiments.

Results

Fitting model. Theory predicts the asymptotic interaction potential for an atom in front of a surface to be a power law of the form

$$V_{\text{a-s}} = -C_{\alpha}(z - z_0)^{-\alpha}, \quad (1)$$

with material-specific coefficients C_{α} (depending on the atomic polarizability and the dielectric function of the substrate), the so-called van der Waals reference plane z_0 [4], and the exponent α which for the dipolar dispersion interaction is 3 (see Supplementary Information Section S3). Since in our experiment the tip-suspended NTCDA, PTCDA and TTCDA molecules are not co-planar with the surface and hence their vertical extensions in z -direction are similar to the molecule-surface separations (see Fig. 1), each molecule cannot be approximated (different from an atom) as a point object. Thus, the measured force-gradient curves in Fig. 2a cannot be fitted directly with the second derivative of Eq. 1 because there is neither an unique value for z nor for C_3 . To be able to analyse our results in terms of the vdW force law, we therefore choose a representation commonly used in theory and *formally* represent the molecule by a collection of (fluctuating) atomic point dipoles. Corresponding to Eq. 1, the molecule-surface vdW potential

$$V_{\text{mol-s}} = - \sum_{i=1}^M \frac{\gamma_i C_{\alpha,X}}{(z_i - z_0)^{\alpha}}. \quad (2)$$

is then obtained by summing over M atoms at the heights z_i (Fig. 1) in each molecule. Since the atomic vdW coefficients defined by this approach, $C_{\alpha,X}$ with $X=(N)TCDA$, $X=(P)TCDA$, or $X=(T)TCDA$ can be different for *NTCDA*, *PTCDA* and *TTCDA*, we go beyond the approximation of additive polarizabilities and vdW potentials, despite formally breaking the molecules up into atomic point dipoles. The reference plane z_0 , being a property of the surface, is identical for all three molecules. The distribution of polarizability within each molecule is estimated with the help of theory. We employ weighting factors γ_i that are taken from the semi-empirical dispersion correction scheme vdW^{surf} [10] (0.29 for hydrogen, 0.67 for oxygen and 1.0 for carbon, see Table S1 and Section S4 of the Supplementary Information). For a meaningful comparison with vdW^{surf} , this choice (well-defined but not unique in the theoretical framework) is preferable. Note that the precise choice of the γ_i has no influence on any of our conclusions.

In fitting our force-gradient data with the second derivative $d^2V_{\text{mol-s}}/dz_{\text{tip}}^2$ of Eq. 2, we proceed in two steps. Initially, we examine the exponent α of the asymptotic behaviour found in experiment. Having established the exponent $\alpha = 3$, we then determine the $C_{3,X}$ coefficients from Eq. 2 and analyze the result.

Force law. To determine the force law we vary the exponent α from 1 to 5 while optimizing z_0 and all three $C_{\alpha,X}$ at each step. We use a weighted least-squares regression minimizing $s(z_0, C_{\alpha,X})$, which is a measure for the goodness of the simultaneous fit of all three Δf curves. More information on data processing and fitting can be found in Sections S2 and S4 of the Supplementary Information. The results of the fit are shown in Fig. 2b. The best fit is obtained for $\alpha = 2.85$,

which is close to the expected value $\alpha = 3$ for the asymptotic vdW potential. Furthermore, there is a clear variation of z_0 with α . In particular, the region of physically sensible values⁴ close to $z_0 \approx d_{\text{Au}(111)}/2 \simeq 1.2 \text{ \AA}$, where $d_{\text{Au}(111)}$ is the Au(111) interlayer spacing, is quite narrow with $2.75 < \alpha < 3.2$. Both results confirm the asymptotic interaction between constituent parts of the molecules ('atoms') and the surface to be

$$V_{\text{a-s}}^{\text{vdW}}(z) = -C_3(z - z_0)^{-3} \quad (3)$$

Further analysis shows that this expression is valid for $z > 4.8 \text{ \AA}$ (see below). This power law proves that in our experiment the vdW interaction dominates the molecule-surface potential, with other interactions playing a minor role. This conclusion confirmed by a detailed analysis of electrostatic forces in our experiments (see below).

