Van der Waals interactions in advanced materials, in memory of David C Langreth

EDITORIAL

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Guest Editors

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The past decade has seen a dramatic rise in interest in exploring the role that van der Waals (vdW) or dispersion forces play in materials and in material behavior. Part of this stems from the obvious fact that vdW interactions (and other weak forces, such as Casimir) underpin molecular recognition, i.e., nature's approach to search for a match between genes and anti-genes and hence enable biological function. Less obvious is the recognition that vdW interactions affect a multitude of properties of a vast variety of materials in general, some of which also have strong technological applications.

While for two atom- or orbital-sized material fragments the dispersive contributions to binding are small compared to those from the better known forms (ionic, covalent, metallic), those between sparse materials (spread over extended areas) can be of paramount importance. For example, an understanding of binding in graphite cannot arise solely from a study of the graphene layers individually, but also requires insight from inter-sheet graphene vdW bonding. It is the extended-area vdW bonding that provides sufficient cohesion to make graphite a robust, naturally occurring material. In fact, it is the vdW-bonded graphite, and not the all-covalently bonded diamond, that is the preferred form of pure carbon under ambient conditions.

Also important is the understanding that vdW attraction can attain a dramatic relevance even if the material fragments, the building blocks, are not necessarily parallel from the outset or smooth when viewed in isolation (such as a graphene sheet or a carbon nanotube). This can happen if the building blocks have some softness and flexibility and allow an internal relative alignment to emerge. The vdW forces can then cause increasingly larger parts of the interacting fragments to line up at sub-nanometer separations and thus beget more areas with a sizable vdW bonding contribution. The gecko can scale a wall because it can bring its flexible hairs sufficiently close to any corrugated—and/or any smooth—surface and thus enforce a strong vdW-type adhesion; it exploits what is then essentially a contact force (dominated by the attraction exerted in the near-surface regions) to defy the pull of gravity on its own bulk.

This *Journal of Physics: Condensed Matter* special issue is dedicated to the memory of David C Langreth. David is a dearly missed friend and mentor who inspired many of us. He was an outstanding condensed matter theorist and a scholar who greatly influenced us through his many-particle-physics based insights into density functional theory (DFT), surface science and related areas. His seminal works range from conserving formulations of interacting nonequilibrium transport [1] and formal-scattering theory [2] to an explicit formulation [3] of the exact DFT exchange-correlation energy in the adiabatic connection formula (ACF), the latter also being derived independently by Gunnarsson and Lundqvist [4]. David's portfolio also includes an analysis [5] that helped catalyze and guide the development of DFT from the local-density approximation (LDA) to the formulations of generalized gradient approximations (GGAs).

Another salient contribution of David's is in the area of vdW interactions in materials. He was a key architect of the vdW density functional (vdW-DF) method [6, 7]. This method was developed in a long-standing Rutgers–Chalmers collaboration between David's group and that of Bengt I Lundqvist, later extending to a wider group of researchers on both sides of the Atlantic. Plasmons are collective excitations that depend on electron-density variation. The plasmon response can be seen as defining the nature of the LDA [4] and their description can thus also be seen as contributing to the success of GGA. The vdW-DF method is a regular constraint-based density functional (for ground-state DFT) which is derived within the ACF framework and which emphasizes the electrodynamical nature of the coupling between these collective plasmon excitations. The vdW-DF method thus seeks to utilise the implicit plasmon nature of the LDA/GGA success to also provide a nonempirical account of the fully nonlocal correlations that underpin the vdW bond [8]. The method retains a seamless integration [6] with the semilocal density functional components. We know that David was pleased to see how this quantitative, material-specific theory helped address problems in a broad class of materials that are sparse, i.e., that contain low electron density regions which are of significant consequence in determining material characteristics [9].

