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Unusual features of the dispersion force in layered and striated nanostructures

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Abstract

A discussion is presented on some physics behind the unusually long ranged dispersion forces recently predicted between one-dimensional and nanolayered structures with a zero electronic energy gap, such as metallic nanotubes and graphitic structures. The various results for these systems, previously obtained via a variety of formalisms, are here re-derived systematically from a single approach.

Keywords: van der Waals; Dispersion force; Nanotube; Nanostructure; Coupled plasmons; Graphene; Low dimensional

1. Introduction

Soft dispersion forces, part of the van der Waals (vdW) interaction, are frequently important in the cohesion of layered and nanostructured systems. For example, vdW forces are generally considered to be involved in the binding of graphene layers to form graphite and its intercalates. Similarly vdW forces cause carbon nanotubes to clump into bundles.

Dispersion forces have been studied for over a century [1,2]. For the interaction between small systems such as atoms at separations R much greater than a conventional bond length, very simple models involving an R^{-6} interaction energy (see e.g. [1,3]) are satisfactory in the electromagnetically non-retarded regime. It has been popular to model larger systems using a sum of such R^{-6} pair forces [1,4]. Since the 1950s one has also had access to more detailed theories for larger systems, such as approaches arising from stochastic electrodynamics [5] or perturbative quantum electrodynamics [6], or the surface plasmon approach [1]. In almost all applications the spatially nonlocal polarizability or dielectric function appearing in these theories had been approximated by a spatially local form. This approximation led ultimately to power-law exponents for the non-retarded energy versus separation curves (E vs D) for extended parallel structures that were the same as from an elementary sum of atom–atom R^{-6} contributions (see column 3 of Table 1). However, until very recently these approaches had not been applied in detail to large systems with a zero electronic energy gap *plus* one or more spatial dimensions in the nanometer range. Thus, it seems to have been widely unnoticed that the usual spatially local approximations for the dielectric function fail for these extremely anisotropic cases. The reasons for this include the ability of electrons to form long-wavelength density fluctuations, plus the lack of strong three-dimensional Coulomb screening [7], a lack attributable to the presence of at least one nanoscale spatial dimension. As a result, zero-energy-gapped systems having, simultaneously, at least one macroscopic spatial dimension and at least one nanoscopic dimension should give unusual slowly decaying van der Waals power laws (see column 2 of Table 1). This was recently exposed as a general phenomenon [7], after the earlier work had uncovered one special case, that of two parallel two-dimensional electron gases [8].

In the following Sections we will discuss the reasons for these results, and in particular why some of them are so different from the predictions of a sum of R^{-6} energy contributions from atom (or bond) pairs. Further investigation

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Table 1
Asymptotic dispersion energy of parallel structures vs. separation *D*

System	Present prediction[a]	Standard prediction
1D metals [7]	$\mathbf{-D^{-2}(\ln(KD))^{-3/2}}$	$-D^{-5}$
1D nonmetals [7]	$-D^{-5}$	$-D^{-5}$
2D metals [8,3,7]	$\mathbf{-D}^{-5/2}$	$-D^{-4}$
π-conjugated layers [7]	$\mathbf{-D^{-3}}$(at $T=0$ K)	$-D^{-4}$
1 metallic, 1 π-layer [7]	$\mathbf{-D^{-3}\ln(D/D_0)}$	$-D^{-4}$
2D insulators [7,24]	$-D^{-4}$	$-D^{-4}$
Two *thick* metals or insulators [3,7]	$-D^{-2}$	$-D^{-2}$

[a] K and D_0 are constants.

of these asymptotic results is timely because (i) the small forces discussed here should be readily observed, in their asymptotic region of validity, via sensitive force microscopy and nanomechanical resonant techniques [11] that have been demonstrated recently and (ii) individual graphene layers have recently been obtained experimentally [9], with a good enough purity to see the quantum Hall effect [10].

2. Formalisms for vdW energies

At a microscopic level, the dispersion interaction arises from the Coulomb-induced correlations between the spontaneous electron density fluctuations on two or more systems (see e.g. [3]). It can be understood qualitatively and quantitatively in a number of ways.

