

THE VAN DER WAALS INTERACTIONS OF CONCENTRIC NANOTUBES

Elsebeth Schröder and Per Hyldgaard

Dept. of Applied Physics, Chalmers University of Technology and Göteborg University,
SE-412 96 Gothenburg, Sweden
E-mail: schroder@fy.chalmers.se

Concentric nanotubes are stabilized by a competition between the short-range repulsion and the long-range van der Waals binding. At the relevant binding distances (3.4 Ångström) we find that traditional first-principle density-functional theory (DFT) calculations can only partially account for these combined interactions and that an accurate quantum-physics account of structure and dynamics must also include a calculation of the van der Waals forces. We use a successful model of the electrodynamic response of the nanotube electron gas to provide such a combined description in which we reflect the important self-consistent screening effects arising within the nanotube electron gases. Our description differs significantly from traditional asymptotic calculations of the van der Waals interactions. Work supported by the Carl Tryggers Foundation, W. and M. Lundgren Foundation, the Swedish Research Council (VR), and the Swedish Foundation for Strategic Research (SSF).

Introduction

Soft and sparse material systems constitute a significant challenge for quantum-physical theory as their structure complicates the necessary calculations. While density-functional theory (DFT) provides an accurate account of most hard and dense materials, the present implementations of the DFT tool meets with important, fundamental problems when applied to the soft materials important for both life and most of our daily-life activities.

The quantum-physical computations are complicated in the soft and sparse materials because these combine *both* chemically-bonded ‘molecular regions’ of high electron density and ‘intermolecular voids’ across which physical interactions are mediated exclusively through the electromagnetic field, reflecting nonlocal correlations of the electron density—the van-der-Waals type of interactions. The difficulties in combining accurate accounts of both the local and nonlocal electron correlations has shifted the emphasis to other, less accurate, phenomenological descriptions (often implemented in molecular-dynamics simulations). However, recent advances [1–3] indicate that the remarkable accuracy of hard-materials DFT calculations can be extended to soft condensed matter.

Here we investigate the quantum-physical interactions within the concentric-nanotube system, Fig. 1. This system constitutes—like graphite [3]—an ideal example of the soft and sparse materials computational problem due to the clear separation of intratube, local, chemical bindings and nonlocal, physical, intertube interactions. For this system we combine first-principle DFT calculations with a successful, if approximate, description of the physical intertube forces.

The nonlocal intertube physical interactions

The multiwalled nanotube, i.e., the concentric nanotube system is stabilized by a competition of the kinetic-energy repulsion and the weak physical attraction mediated by the electromagnetic fields. Our calculation of this physical intertube attraction is based on accurate first-principle DFT calculations of the kinetic repulsion and the following approximate treatment of the intertube attraction.

Adapting the successful model description of Ref. [1] we approximate the local nanotube response by the bare dynamic susceptibility at (complex) frequency u :

$$\chi_0(n(r), u, u_0) = \frac{n(r)}{u^2 + u_0^2}. \quad (1)$$

This is a function of the nanotube electron density $n(r)$ (at distance r from the nanotube center) which we determine directly from first-principle DFT calculations [4]. The frequency cut-off u_0 is defined by a separate first-principle calculation of the static nanotube susceptibility.

From this model of the local susceptibility we obtain a corresponding effective susceptibility tensor χ_{eff} which describes the ratio of the locally induced polarization to the externally applied

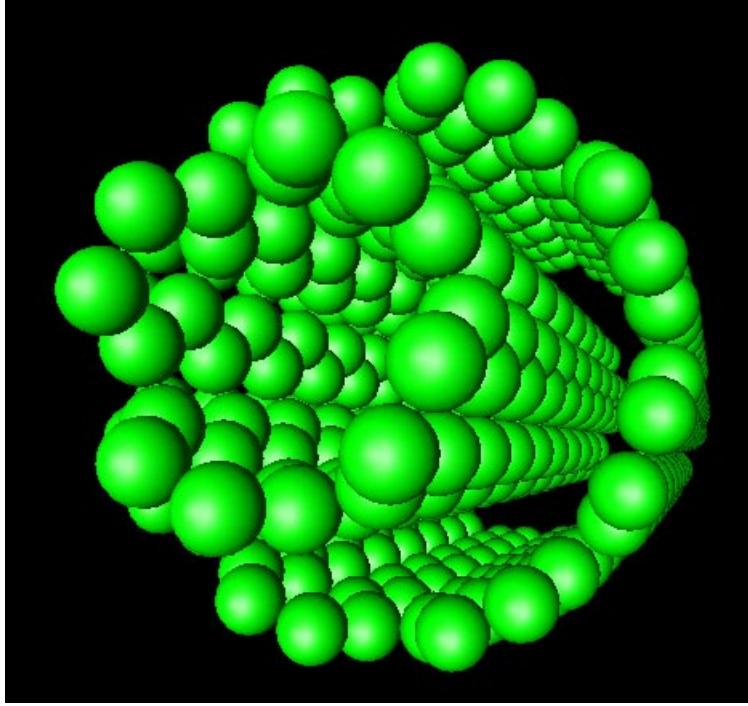


Figure 1: A quantum-physical description of the interactions within two concentric nanotubes requires both accurate calculations of the strong, local intratube chemical bindings and of the weak, nonlocal intertube physical interaction that stabilize the multiwalled nanotube. This intertube interaction arises as a competition of a kinetic-energy repulsion and a van-der-Waals type attraction. Our standard density-functional theory (DFT) implementations provides an excellent account of the intratube interactions but not of the intertube forces. We combine first-principle DFT calculations [4] of the nanotube electron density with a model [1–3] of the electron response, to provide a detailed quantum-physical description of the multiwalled nanotube structure and stability.

electric field. This effective susceptibility is a *functional* of the electron density:

$$\chi_{\text{eff}}[n(r)](u, u_0) \neq \frac{\chi_0}{1 + 4\pi\chi_0} \quad (2)$$

but can be calculated from a separate determination of the self-consistent screening within and between the nanotubes.

Our description differs significantly from the traditional, approximative and asymptotic account of the van der Waals interaction because of the finite screening effect by the nanotube electron density. Moreover, our description of the physical intertube attraction offers a direct integration with the first-principle DFT calculations [4] necessary for an accurate description of both the intratube chemical binding and the kinetic-energy intertube repulsion.

Conclusion

In summary, we report a quantum-physical calculation that combines both the chemical intratube and physical intertube interactions. Present standard DFT functional calculations alone can not provide a complete account of the nanotube structure and dynamics but must be supplemented by calculations of the intertube physical interactions. We have adapted a successful model [1] for these calculations of the physical interactions, based directly on the calculated [4] nanotube electron density.

References

- [1] E. Hult, H. Rydberg, B. I. Lundqvist, and D. C. Langreth, *Phys. Rev. B* **59**, 4708 (1999).
- [2] H. Rydberg, B. I. Lundqvist, D. C. Langreth and M. Dion, *Phys. Rev. B* **62**, 6997 (2000).
- [3] H. Rydberg, N. Jacobson, P. Hyldgaard, S. I. Simak, B. I. Lundqvist, and D. C. Langreth, *Hard Numbers on Soft Matter*, Applied Physics Reports 2001-48.
- [4] Computer code DACAPO, <http://www.fysik.dtu.dk/CAMPOS/>