Many-Body Terms in van der Waals Cohesion Energy of Nanotubes

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Abstract. We have developed a model for the calculation of van der Waals force for layered systems with axial symmetry. Our result can be applied to compute the cohesion of a carbon nanotube to a substrate, the cohesion between nanotubes, and between shells of multiwall nanotubes. We have obtained unusal power laws for the distance dependence of the many-body van der Waals potential.

Keywords: nanotube, plasmon, many-body theory, van der Waals cohesion

1. Introduction

Van der Waals interactions have been studied over a considerable period of time. Starting with the phenomenoligical work of van der Waals (van der Waals 1873), our understanding has developed from classical models (Reinganum 1912) to quantum mechanics (London 1930) and to full statistical quantum electrodynamics (Dzyaloshinskii, Lifshitz and Pitaevskii 1961). The earlier semi-empirical approach is still considered accurate and adequate for the description of many phenomena and involves transparent physics even for very complex systems.

In this letter we present a calculation of many-body corrections to the van der Waals (dispersion) forces for nanosystems with cylindrical symmetry. This geometry has received considerable attention owing to the close relation to the theory of biological ion channels and carbon nanotubes. The accurate calculation of the dispersion force is also important for the engineering of nanodevices: nano-electromechanical systems and elements of nanoelectronics (Dequesnes, Rotkin and Aluru 2001). The van der Waals (vdW) force changes drastically the system behavior at the nanoscale.

We follow here the dielectric function approach to model the vdW cohesion. (Repulsion is due to the Pauli

principle (Girifalco, Hodak and Lee 2000) and will not be addressed here.) This method was shown to be useful for various solids (Dzyaloshinskii, Lifshitz and Pitaevskii 1961). In general, it requires the calculation of the dispersion of elementary excitations of the system. The term of the total van der Waals energy (vdWE) is not taken into account by standard one-body models. The contribution of one-dimensional collective modes is of primary importance for us. It gives a first-order correction within many-body approximations and beyond the 6–12 Lennard–Johns (LJ) potential (Lennard-Jones 1930). A complete description of the vdWE is possible if the system dielectric function is fully known. Unfortunately, it is not available for biological systems. Hence, we consider here nanotubes since their electronic structures can be calculated explicitly.

2. Calculation of Collective Modes

The theory starts with the calculation of the dielectric function of a single SWNT in RPA neglecting all modes except the collective plasmon modes which have most of the oscillator strength. These modes contribute the major input to the total vdWE.

Instead of writing the complete polarization function (refer to paper (Benedict, Louie and Cohen 1995)) and obtaining its high-frequency limit, we derive the answer from the equations of motion of the charge on

a cylinder surface:

$$\begin{cases} \dfrac{\partial j}{\partial t} = -\dfrac{ne^2}{m}\nabla\varphi \\ \dfrac{\partial \sigma}{\partial t} + \nabla j = 0 \end{cases}, \qquad (1)$$

where $n = 16/3\sqrt{3}b^2$ is the surface graphite electron density, m, e are the electron mass and charge, φ is an acting potential on the surface of the SWNT, which includes the induced potential of all charges on the surface, σ is the fluctuation of the charge density related to the plasmon mode, j is its current, ∇ is 2D gradient operator along the surface.

To close the set of equations we write the surface boundary condition for the fluctuation density $\sigma_{k\mu}$ using the Gauss-Ostrogradskii theorem:

$$4\pi\sigma_{k\mu} = \varphi\,\frac{1}{R\,K_\mu(kR)I_\mu(kR)}, \qquad (2)$$

where $K_\mu(kR)$, $I_\mu(kR)$ are Bessel functions of imaginary argument and of order μ taken at the SWNT radius R. k is the co-axial momentum of the mode, μ is the circumferential quantum number of the mode. The plasmon mode frequencies are given by the 1D series for each of allowed $\mu = 0, \ldots, N_{at} - 1$, where N_{at} is the number of atoms along the circumference in the real space unit cell of a SWNT. For example, for [10,10] armchair metallic nanotube it equals 20. The SWNT plasmon dispersion is:

$$\omega_{k\mu} = \omega_p\sqrt{R^2\left(k^2 + \frac{\mu^2}{R^2}\right)K_\mu(kR)I_\mu(kR)}. \qquad (3)$$

Here we use the notation $\omega_p = \sqrt{4\pi ne^2/mR}$ for the 2D plasma frequency at a characteristic length scale given by the SWNT radius, R. This frequency sets the energy scale for collective modes of the tube and, hence, for the vdWE.

3. van der Waals Cohesion Energy

The vdWE is given by the difference in the total energy of the modes of the electromagnetic vacuum due to the interacting systems approaching each other. The simplest way to calculate it is to find the collective mode frequencies as a function of the distance between the systems. The frequencies depend on the distance because of the Coulomb interaction between the shells.