As an important benchmark for theory, we find a sharp minimum in s precisely at the theoretically well-founded van der Waals reference plane position $z_0 = d_{\text{Au}(111)}/2$ if we fix α to the asymptotic value of 3 (Fig. 2c).

C_3 coefficients. We now turn to the determination of precise C_3 coefficients within the theoretical model given by Eq. 2. For a correct recovery of the (by definition asymptotic) C_3 values, it is crucial to exclude the z_{tip} -interval where the height z_{mol} of the lower end of the molecule above the surface (Fig. 1) is small and deviations from Eq. 3 are expected, due to Pauli repulsion, higher order terms of the van der Waals multipole expansion, and the invalid point dipole approximation. To identify the minimal allowed z_{mol} , we fit the experiments in intervals that start between $z_{\text{mol}} = 3.5 \text{ \AA}$ and 7.0 \AA (yellow regions in Fig. 3a) and end at the largest z_{tip} values reached. We find that all fit

parameters (Fig. 3b) and the fit quality s (inset of Fig. 3a) converge to a plateau for $z_{\text{mol}} \geq 4.8 \text{ \AA}$. Below this threshold, the fitted parameters depend strongly on the starting value of the fit region, with z_0 becoming unphysically small. The value of the threshold is consistent with calculations in the random phase approximation (RPA)³³ (see Supplementary Information Sections S7 and S8). Fits for a starting value of $z_{\text{mol}} = 5.3 \text{ \AA}$ are displayed in Fig. 3a, while Fig. 3c shows how the fit quality depends on the individual $C_{3,X}$ values. For all three molecules we find a clear minimum in s , for NTCDA at $C_{3,N} = 24.9 \text{ kcal/mol\AA}^3$, for PTCDA $C_{3,P} = 25.9 \text{ kcal/mol\AA}^3$, and for TTCDA $C_{3,T} = 28.0 \text{ kcal/mol\AA}^3$. The respective data points are plotted in Fig. 4a.

Non-additivity of experimentally determined C_3 coefficients. The C_3 coefficients determined with our approach show a clear trend of increasing with molecular size, i.e., the per-atom molecule-surface interaction rises in the sequence NTCDA, PTCDA, TTCDA. This is a clear signature of cooperative effects between the atoms in the extended π -electron system, confirming the importance of the non-additivity in the molecular polarizabilities without which our experimental findings cannot be explained. This superlinearity accounts for $\sim 10\%$ of C_3 for TTCDA if compared to NTCDA.

Fig. 4a also displays C_3 coefficients from the computationally expensive DFT + RPA method. It calculates the macroscopic response of the molecule to electrical fields from a full microscopic quantum theory of the molecule, allowing insight into the role played by the quantum mechanical electronic states. Apart from slightly larger absolute values, it predicts a superlinearity in good agreement with experiment. The origin of the superlinear rise of C_3 is the increasing deconfine-

ment of electrons in the direction of the long molecule axis. This leads to a strong increase in the per-atom polarizability of the carbon atoms (averaged over all carbon atoms in each molecule) for NTCDA, PTCDA, and TTCDA at small imaginary frequencies along the respective axis (Fig. 4b). The anisotropy originates from the anisotropic shape of the molecules. For an infinitely long molecule, electrons would form a metallic band and the static polarizability in this direction would diverge. For finite molecules, the band breaks up into confined states, which are the molecular orbitals³⁴. The longer the molecule, the more closely spaced are these confined states on the energy axis. This leads to increasing contributions of corresponding electronic transitions to the low-frequency molecular polarizability and hence to C_3 . Indeed, we find that the rising weight of the transition between the highest occupied and lowest unoccupied orbitals alone is responsible for more than 90% of the superlinearity from NTCDA to TTCDA (Supplementary Figure S9). In essence, the deconfinement of valence electrons washes out the ‘atomic individuality’ in the molecule and introduces cooperative behaviour. More details can be found in Supplementary Information Section S9.

By construction, the semi-empirical dispersion correction vdW^{surf} does not exhibit a superlinear increase of C_3 (Fig. 4a), because it is based on volume-scaled atomic polarizabilities (see Supplementary Information section S6). However, the fact that its deviation from experiment is of similar size as the experimentally observed superlinearity suggests that with vdW^{surf} a semi-empirical correction scheme of sufficient accuracy is available such that efforts to include cooperative effects would make sense. We stress that this would constitute a most important advance, because for systems involving larger molecules, such as functional self-assembled monolayers or

surface-immobilized biomolecules, 10% of the total van der Waals interaction, which may amount to several eV, are a significant energy that can influence the properties profoundly. The conclusions drawn here are valid not only for dispersion corrected DFT methods but for the entire class of force-field based simulations of conjugated molecules.