2.1. Perturbation in the inter-system Coulomb potential, useful in the non-overlapping regime

In order to study the distant part of the vdW interaction, we will focus first on a form of perturbation theory that is able to give at least qualitatively correct results for all the cases of interest in the present paper.

Consider the perturbation theory with respect to the interaction w_{12} between two separated electronic subsystems (w_{12} is assumed to be the non-retarded Coulomb interaction). The dispersion energy arises at the second-order level of perturbation, giving in the first instance a typical expression involving Coulomb matrix elements between many-electron wavefunctions, divided by an energy denominator. Of the many different ways to re-express this result we exhibit one here, due to Longuet-Higgins and others, [12,13] which will be particularly useful for present purposes:

$$E^{(2)} = \frac{-\hbar}{2\pi}\int_1 \mathrm{d}^3r_1\mathrm{d}^3r_1' \int_2 \mathrm{d}^3r_2\mathrm{d}^3r_2' \frac{\mathrm{e}^2}{|\vec{r}_1-\vec{r}_2|}\frac{\mathrm{e}^2}{|\vec{r}_1{}'-\vec{r}_2{}'|} \times \int_0^\infty \chi_1(\vec{r}_1,\vec{r}_1{}',\mathrm{i}u)\chi_2(\vec{r}_2,\vec{r}_2{}',\mathrm{i}u)\,\mathrm{d}u. \tag{1}$$

Here $\chi_1(\vec{r},\vec{r}\,',\mathrm{i}u)$ is the linear density–density response function of electronic system #1 in the absence of system #2, and similarly for χ_2. In general $\chi(\vec{r},\vec{r}\,',\omega=\mathrm{i}u)\exp(ut)$ is defined to be the linear density perturbation at $\vec{r}$ induced by a perturbation to the electrons' external potential energy function of the form $\delta V^{\mathrm{ext}}(r,t)=\delta^3(\vec{r}-\vec{r}\,')\exp(ut)$. Eq. (1) is meaningful only when the electronic charge clouds of the two subsystems can be considered as non-overlapping, so that electrons belonging to the two subsystems can be considered as distinguishable. Then, for example, Pauli exchange effects due to overlap can be ignored. With this proviso, (1) includes in principle the effects of Coulomb interactions within each subsystem to all orders, via the exact density–density responses χ_1, χ_2 of the isolated systems: only the Coulomb interaction *between* the subsystems is treated perturbatively. Of course χ_1 and χ_2 have to be approximated in practice. For the qualitative purposes of the present paper, the random phase approximation (RPA, time-dependent Hartree approximation) will be used.

2.2. Moeller–Plesset (MP) perturbation theory

This form of perturbation theory [14] starts with a Hartree–Fock description of the coupled system, then treats *all* electron–electron Coulomb interactions beyond this in second-order perturbation theory. The second-order energy thus includes both terms that relate to Coulomb interactions inside a subsystem, and terms that describe Coulomb interactions between the subsystems. Only the latter form part of the dispersion energy. Because two orders of perturbation theory are already used up in creating a dispersion term of order w_{12}^2, the dynamics due to Coulomb interactions w_{11}, w_{22} are left out of the Moeller–Plesset second-order dispersion interaction E^{MP2}. As a result, for non-overlapping systems MP2 theory is equivalent to (1) except that only the *bare* (independent-electron) responses $\chi_1^{(0)}$, $\chi_2^{(0)}$ of the subsystems appear, in contrast to the fully interacting ones χ_1, χ_2. This can be a serious error for some systems (e.g. a Be atom, or a 2D electron gas) where the bare and interacting responses are significantly different. Going to a higher-order in the Moeller–Plesset perturbation scheme (e.g. MP4) can improve matters, particularly for small systems, but this is neither adequate nor numerically tractable for the large metallic and near-metallic systems that we will be studying here. On the other hand, MPx treats exchange properly and remains valid as systems are brought together into the charge-overlapped regime where (1) is not valid.

2.3. Symmetry-adapted perturbation theory

This is a hybrid method that allows one to focus on the inter-system Coulomb interaction w_{12} as in Section 2.1, but projects out terms that violate exchange symmetry, thus permitting overlapped systems to be studied [15]. This method is currently having good success for small vdW-interacting systems but is not currently tractable for the systems of interest here, which have at least one macroscopic dimension.