The Coulomb interaction mixes the modes which are independent for infinite separation. We do not address here the problem of the interaction between systems with lattices which are not commensurate. We found that the correction to the result presented in this paper is small and diminishing as the inter-subsystem interaction becomes smaller than the bare plasmon energy. It will be discussed elsewhere (Rotkin and Hess unpublished). The Hamiltonian in the space of elementary excitations (plasmons) has the diagonal form:

$$H_o = \sum_{k,\mu}\hbar\omega_{k\mu}\left(n_{k\mu} + \frac{1}{2}\right), \qquad (4)$$

where $n_{k\mu}$ is the number operator for plasmons and $\omega_{k\mu}$ is the plasmon frequency which is given by Eq. (3) in the absence of any interaction. In the zero temperature limit (which is appropriate for distances smaller than 1000 nm), only the zero-point oscillation term survives. The van der Waals force is the derivative of Eq. (4) with respect to the distance which is implicitly included in the plasmon frequency.

3.1. Intertube van der Waals Attraction

In this section we calculate the attraction energy between two parallel nanotubes (Fig. 1C). We derive the plasmon frequencies from the quantum mechanical Lagrangian within the second quantization formalism. The Lagrangian for a single shell is:

$$L_1 = \frac{1}{2}\sum_{k,\mu}\left(\frac{\omega^2}{\omega_{k\mu}^2} - 1\right)\sigma_{k\mu}^\dagger\varphi_{k\mu} + h.c., \qquad (5)$$

where we use the Heisenberg operators of the classical potential, φ, and the classical charge density fluctuation, σ. This form of the continuum Lagrangian is consistent with the equations of motion as given in Eqs. (1) with Hamiltonian (6). The generalization of the Lagrangian for the case of two tubes (two shells) is straightforward:

$$\begin{aligned} L = &\frac{1}{2}\sum_{k,\mu}\left(\frac{\omega^2}{\omega_{k\mu}^2(1)} - 1\right)\sigma_{k\mu}^\dagger(1)\varphi_{k\mu}(1) \\ &+ \frac{1}{2}\sum_{K,M}\left(\frac{\omega^2}{\omega_{KM}^2(2)} - 1\right)\sigma_{KM}^\dagger(2)\varphi_{KM}(2) \\ &- \frac{1}{2}\sum_{k,\mu;K,M}V(1-2)\big(\sigma_{k\mu}^\dagger(1)\varphi_{KM}(2) \\ &+ \sigma_{KM}^\dagger(2)\varphi_{k\mu}(1)\big) + h.c. \end{aligned} \qquad (6)$$
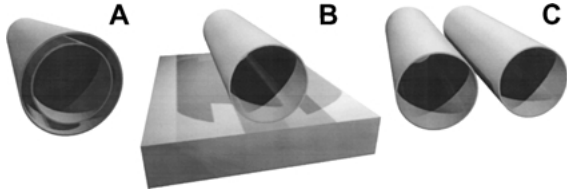
Figure 1. The 1D systems considered in the paper. (A) Double-shell nanotube. (B) Nanotube on a substrate. (C) Two nanotubes.

Figure 2. The calculated van der Waals potential: (upper) for nanotube on a substrate; (lower) for two identical nanotubes of $R = 7$ Å.

where the first two terms are the free Lagrangians of the plasmon subsystems and the last term represents the interaction between subsystems (1) and (2) which we treat perturbatively. The matrix elements which represent the Coulomb interaction between the tubes in the continuum limit are the combinations of the Bessel functions, comparing with the exponents in the planar problem (Chaplik 1971) and the Legendre polynomials in the spherical problem (Rotkin and Suris 1996, 1998). In order to proceed further analytically we restrict the expression for the Coulomb matrix to the components with $k = K$ and $\mu = M$. This approximation has the same accuracy as used before because the dimensionless ratio of the interaction to the plasmon frequency is small in our problem. We have to keep only the first order of this parameter in the secular equation for the plasmon mixing:

$$\sqrt{\left(-\frac{\omega^2}{\omega_{k\mu}^2(1)} + 1\right)\left(-\frac{\omega^2}{\omega_{k\mu}^2(2)} + \frac{K_\mu(kR_2)I_\mu(kR_2)}{K_\mu(kR_1)I_\mu(kR_1)}\right)}$$
$$= \mp \frac{I_\mu(kR_2)K_{2\mu}(kD)}{K_\mu(kR_1)} \qquad (7)$$

here D is the distance between the tube centers and R_1 and R_2 are the radiuses. The shifts of bare plasmon energy levels decrease with k and μ along with the Coulomb matrix element itself (given by RHS of Eq. (7)): in the limit of $kD \gg 1$ it is approximately equal to $1/\sqrt{2\pi kD} \exp(-k(D - 2R))$.