In a DFT framework, the vdW-DF method supplements other nonlocal functional descriptions [10] and the DFT-dispersion class of methods, extending GGA-DFT with an atom-based asymptotic description which relies on the vdW interaction coefficients [11]. The recent quest to understand the role of vdW forces in materials has certainly been facilitated and intensified by the set of recent developments in DFT itself. This is because these vdW-aware methods provide an opportunity to deliver a computationally effective account of the quantum-physical behavior even when the materials are sparse. It is the expectation that with such new-found theoretical capability, one may further extend the immense progress already attained by traditional (GGA) DFT calculations in reliably predicting the characteristics of materials and phenomena in materials, nanoscience, chemistry and other related fields [12].

This special issue contains a wealth of exciting contributions, mostly on vdW forces in materials. The special issue was suggested following the well-attended first focused vdW and materials session arranged by the Division of Materials Physics (DMP) of the American Physical Society (APS) at the March Meeting in 2011. The sad and unexpected passing of David in the spring of 2011 caused some rethinking and at the memorial symposium, held by David's colleagues at Rutgers in November 2011, we proposed to dedicate this special issue to David's contributions to the field. We are delighted with the overwhelmingly positive reaction that we received in response to our call for papers. We are also delighted to now be able to bring so many exciting contributions to you.

The papers included in this special issue focus, in general, either through experiments or through theoretical characterization, on material properties in which vdW forces represent a central component. These articles contain arguments for and against a broader usage of DFT with vdW to account for material description, as well as establishing benchmarks which measure progress in the field. This special issue also includes fundamental theoretical analysis and suggestions for sensitive experiments that can resolve outstanding issues underlying the nature and role of the interaction. We believe that these papers will help stimulate further material-theory developments and, even more importantly, more discussions and feedback between theory and experiment.

Physisorption is important to enable lubrication. This is because physisorption keeps the lubricating molecules at the interface at which a pair of internal surfaces must be free to move relative to each other. In turn, physisorbed (or perhaps weakly chemisorbed) lubricants prevent, for example, the formation of stronger bonding that will impede mechanical operation. However, it is also important to

further characterize the nature and dynamics of the vdW bonding of lubricants: while physisorption means a weak binding further from the surface, there are still important friction effects. Walker *et al* present an experimental study, along with theoretical analysis, that directly determines the frictional heating of a Kr overlayer on graphene through quartz crystal microbalance measurements.

The properties of materials reflect their atomic structure and hence indirectly their bonding nature and character. We can explore the role of dispersion forces by examining the impact their inclusion has on predictions of material properties. On the other hand, the experimental and theoretical study of Casimir forces also plays a vital role in the exploration of material behavior. vdW forces are related to the Casimir force but lack retardation effects. While the vdW bonding depends on additional effects (for example, the multipole contributions that reflect image-plane effects), the study of Casimir forces provides direct (and not indirect) measurements of the nature of interactions.

Klimchitskaya *et al* note that to reconcile explicit measurements of the Casmir forces between semiconductor fragments within the Lifshitz description, it is relevant to question the Drude-like description of the contributions from free carriers and instead proceed with a formulation based only on optical observations of the permittivity. This optical response can be seen as a reflection of a more plasmon-like behavior. The authors suggest an experiment involving the study of the impact on the Casimir forces by a Mott transition in doped semiconductors. Such an experiment would permit explicit testing of the validity of the present model for Casimir forces and hence provide additional perspectives on the nature of dispersive interactions.

There is an effort to store energy, e.g. H_2 or CO_2, inside a range of open cage-like structures, such as metal organics frameworks (MOF) or clathrates. The fact that the internal molecular adhesion is dominated by vdW forces suggests that the storage and retrieval costs could perhaps be lowered as compared to an approach that involves more traditional chemical compounds. Nijem *et al* have provided spectroscopic characterization of vdW interactions of both hydrogen molecules and CO in a specific MOF. The study includes a vdW-DF calculation of structure and a theoretical prediction of expected infrared activity.

The potential applications to energy materials have motivated more theoretical characterizations. Li and Thonhauser use the vdW-DF method to investigate the limitations and hydrogen storage potential of hydrogen–methane compounds in a MOF. Similarly, Ihm *et al* combine vdW-DF studies with a thermodynamics argument to characterize the potential for molecular hydrogen uptake in expanded graphite, for example, through intercalation.

