Direct Measurement of Nonadditive van der Waals Forces From Graphene Nanostacks

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Abstract

Theoretical evidence suggests strong nonadditivity of van der Waals (vdW) forces at the nanoscale^(1,2), but direct experimental confirmation is missing⁽³⁾. By aligning the underlying surface sample with a macroscopic tipless Si cantilever, we present essentially noise-free vdW force measurements up to micrometer separations from multilayered graphene (MLG) nanostacks of variable thickness (1-21 layers) adsorbed on SiO₂ as well as from macroscopically-thick highly ordered pyrolytic graphite (HOPG). At contact cantilever-surface separation, the vdW force increases non-additively but monotonically from graphene to HOPG. Conversely, at separations $D > 100$ nm the vdW forces from MLG exhibit tunable power laws and the magnitude of the force on top of thick MLG nanostacks substantially exceeds the force measured on top of HOPG, despite the latter showing a slower decaying power law (D^{-4} for MLG vs D^{-3} for HOPG). Such a strong nonadditivity and tunable power laws of vdW forces at the nanoscale are rationalized by many-body calculations that include the nonlocal polarization response in graphene nanostacks.

Full Text

Van der Waals (vdW) forces play a crucial role in matter^{4,5}, for example, they drive the formation of two-dimensional multilayered functional devices with novel electronic^{6,7}, magnetic⁸, and optical properties⁹. Noncovalent vdW forces are well understood when interactions involve small molecules^{10,11} or macroscopic bodies^{5,12,13}. The situation is much less obvious when at least one of the interacting objects has nanoscale size. Crucial questions remain about the strength and the distance scaling of vdW forces at the nanoscale^{1,3,14,15}. For example, vdW forces between graphene and solid surfaces lead to a surprisingly extended and strong μm -scale adhesive stress upon delamination^{16,17}. In contrast, a layer of graphene adsorbed on SiO₂ exhibits a “Faraday cage” effect¹⁸⁻²⁰, effectively eliminating the vdW force between a sharp microscope tip and the SiO₂ surface. In addition, theoretical models predict that wavelike charge density fluctuations are responsible for the emergence of nonadditive modifications of the power laws that govern vdW interactions at the nanoscale^{1,2,21}. Here we present a direct experimental confirmation of strongly nonadditive van der Waals forces from graphenic nanostacks. This sensitive measurement is enabled by a novel force microscopy setup which allows the alignment of the underlying surface with a macroscopic tipless Si cantilever.

Experimental setup for the accurate measurement of nanoscale vdW forces

Figure 1a(inset) shows a schematic model of a novel AFM experimental setup that allows carrying out sensitive measurements of vdW forces between a macroscopic Si cantilever and arbitrary substrates. First, since the presence of a sharp pyramid probe on the cantilever results in micron-sized separations between the cantilever and a sample, we decided to conduct experiments with a tipless Si cantilever. Second, we implemented a goniometer into the AFM setup, Fig. S1a, allowing us to reduce the tilting angle between the cantilever and the force measurement sample to 1° (Supplementary Note 1). Finally,

mutual laser reflections from the cantilever and the substrate present at low tilting angles were removed by carrying measurements at the edge of the sample and by shifting the laser spot of the feedback laser away from the sample, Fig. S1b. We note that precise measurements of contact separation distances between Si cantilever and a surface are not possible as the reflected laser is not positioned at the tip of the cantilever. However, such uncertainty does not influence our conclusions since we used an extended cantilever with an aspect ratio of 100x500 μm (Methods) and concentrate on large separation distances. In consequence, the presented experimental strategy allows us to record essentially noise-free force-displacement (F-ds) measurements on a freshly cleaved highly oriented pyrolytic graphite (HOPG) surface with reliably measurable attraction forces between Si cantilever and the substrate up to at least 2 μm separation distances, see Fig. 1a and Fig. S3. We observed that a gradual reduction of the tilting angle of the HOPG surface to the Si cantilever from $\alpha=11^\circ$ to $\alpha=1^\circ$, resulted in a 100-fold increase in attraction force at the contact distance (F_{Contact}), Fig. 1b and 1c. Herein, the contact between the cantilever and the substrate is taken from the F-ds curves at the minimum force value prior to the onset of the linear bending of the cantilever, Fig. 1a. An analytical model (see Supplementary Note 2), which describes the variation of attraction forces between the cantilever and a surface as a function of the cantilever tilting, results in the same amplification factor, in excellent agreement with the experimental evidence. Within this model, one assumes that the cantilever forms an angle α with respect to the surface, and that the force acting on a small segment of the cantilever scales as D^p . Under these assumptions one finds that