The specific van der Waals energy per atom of the system is the sum of the plasmon zero point oscillation energies divided by the total number of modes. The integral over the first Brilluine zone of the SWNT is substituted for the sum. We have considered the interaction between two tubes of the same radius $\sim$7 Å which is often used in simulations. The vdWE derived from the zero-point oscillation of those mixed modes decays with D as $D^{-4.5}$ (presented in Fig. 2). In contrast to one-body models this vdWE has a fractional exponent
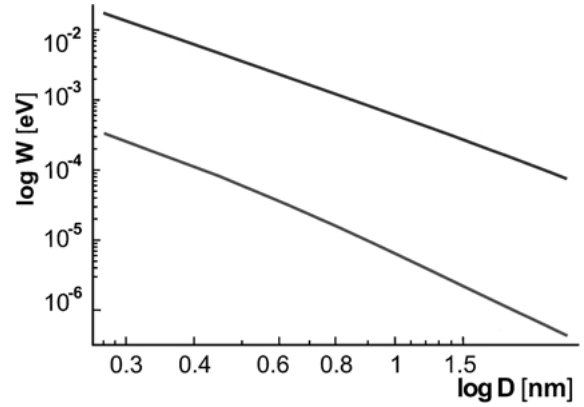
which reflects the specific square root dispersion of the bare plasmon frequency as given by Eq. (3).

3.2. Cohesion to Metal Substrate

The solution obtained for the tube-tube interaction can be readily used to yield the cohesion of the SWNT to the metallic substrate (Fig. 1B) because the electric field distribution near the flat conductor is given by the image charge of the opposite sign. Hence, one can choose the odd solution (with the minus sign) of the secular Eq. (7) while the even solution has to be discarded. The same integration over the Brilluine zone gives now a slower decay of the vdWE. It is because only one subsystem (SWNT) possesses the 1D plasmon modes in this case. The exponent is approximately -3.5 compared to -4.5 for two SWNTs (Fig. 2).

3.3. Inter-Wall Cohesion in DWNT

The energy of the inter-wall attraction in a multi-wall nanotube seemed to be an unmeasurable parameter before the discovery of the peapod structures, C_{60}@SWNT, and their transformation in double wall nanotubes. The process of creation of the second wall inside the initial nanotube is favorable owing to the energy of the inter-wall cohesion.

The Coulomb interaction between shells is given by continuum electrostatics. Because of the axial symmetry of the problem only modes with the same quantum numbers ($\mu = M$, $k = K$) are mixed and the interacting plasmon Lagrangian (5) is exactly diagonal in Fourier space. The secular equation is as
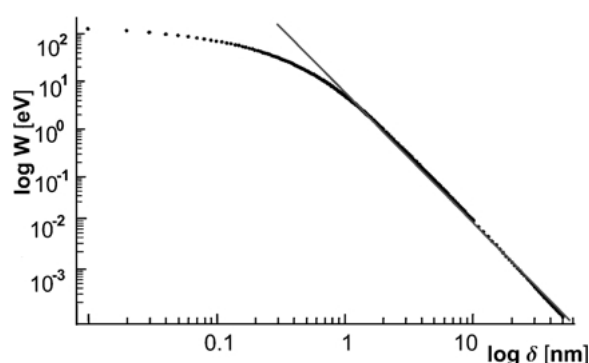
Figure 3. The dependence of the van der Waals potential for a double wall nanotube on the distance between shells, δ (dots); and the linear fit (solid line) with the exponent -2.5.

follows:

$$\sqrt{\left(-\frac{\omega^2}{\omega_{k\mu}^2(1)}+1\right)\left(-\frac{\omega^2}{\omega_{k\mu}^2(2)}+\frac{K_\mu(kR_2)I_\mu(kR_2)}{K_\mu(kR_1)I_\mu(kR_1)}\right)}$$
$$= \mp\frac{K_\mu(kR_2)}{K_\mu(kR_1)} \tag{8}$$

The plasmon frequencies depend on the radii of both shells. We plot here the vdW cohesion energy as a function of the intershell distance (Fig. 3). Both parameters can vary and be measured experimentally (Bandow *et al.* 2001).

In summary, we have developed a continuum theory which gives a fast and accurate qualitative estimation of the many-body contribution to the dispersion attractive force for 1D tubular systems made from layered materials. We have used the formalism of dielectric function and have assumed that the main term in the many-body van der Waals cohesion is from the collective modes (plasmons). The frequencies of the plasmons which are mixed by the Coulomb interaction are explicitly calculated. As a result of the mixing, the total system energy is lowered by the van der Waals contribution. Our approach is applicable to a wide class of shell systems with axial symmetry. For example, the van der Waals attraction between carbon double wall nanotube shells, parallel tubes as well as cohesion to the metal substrate are readily modeled.

The interesting result is the distance dependence of the new (many-body correction) term which has a fractional exponent, 5/2 for the tube-metal cohesion and 7/2 for tube-tube interaction, unlike an one-body energy given by LJ 6–12 potential. It was known that the direct summation of atom-atom interactions for carbon nanotubes gives the exponents of 4 and 3 for intertube and tube-substrate cohesion, respectively.

Our approach is almost independent on the commensurability issue which is in contrast to the one-body LJ potential. It can be easily applied for the cohesion of the tube to a substrate which is not graphite. Therefore, this contribution is especially important for the description of recently studied friction properties of nanotubes (Yu, Yakobson and Ruoff 2000, Cumings and Zettl 2000, Falvo *et al.* 2000).

Acknowledgments

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