Surface holding potential. We briefly note here that in conjunction with the analysis of Ref. 23 the results of the present work mean that the *complete* adsorption potential of a large organic molecule by force experiments has been mapped out, including the asymptotic (this paper) and the short-distance (Ref. 23) regimes (see Section S10 of the Supplementary Information). The asymptotic potential is plotted in Fig. 4c (green). We have reported here that for $z < 4.8 \text{ \AA}$ the asymptotic potential loses its validity. In this region, the potential extracted from force measurements with the molecule close to the surface (orange)²³ is a good approximation.

Conclusion

We end the paper by discussing two possible sources of systematic errors. Firstly, the presence of electrostatic forces in the junction; since these are also long-ranged, they could add to measured force gradients. Secondly, a deviation of the orientation of the molecule in the junction from the vertical; this could invalidate the atomic positions which enter our fitting procedure. Our analysis shows that both electrostatic forces and deviations from the vertical orientation do not play a significant role.

While it is generally true that precise positions of molecules in scanning probe junctions are

difficult to establish, our experiment offers an exceptional degree of control: Since we attach the tip to the molecule while it is still flat on the surface and then retract the tip gradually, we can be sure that at the point when the molecule leaves the surface it does so in the upright geometry. The force gradient data prove this unambiguously. The crucial question is whether this geometry is maintained when the tip is retracted further. In order to analyse this question, we have determined the directionality of the tip-oxygen bond, since a significant directionality of this bond would be one mechanism that could tilt the molecule out of the vertical once the contact to the substrate is broken. A DFT calculation (see Supplementary Information Section S5) shows that there is essentially no directionality of this bond in a broad angular range. While this means that the tip-oxygen bond will not rotate the molecule out of the vertical, it also implies that it will not pull it back into the vertical if for some other reason it tilts out of the vertical. But as we will argue now, the absence of a restoring force from a directional bond means that any tilting is easily detectable in experiment (and indeed sometimes detected).

Hypothetical asymmetries in the tip would induce a torque on the tip-suspended molecule. If the molecule responds to this torque by rotating around the tip-oxygen bond, the torque increases further and finally flips the molecule completely to the tip. Experiments where we observe this effect have been excluded from our analysis (see Supplementary Information Section S2). If the molecule does not flip up, the torque must be so small that *even at the largest tip surface distances in the experiment* the restoring force originating from the molecule-surface attraction stabilizes the molecule in a vertical orientation. Since those restoring forces increase rapidly as z^{-4} when approaching the surface (whereas the tilting torque arising from the tip asymmetry is independent

of the tip surface distance and thus remains small), they completely dominate any tip-induced torque in the relevant part of the experiment. The molecular orientation is thus determined by the molecule-surface interaction only, as in our molecular mechanics model that yields the employed z_i , with the result that the orientation of the molecule is vertical.

Regarding the electrostatic forces, we have calculated the electrostatic interaction energy between the three tip-attached molecules and the surface for an exemplary molecular height of $z_{\text{mol}} = 7 \text{ \AA}$. We find that this interaction is only a few meV for all three molecules (-3.1 meV for NTCDA, -5.1 meV for PTCDA and -2.1 meV for TTCDA, see Supplementary Information Section S5). At this distance, the van der Waals interaction energy as calculated with vdW^{surf} is approximately one order of magnitude larger. The reason for the very small electrostatic interaction is the fact that there is no large-scale charge transfer between tip and molecule; all bond-related charge reorganization takes place in the direct vicinity of the local tip-oxygen bond. Hence, electrostatic forces are not expected to influence the measured frequency shift curves, in full agreement with the observed force law exponent $\alpha = 3$.

