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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 London, Casimir, and Lifshitz. 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 considered. Hence, semi-empirical correction schemes are often used that simplify the vdW interaction to a sum over atom-pair potentials. A similar gap exists between successful measurements of vdW and Casimir forces for single atoms on the one hand and macroscopic bodies on the other, as comparable experiments for molecules are absent. I will present experiments in which long-range vdW potentials between a series of related molecules and a metal surface have been determined experimentally. The experiments rely on the extremely sensitive force detection of an atomic force microscope in combination with its molecular manipulation capabilities. The results allow us to confirm the asymptotic force law and to quantify the non-additive part of the vdW interaction which is particularly challenging for theory. In the present case, cooperative effects account for 10% of the total interaction. This effect is of general validity in molecules and thus relevant at the intersection of chemistry, physics, biology, and materials science.