$$F(\alpha) \propto \frac{1}{\cos(\alpha) \tan(\alpha)^p}. \quad (1)$$

Hence, by setting $p=2$, (as obtained experimentally at short cantilever-surface separations) one obtains that a 10-degree reduction in the tilting angle α yields (for small angles) a 100-fold amplification in the substrate-cantilever force. Here, we will demonstrate that the proposed experimental strategy shows high sensitivity to vdW forces arising from nanoscale objects, while the previous seminal strategies were mainly focused on vdW/Casimir²² and hydration¹² interactions present between solid materials in vacuum and water respectively.

Stability and reproducibility of vdW force measurements

Before discussing vdW forces arising from graphene nanostacks, we first assess the ability of our setup to reproduce previous seminal force measurements on top of HOPG¹³ and a single graphene layer¹⁸. Our experiments on top of HOPG showed a power law approaching D^3 as the separation distance between the Si probe and HOPG increased to 1 μm , Fig. S4. These results reproduce the interaction power law between two solid materials, Fig. 1c(inset). In addition, forces measured at distances close to contact (i.e., F_{Contact}) showed a D^2 power law, which is in line with the seminal experiments of Prosser and Kitchener¹³.

From the analysis of F-ds curves upon retraction recorded on HOPG at $\alpha=1^\circ$, we conclude that the cantilever forms a physical contact on HOPG with its isosceles triangular part (i.e., base 100 μm , height 86.6 μm and angle of $\beta=60^\circ$) having a length $l=4\text{ }\mu\text{m}$, which results in an overall contact area of 9.28 μm^2 (Supplementary Note 3), Fig. S5. Next, by integrating the F-ds curve recorded on HOPG at $\alpha=1^\circ$ and normalizing its value per contact area, we calculated the delamination energy of Si cantilever from HOPG being equal to $0.10\pm0.02\text{ N/m}$, which coincides with reported values from other experimental strategies (Fig. S5d)¹⁷. Moreover, to confirm the negligible role of the water bridge forming between Si cantilever and HOPG, which may affect attraction forces in nanoscopic experiments with sharp probes, we conducted F-ds measurements of vdW forces in “contactless” mode on top of HOPG surface (Supplementary Note 4). In detail, after the typical F-ds measurements with Si cantilever on HOPG were established, we lowered the HOPG substrate, which resulted in a gradual reduction of the linear deflection of the cantilever and eventual loss of contact with the surface, Fig. S6a. Our experiments showed stable vdW attraction forces even after 1000-cycles of F-ds measurements, Fig. S6c. We also note that F-ds curves measured at a fixed position on top of HOPG showed reproducible forces with an error bar below 3%, Fig. S7. In addition, we recorded multiple F-ds curves along the HOPG sample edge, which again demonstrated high reproducibility and stability with an error bar below 5%, Fig. S8. We note that measured vdW forces were essentially suppressed on uncleaned Si/SiO₂ surfaces, demonstrating the high sensitivity of force measurements to electrostatics induced by impurities such as water, hydrocarbons, and polymers (Fig. S9, Supplementary Note 5). However, we observed that extensive cleaning of Si/SiO₂ samples reproducibly restored long-range vdW forces (Fig. 1d and Fig. S10).

