van der Waals–London dispersion interactions for optically anisotropic cylinders: Metallic and semiconducting single-wall carbon nanotubes

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We investigate the van der Waals–London dispersion interactions between a single-walled carbon nanotube immersed in water and interacting with three different objects: an optically isotropic planar substrate, an optically anisotropic planar substrate, and another single-walled carbon nanotube of identical chirality. These interactions were derived from \textit{ab initio} optical properties and an appropriate formulation of the Lifshitz theory. We derive two analytically tractable limits for the van der Waals interaction: the far limit at separations much larger than the cylinder radius, and the near or Derjaguin limit where surface-cylinder separation is much smaller than the radius. We investigate in detail the effect of relative geometry and the relative separation on the magnitude of the dispersion interaction.

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I. INTRODUCTION

Single-wall carbon nanotubes (SWCNTs) have received an extraordinary amount of attention since their discovery in 1991.1,2 One unique feature of this class of materials is how much their electronic properties can change with respect to subtle changes in the wrapping angle, or chirality, of each particular carbon nanotube (CNT).3,4 Many researchers classify SWCNTs into two broad categories: metallic and semiconducting.5 The metallic tubes have a chirality such that \[(n-m) \mod 3 = 0\], where \(n\) and \(m\) are the lattice translation vectors for a simple sheet of graphene. All other combinations of \(n\) and \(m\) yield SWCNTs with a band gap and are thus semiconducting. The origin and reasoning behind the electronic structure’s dependence on chirality are well documented from both band-structure theory and experimental results, and are based heavily on the continuous nature of the graphene band structure becoming discretized because of the imposed finite distance in the circumferential direction. The metallic tubes are the SWCNTs that have these allowable states cross the \(k\) points of graphene.6

The literature often ignores the full frequency-dependent dielectric spectrum of the SWCNTs. This is largely due to two major reasons: First, people interested in electronic conduction focus particularly on the band gap. Second, it is nontrivial to measure accurately full spectral data. While it is true that these data are not necessarily important for the performance of a particular device, they are critical for making devices that involve the placement and/or arrangement of SWCNTs. Fortunately, computational power and efficient, robust quantum-mechanical codes have been developed to give us the very accurate spectral data needed for analyzing these interactions.7,8,9 Additionally, it has been discovered that the dielectric spectral data nonlinearly depend on chirality and some SWCNTs even exhibit significant optical anisotropy between their radial and axial directions.10,11 For the purposes of this paper, one CNT was selected out of each of the two major SWCNT classes (the \([6,5,s]\) semiconducting and \([9,3,m]\) metallic, which have been previously analyzed12). This is not to suggest that all or even any tubes in each category will behave alike. In fact, it is possible to group SWCNTs into three different classes (metals, semimetals [very small gap semiconductors], and semiconductors), by families,13 or have no classification system at all. While the taxonomy and correlation of van der Waals–London dispersion (vdW-Ld) spectra to chirality is very interesting in itself, it is not the focus of this paper and will be analyzed in the future. Rather, the focus is on the methodology of going from each SWCNT’s van der Waals–London dispersion spectrum to calculate the van der Waals–London dispersion interaction energy that results from the SWCNT’s shape and optical anisotropy.

The van der Waals–London dispersion interactions dominate systems that have no net charge and in which typical separations are much larger than those characteristic of molecular and atomic bonds. They are particularly important in colloidal systems and, in fact, determine the colloidal stability as formalized within the standard Derjaguin-Landau-Verwey-Overbeek theory.14 A proper understanding and a consistent theoretical formulation of the van der Waals–London dispersion interaction have been fully achieved within the Lifshitz theory of dispersion interactions.15,16 It provides the link between dielectric dispersion spectra and the magnitude of these interactions for geometries that are either analytically tractable or easily approximated into simpler geometries. For systems with anisotropic dielectric response, such as SWCNTs, the van der Waals–London dispersion interaction is much richer than in the case of simple isotropic systems. The anisotropy of dielectric response leads straightforwardly to orientation-dependent interactions and the van der Waals–London dispersion torques, which can, in turn, introduce strong alignment forces either between
and orientation behaviors in the far-limit Hamaker calculations for a metallic \([9,3,m]\) over a substrate comprised of a hexagonal packed array of \([9,3,m]\) CNTs in water, predicting to drive an orientational ordering or torque upon approaching CNT from an orthogonal to a collinear configuration. We have also shown that, contrary to a \([9,3,m]\) CNT, the \([6,5,s]\) CNT has a much weaker directionally dependent Hamaker coefficient for both the rod-rod and rod-substrate systems in either limit. These results should guide future formulations that consider retardation, salt within the medium, and multilayer geometrical arrangements.\(^{32-34}\)

The formulations are different from previous semi-infinite plane-plane interactions in that they introduce other components \((\Delta_\parallel, \Delta_\perp, \text{ and } \gamma \text{ as well as trigonometric functions}) which alter the influence on how strongly the spectral mismatches influence the resulting Hamaker coefficient. Their importance lies in the calculation not only of orientation effects but also of the overall difference in magnitude between different SWCNT chiralities and a substrate. Knowing the difference of these magnitudes is useful for those interested in solution separation of SWCNTs based on the chirality-dependent vdW-Ld interaction energies.

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\(^{5}\) One important thing to note is that these labels only describe the electronic conduction properties along the axial direction of the SWCNT and are unrelated to the electronic conduction properties in the radial direction and the SWCNTs’ optical properties in either direction.


\(^{23}\) See http://sourceforge.net/projects/geckoproj


\(^{25}\) The nonretarded case applies at small induced-dipole separations when \(od/c\) is small and no phase lag develops between the oscillations of the induced dipoles due to a finite speed of light, \(c\).


