

1 Molecular systems, growth and overlayers: van der Waals density functional and first-principle thermodynamics calculations

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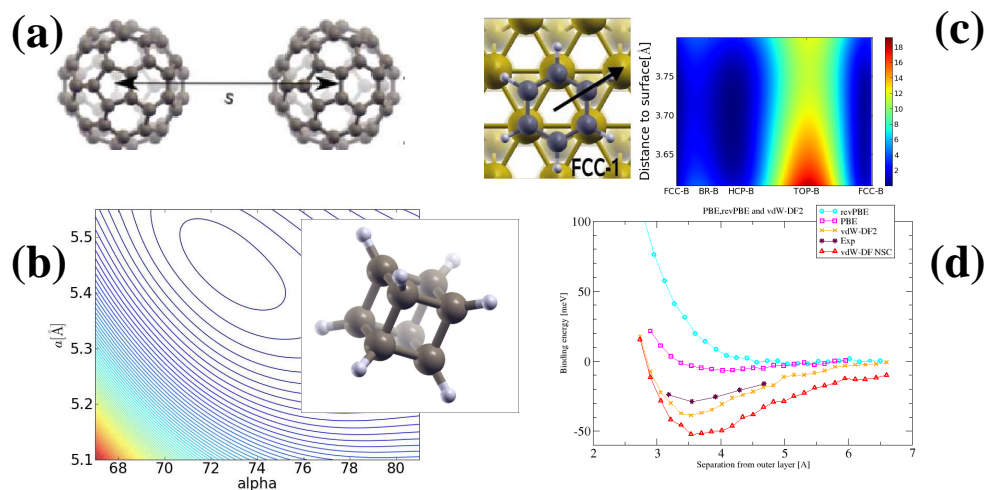


Figure 1: Molecular systems which are part of our computational laboratory for development and accuracy calibration of van der Waals density functional (vdW-DF) calculations [1]. With SNIC resources we pursue projects to determine binding in graphitics test systems — from C₆₀ dimers (a) to graphene exfoliation [2] — and in molecular crystals such as cubane (b) [3]. We furthermore use vdW-DF to characterize molecular physisorption and adsorbate diffusion barriers (c) [4]. Unlike most semi-empirical approaches (like DFT-D), the vdW-DF method^{1, 2} provides a natural framework for inclusion of image-plane effects [5], a prerequisite for achieving transferability across a range of distances [3, 5, 6]. It is gratifying that a detailed calibration against the measured shape of the physisorption well for H₂ on Cu(111) (d) [7] suggests a strong performance particularly for the most recent formulation,² vdW-DF2, and a possibility to refine descriptions of, for example, lateral adsorbate interactions [4] and DNA structure [8].

Sparseness [1] is a defining property of a very broad class of condensed-matter phenomena but it represented, until recently, an outstanding challenge for efficient investigation through use of density functional theory (DFT). Materials are sparse

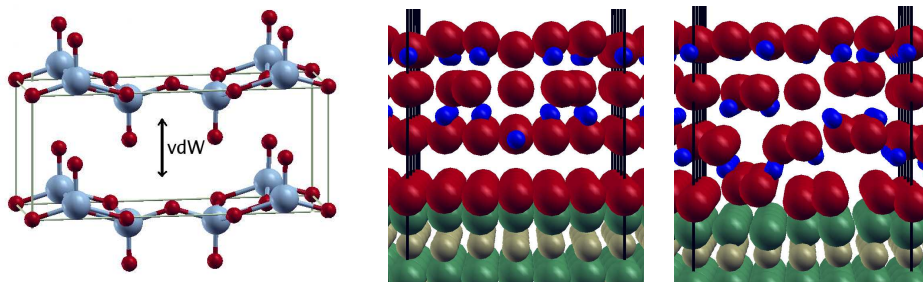


Figure 2: Nature of adhesion and role of nonequilibrium deposition environment in oxides and oxide nucleation. Inclusion of van der Waals forces is essential for a correct description of layered oxides like V_2O_5 (left panel [6]) and for an exfoliating alumina/TiC overlayer (structure motifs predicted in middle panel [9]); traditional covalent and ionic binding describe the adhesion in a wear-resistant alumina/TiC coating (right panel [9]). Inclusion of the nonequilibrium nature of deposition growth [10, 11] corrects the thermodynamical predictions of the nature of alumina/TiC overlayer nucleation (from exfoliating) to wear resistant, a coating.

when they contain important regions with low electron concentration where van der Waals (vdW) forces contribute significantly to the structure and behavior. Examples are molecular crystals and supramolecular complexes, physisorption and/or weak adsorption of molecules on surfaces and self-assembly of functional overlayers. Sparseness is also important in hollow materials and grain boundaries, as well as for the broad class of layered materials, particularly those which undergo facile exfoliation. Such systems did represent a challenge for DFT only because the density functional was approximated from a local or semi-local variation in density. As partners in a Rutgers-DTU-Chalmers collaboration we are helping to develop a new truly nonlocal approximation for the density functional.^{1, 2} A new method, called vdW-DF, is proving itself useful in extending the power and efficiency of first-principle DFT from hard materials to the even greater class of sparse-matter challenges [1].

Nonequilibrium thermodynamics often plays an essential role in materials and nano science. It is possible to couple traditional DFT calculations with kinetic simulations of, for example, materials growth and nanoscale transport. However, a thermodynamical atomistic description (with a full quantum-physical account of the electron behavior) is still highly desirable. Unfortunately, the nonequilibrium nature and open boundary conditions contradicts the ground-state, canonical-ensemble foundation of standard DFT and we are motivated to seek formal extensions. Progress includes a formal proof for a DFT for nonequilibrium tunneling.³ We have also developed a new *nonequilibrium* thermodynamical account of deposition growth [10].

Allocations of SNIC resources have been instrumental for progress. The programs involve both basic and applied research. We are grateful that SNIC shares our view that the catalytic value is enhanced by a direct coupling to advanced computation projects on problems with materials and nano-science relevance. Due to space limitations we can only exemplify — using figures and figure captions — the set of projects pursued with computer resources provided by our SNIC allocations. We refer to the above-listed web pages for a more complete account.

Publications

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