Moving to a nanostructured surface, we measured vdW forces on top of a single layer of graphene (1LG) fabricated by chemical vapor deposition (CVD) and transferred to Si/SiO₂ substrate with the help of poly-methyl-methacrylate (PMMA) polymer, as described before (Methods)^{23,24}. Our experimental strategy showed two important findings. Conducted angle-dependent F-ds measurements with Si cantilever across multiple Si/SiO₂/1LG samples showed a reduction of $\sim 75\%$ in vdW attraction forces at contact (i.e., F_{Contact}) (Fig. S10), compared to HOPG or Si/SiO₂ (the last one was exposed to the same experimental conditions), Fig. 1d. These experiments demonstrate that a stronger reduction of vdW forces is observed at the contact with the surface rather than at larger separation distances, which is in a qualitative agreement with the theoretical model describing vdW screening by 1LG (Supplementary Note 6)^{20,25}. Therefore, our experiments establish a quantitative benchmark for the screening of vdW interactions by 1LG with a remarkably large value of 75% at small separation distances.

Finally, to demonstrate the high sensitivity of our experimental technique towards other 2D materials, we studied a single layer of CVD-grown molybdenum disulfide (1LMoS₂). Similar to 1LG, 1LMoS₂ showed a 60% reduction in attractive vdW forces with respect to non-covered Si/SiO₂ surface, being in line with recent theoretical calculations¹⁹, Fig. S11.

Nonadditivity of vdW forces from graphene stacks

Having established the accuracy and reproducibility of our setup for measuring vdW forces, we now proceed to discuss force measurements on top of graphenic nanostructures. Multilayered graphene stacks (MLG, 1→2→4→7→14→21 layers) were fabricated on top of Si/SiO₂ by CVD as described in Methods²⁴. X-Ray reflectivity measurements found that the average interlayer distance in CVD-grown graphene stacks lies between 0.33 and 0.44 nm, hence we expect a linear growth of the thickness of MLG upon increasing the number of layers²⁶.

Figure 2a shows $F_{Contact}$ values obtained from the measured F-ds curves (Fig. S12) on top of MLG. Here we observe a slow convergence of the force towards values characteristic for HOPG bulk samples with an increasing number of layers. This overall trend is expected because in the limit of infinitely-thick MLG one should recover the HOPG limit. However, the slow convergence of the force with the number of layers can only be explained by a nonadditive many-body theory²⁷ (to be analyzed below) that takes into account the non-locality of graphene intralayer polarization response as well as a 3-5-fold weakened interlayer coupling compared to HOPG. In contrast, the more conventional theory based on pairwise interactions or full-strength interlayer coupling would yield a force that converges already at 3-4 layers of graphene at small separation distances. This obviously disagrees with our measurements in Fig. 2a and is already indicative that we measure a strongly nonadditive polarization response in MLG.

The most striking results are found at cantilever-substrate separations beyond 100 nm, as shown in Fig. 2c and Fig. S13. Here we observe that vdW attraction forces measured on top of 7LG, 14LG, and 21LG samples are stronger than in the case of HOPG. For example, the 21LG sample at $D=500$ nm shows a 5-fold stronger force than on top of HOPG, see Fig. 2c. These observations can be attributed to a greatly enhanced polarization response of MLG nanostacks compared to HOPG (discussed below and in Supplementary Note 8). At a first glance, the enhancement of vdW force on top of MLG is surprising, given that an infinitely-thick MLG should exhibit the same interaction as HOPG. In practice, however, it is well known that CVD-grown MLG is not pristine, but may contain defects as well as water and other interlayer impurities. One may expect such imperfections to decouple the graphene layers leading to a reduction of the vdW force measured by the cantilever. However, our measurements yield the opposite result.