The relevance of vdW-aware DFT calculations and the usefulness of such methods reaches beyond the study of molecules, surfaces and adsorption/absorption problems. Moellmann *et al* present a dispersion-DFT study of TiO_2 bulk and surfaces, which illustrates that vdW forces can also play a prominent role when comparing the energies of different oxide structures.

Perdew *et al* present a spherical-shell model and a simplified classical electrodynamical determination of the vdW interaction coefficients that describes the asymptotic interaction between fullerenes or other nearly spherical nanoclusters. The overall modeling framework also permits a formal expression of multipole contributions. Dappe *et al* used a combination of DFT and second-order perturbation theory to analyze the interactions between graphene layers, thus also exploring the role of dynamical screening in the vdW binding.

The work of Sabatini *et al* extends the vdW-DF description with accounts of the stress tensor, providing the method with the same versatility as one has grown to expect in traditional LDA/GGA-DFT calculations. The method is illustrated with investigations of amino acid crystals under various pressures.

The vdW-DF method was originally perceived as computationally more expensive than other approaches. It has now benefited from the development of

efficient algorithms so the computational cost is comparable to that of traditional GGA-DFT calculations. As is also the case for some of the dispersion-DFT methods, there is an overhead when these are implemented self-consistently. Noting that sparse-matter structure determination and relaxations may well employ a sequence of methods, Le *et al* have suggested a simplified (cost-free relative to GGA) formulation of self-consistent dispersion-DFT calculations that is cost-free in the evaluation of forces and yet adapts the atom-centered pair-wise interaction coefficients through the change in local electron distributions.

There is a need for continued testing of accuracy in the description of material properties and of the robustness and transferability of predictions across systems and length scales. This need is widely appreciated and is also reflected in the fact that many of the contributions touch on, suggest, or pursue a systematic benchmarking. There is an interest in careful analysis of detailed experiments on the physisorption of inert atoms, light molecules and organic molecules on smooth surfaces. Chen *et al* investigated the role of vdW forces in noble gas adsorption on various metal surfaces. Londero *et al* analyzed a set of experimental results for the desorption of n-alkanes from graphene in a program that had undergraduate participation. Lee *et al* benchmarked the performance of the vdW-DF2 functional and other methods against the physisorption potential curve that can be established from a rich data set of resonant backscattering of hydrogen molecules on various facets of Cu crystals.

A few of the investigations included here noted that the vdW-DF method permits a more detailed analysis of the nature of strong physisorption and/or weak chemisorption cases than do DFT-dispersion methods *and* discussed the ramifications of the fact that GGA-DFT often, and vdW-aware DFT sometimes, pose difficulties for systems with a partial vdW component in the binding. Caciuc *et al* thus present a combined *ab initio* and semi-empirical vdW study comparing benzene/triazine/broazine adsorption on graphene and on boron-nitride sheets. On a more strategic note, Lazic *et al* broadened the discussion of a graphene/Ir(111) system and used the documented limitation of a GGA description to discuss a rationale for considering a more general switch to nonlocal functionals. Graziano *et al* note that the accuracy in the description of some soft layered systems like graphene and boron-nitride can be increased by changing the exchange description away from what was suggested in the original vdW-DF method. Hanke *et al* focused on the weak chemisorption of ethene on the various Cu facets that have an increasing degree of openness and provide a method for benchmarking through comparison with experimental observations.

Finally, Björkman *et al* raise the question 'Are we van der Waals ready?' and proceed to test our readiness by benchmarking the performance of a range of vdW-aware methods for the group of 96 known layered structures.

We have also included in this special issue one study of nonequilibrium transport which is linked to David's work in formal scattering theory [1, 2] and which observes that vdW forces (and possible generalizations to nonequilibrium transport conditions) will be of central importance in a richer computational characterization of molecular electronics under operational conditions.

David was always keen to spearhead the development of tools that improved descriptions of nature and addressed actual experiments. We know that he was happy that DMP started the focused session on vdW and materials in 2011. We know that he would have thoroughly appreciated the articles in this special issue. He would have hoped, as we do, that materials theory may continue to learn how to tackle even more exciting experimental problems and that we may continue to deepen our understanding of materials and their functionality.

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