To conclude, we have employed the extremely sensitive force detection of an atomic force microscope and measured the long-range vdW potentials between a series of related molecules and a metal surface. In particular, the exponent of the force law, the reference plane position z_0 , the validity range of the asymptotic force law, the absolute values of the C_3 coefficients, and their superlinearity have been determined, all in excellent agreement with theory. An analysis of the mechanical and electronic properties of the bonding between the XTCDA and a Au covered tip has

shown that crucial properties of this material system which allow the quantitative determination of van der Waals forces between a single molecule and a surface, even up to the possibility to record the superlinearity of van der Waals forces, are on the one hand the almost complete absence of a directionality of the bond between the functional oxygen atom and the tip, and on the other hand the absence of any significant charge transfer between tip and molecule.

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Figure 1 Schematic sketch illustrating the experiment. Within each experiment a single, isolated molecule is contacted at one of the reactive carboxylic oxygen atoms, detached from the surface, lifted about 2 nm further, and brought back into the adsorbed state. While repeating this cycle up to 45 times the force gradient dF_z/dz is constantly recorded. The tip-surface and molecule-surface distances z_{tip} and z_{mol} , as well as the distance z_i between each atom i and the surface are indicated. The chemical structures of the three investigated molecules are shown on the right (from left to right: NTCDA, PTCDA, and TTCDA).

Figure 2 Determination of the force law. a Averaged frequency shift Δf curves from individual contacting experiments. The Δf upon tip approach has been subtracted from the curves (Fig. S4 of the Supplementary Information). All curves are z -aligned at large z_{tip} where molecule and surface are well separated. The absolute z -scale is obtained by comparison to simulations²³ (Fig. S5 of the Supplementary Information). The arrows indicate where each molecule is detached from the surface with cartoons at the top showing the respective geometries. The inset exemplifies reproducibility and noise level for TTCDA. The gray background marks the part of each curve that is used in the fit. **b** Fit quality s and fit parameter z_0 for different force law exponents α . The best fit is obtained for $z_0 = 1.3\text{ \AA}$ at $\alpha = 2.85$ (dotted lines). The corridor of physically reasonable z_0 values (and of the respective exponents α) is shaded grey. **c** Fixing the exponent to $\alpha = 3$ we obtain a sharp minimum in s at $z_0 = d_{\text{Au}(111)}/2$ (dotted line).

Figure 3 Determination of the asymptotic van der Waals coefficients. **a** Plot of the experimental Δf data for the detached molecules (on a $(-\Delta f)^{-1/5}$ scale). The starting point of the fit intervals was varied within the yellow-marked regions that correspond to molecular heights $3.5 \text{ \AA} < z_{\text{mol}} < 7.0 \text{ \AA}$. The displayed fits to the experimental data (solid lines) have been obtained for a starting point of $z_{\text{mol}} = 5.3 \text{ \AA}$. The inset shows how the fit quality s depends on the starting point of the fit interval. We show the residuals of each fit and compare them to the residuals (marked by an asterisk) obtained in a fit where all $C_{3,X}$ are constrained to be identical, i.e., without superlinearity. **b** Best fit parameter values z_0 , $C_{3,N}$, $C_{3,P}$, and $C_{3,T}$ as a function of the fit interval starting point. We obtain unphysical values if the asymptotic force law of Eq. 3 is used too close to the surface. **c** Dependency of the fit quality s on the change of a single $C_{3,X}$ parameter. The three other fit parameters remain at their optimal values from panel b. The start of the fit interval was set to $z_{\text{mol}} = 5.3 \text{ \AA}$.

Figure 4 Experimental results and comparison to theory. **a** Summary of the experimentally obtained C_3 values. The experimental error bars indicate the uncertainty in the C_3 coefficients due to the influence of the experimental noise on the fitting routine. Calculated values from the semiempirical dispersion correction scheme vdW^{surf} and from DFT+RPA are also shown. **b** Dynamic per-atom polarizabilities of carbon for NTCDa, PTCDa, and TTCDa as resulting from RPA calculations. The coordinates x , y , and z refer to the directions along the long axis, short axis, and perpendicular to the plane of each

molecule. **c** The true van der Waals potential of PTCDA (coplanar to the surface) deviates from the asymptotic form (green) at small molecule-surface separations (compare Fig. 3b). The potential close to the adsorption height is estimated by the orange curve calculated on the basis of Ref. 23, while the true van der Waals potential is an interpolation between the two branches. The invalid parts of both potentials are dashed.