To rationalize the experimental measurements we developed a minimal theoretical model, which includes the relevant many-body quantum mechanical effects arising in the vdW interaction between the cantilever and the underlying surface. To make calculations feasible and explainable, we treat the cantilever as a point-polarizable object. Such an approximation neglects the finite extent and non-local polarization response of the cantilever due to surface plasmons, but it retains the main non-additive features of the substrate-cantilever interaction (see Supplementary Note 6). We then couple the density-density response function of the cantilever χ_A computed at imaginary frequency $i\omega$ to the surface susceptibility, χ_s , through the Coulomb interaction v . Here χ_A is peaked at zero frequency to effectively mimic the energetic range of delocalized plasmon-like modes. The

density response of the substrate (graphene multilayers or HOPG) is obtained by solving the self-consistent Dyson's equation and it includes the relevant quantum many-body effects of the system, within the random phase approximation (RPA). Due to the relatively large substrate-cantilever separations involved in this work and the finite thickness of MLG, the substrate-cantilever coupling ν is treated using second-order perturbation theory, since the strongest many-body effects are presumed to be confined within the substrate (see Supplementary Note 7). Hence, the vdW force arising between substrate and cantilever is finally expressed as:

$$\vec{F}_{vdW} = -\vec{\nabla} E_{vdW,bind} = \vec{\nabla} \int_0^\infty d\omega \frac{\hbar}{2\pi} \text{Tr}[\chi_A(i\omega) \nu \chi_S^{RPA}(i\omega) \nu]. \quad (2)$$

Full detail on the computation of eq. (2) is provided in the Supplementary Note 6. In addition to the nonadditive vdW forces computed at the RPA level, we provide comparison to standard pairwise vdW forces, derived from interatomic summation of semi-classical Lennard-Jones terms.

The measured force at the contact distance, $F_{Contact}$ deviates qualitatively from pairwise vdW predictions (Fig. S14), and can be explained instead semi-quantitatively by many-body vdW theory (see Fig. 2b). Many-body interlayer coupling qualitatively changes vdW forces, causing deviation from linear growth of $F_{Contact}$ and slow convergence of the vdW force with respect to the number of layers. To account for weakened intralayer response (due to defects) and screened interlayer Coulomb coupling (due to possible interlayer water and impurities - see Supplementary Note 7)^{28,29}, the substrate response χ_S^{RPA} for multilayer graphene is computed by introducing an effective screening factor ϵ^{-1} , that renormalizes the interlayer Coulomb coupling. Setting $\epsilon^{-1}=0.2$, one finds qualitative agreement with experimental observations, with a predicted vdW enhancement factor of 3 passing from 1LG to 21LG at the contact with the surface (i.e., $F_{Contact}$), which is in excellent agreement with the experimental observations, Fig. 2b. We note that Si/SiO₂ roughness may induce stronger decoupling between graphene sheets in the first layers of the MLG stacks, which is not considered in the current model, suggesting one explanation for the difference between the many-body calculations and experimental measurements in Fig. 2a for thin MLG stacks. Also, the finite size of the cantilever neglected in our model is expected to cause slower force convergence with respect to the number of layers in better agreement with experiment. Of course, our model with a single interlayer dielectric screening parameter may not be sufficiently flexible to capture all the effects in the vdW force between a macroscopic cantilever and MLG nanostacks of varying thickness.

In addition, our many-body calculations confirm a strong force amplification from MLG seen at greater separation distances D (Fig. 2c), that are again in stark contrast with pairwise predictions (Fig. 2d(bottom panel)). The force amplification at large D is also qualitatively different from previous AFM experiments conducted with a sharp probe at separation distances of a few nm¹⁸, where increasing the number of layers up to the bulk structure was observed to lead to a monotonic increase in the vdW force. In contrast, our experiments showed 5-fold stronger vdW forces on 21LG than on HOPG at a separation distance

of 500 nm. Within our many-body theory, the response function of HOPG is described through the Lifshitz-Zaremba-Kohn (LZK) approach³⁰, using the dielectric permittivity of HOPG. This allows differentiating between the many-body screening properties of bulk HOPG and CVD graphene stacks. In fact, given the reduced interlayer coupling in CVD graphene, the density response of different layers effectively *sums up* in multilayer stacks, exceeding the LZK density response of HOPG, and leading to 5-fold stronger vdW forces at large separations, Fig. 2d(top panel), in agreement with our experiments.

Tunable power laws of nanoscale vdW forces

We proceed to analyze the difference in vdW power laws measured on top of MLG and HOPG and their implications for understanding cantilever-substrate interactions at different distances. On top of HOPG, the force asymptotically approaches D^{-3} at large separations in agreement with Lifshitz's theory for thick slabs³¹, see Fig. 3a. Conversely, the vdW force decays as D^{-4} on top of MLG, see Fig. 3a and 3b. This is most evident in thicker graphene stacks, where larger vdW forces imply smaller experimental noise. At close distance, instead, the power law decay tends to slow down, again in line with Ref.¹³. This is attributed to the non-trivial shape and large size of the cantilever (which become most relevant at small D where the largest deformations also occur), and to a possible partial contact between surface and cantilever. In the large D limit (such that the cantilever thickness is $\ll D$), pairwise theories based on the interatomic summation of Lennard-Jones potentials predict that the substrate-(pointlike)cantilever force should scale as $\sim D^{-4}$ on HOPG ($\sim D^{-5}$ on multilayer graphene), at variance with experimental evidence³⁰. The slower power law scaling shown by our experiments is thus attributable to the finite thickness (~ 0.7 μm) of the cantilever and the possible relevance of collective plasmon-like excitation modes in the interaction between the substrate and the cantilever - an intrinsic many-body effect that cannot be captured by pairwise approximations. In fact, it was demonstrated⁷ that the emergence of wavelike charge density oscillation modes in anisotropic nanoscale systems implies a sizable slow-down of the vdW power law decay, an observation that is compatible with our direct measurements. We also remark that different power law scalings were predicted in graphite for cleavage and exfoliation processes³², so that even cantilever bending could play a relevant role in determining the short-distance behavior.

Given the different power laws for the vdW force on top of MLG and HOPG, it is insightful to analyze the effective polarizability ratio per carbon atom in the two systems upon assuming a continuum pairwise-additive model for cantilever-surface vdW interactions (see Supplementary Note 8). The effective polarizability ratio $\alpha_{\text{MLG}}/\alpha_{\text{HOPG}}$ turns out to be inversely proportional to the cantilever-surface distance D . For example, for $D=500$ nm, $\alpha_{\text{21LG}}/\alpha_{\text{HOPG}} \sim 800$. Using the single-frequency approximation to atomic transitions (the quantum Drude oscillator model⁷), the ratio between atomic Hamaker constants (or vdW C_6 coefficients) is equal to the ratio of polarizabilities. Hence, in a continuum pairwise-additive model the polarizability and vdW coefficients become *running coupling constants* as a function of distance from MLG. This analysis reinforces the importance of robust quantum-mechanical treatment of non-local dielectric response of nanostructured materials in the context of vdW interactions.

We finally remark that vdW-induced structural deformations of the cantilever and the substrate were neglected here for simplicity. However, structural deformations can interplay with many-body vdW interactions beyond the nanometer scale³³, yielding enhancement in interface forces upon separation. Further interaction enhancement could also occur due to interfragment coupling between zero-point phonon vibrations, for analogous reasons. By the combined account of many-body vdW contributions and missing geometrical/quantum-mechanical lattice-vibration effects, micrometer-range interface forces can be expected, according to Ref.³³ and compatible with the present experimental findings.

Conclusions

We have presented an experimental strategy that enables noise-free measurements of vdW forces between a macroscopic cantilever and a nanoscale surface, allowing us to accurately interrogate noncovalent interactions for cantilever-surface separations of up to a few micrometers. The measured vdW forces on top of multilayered graphene stacks exhibited high stability and reproducibility with an error bar below 5%. The most remarkable observation is that the vdW force exhibits faster power law decay with distance on top of MLG compared to HOPG, yet the magnitude of the force is substantially greater for MLG surfaces. This finding cannot be explained by pairwise Lennard-Jones potentials or continuum theories for vdW interactions, but turns out to be in excellent agreement with quantum-mechanical many body calculations that include non-locality of dielectric response. The remaining discrepancy between our many-body calculations and experiments at large cantilever-MLG separations suggests that, among other factors, delocalized surface plasmons on the cantilever make a non-negligible contribution to the vdW force. Therefore, our findings pave the way for the development of experimental tools to understand complex interactions in materials owing to the sensitive dependence of dielectric properties on material thickness³⁴, as well as non-additive interactions present in nanoparticles³. Our work might also be useful for other phenomena including the development of functional 2D colloidal micro-Janus particles³⁵, interacting microscopic robots³⁶, and the self-assembly of microscopic optical devices driven by long-range vdW/Casimir forces³⁷.

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Methods

All experimental techniques and theoretical models are available in the **Supporting Information** section.

Data and materials availability

All data are available in the main text or the supplementary materials

Declarations

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Author contributions

PG, AA, MSS and AT designed experiments. PG performed samples fabrications, measurements and data analysis. AA and AT developed theoretical models. PG, AA and AT wrote the manuscript.

Competing Interests Statement

Authors declare no competing interests

Additional information

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Figures

Figure 1

(a) Measurements of vdW forces with a distance range reaching 2 μm achieved with the developed highly-sensitive AFM setup, specifically by tilting the bottom substrate and placing a reflective feedback laser outside of the measured sample. The schematic picture shows planarization of two surfaces upon tilting HOPG. (b) Measured F-ds curves demonstrate a gradual increase in attraction forces upon reducing the angle between the Si cantilever and the bottom HOPG surface. Schematic images of non-tilted (top) and tilted (bottom) surface are shown as insets. (c) An increase in attraction force measured at the contact with the HOPG surface (F_{Contact}) with an amplification factor of 100. The orange arrow shows an increase of vdW forces. The inset demonstrates the analytical model applied in eq.(1) that confirms the amplification factor of 100 (Supplementary Note 2). (d) The effect of the first graphene layer on the screening of attraction forces measured with a Si cantilever on top of the Si/SiO₂/1LG sample. A 75% reduction of vdW forces at F_{Contact} due to the many-body dielectric response of graphene is observed. Reference experiments are done on Si/SiO₂ substrate exposed to the same preparation conditions as the Si/SiO₂/1LG sample. The orange arrow shows a reduction of vdW forces.

Figure 2

(a) A plot of $-F_{\text{Contact}}$ vs N (number of graphene layers) recorded on different multilayers stacks (1-21LG) showed an increase in attraction forces upon increasing the number of graphene layers. The many-body RPA calculations for $F_c(N)/F_c(1)$ (F_c is equivalent to F_{Contact}) are presented in red for interlayer screening parameter $\epsilon^{-1}=0.2$, demonstrating semi-quantitative agreement with experiments after multiplication by a constant factor of 5. (b) The ratio between substrate-cantilever attractive force computed on N graphene layers and a monolayer ($N=1$). The cantilever-substrate separation is fixed to 5 nm. Comparison is given between RPA calculations by considering different values of the ϵ^{-1} parameter. The plot also shows experimental data, which is in agreement with RPA calculations for $\epsilon^{-1}=0.2$. (c) $F_d(N)/F_d(\text{HOPG})$ plot demonstrates stronger attraction forces for MLG compared to HOPG ($d=0, 200, 500\text{nm}$), observed in samples with 7, 14, and 21 layers of graphene, respectively. Many-body RPA calculations for $F_d(N)/F_d(\text{HOPG})$ are also presented. Note that the error bars here appear visually larger than in panel (a)

because of the different ordinate scales (absolute in panel (a) and relative in panel (c)). (d) The RPA model for $F_d(N)/F_d(\text{HOPG})$ demonstrates agreement with the experimental data (top panel), while the pairwise model shows a drastically different behavior (bottom panel).

Figure 3

(a) Log-log plots of F_d s recorded on MLG and HOPG surfaces. F_d s show the power law of the vdW force approaches D^{-4} upon an increase in the number of graphene layers, where stacks with 7LG, 14LG, and 21LG have much stronger attraction forces than HOPG. (b) The F_d s recorded on 21LG shows an attraction power law of D^{-4} , supported by our quantum-mechanical many-body model.

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