Evaluation of the van der Waals force for atomic force microscopy

L. W. Bruch
Department of Physics, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA
(Received 22 February 2005; revised manuscript received 27 April 2005; published 18 July 2005)

The attractive van der Waals force between a conical silicon atomic force microscope tip and a carbon single-walled nanotube SWNT is calculated using parameters derived from the bulk dielectric response of silicon and of graphite. This configuration was used in a recent experiment [Phys. Rev. Lett. **93**, 136101 (2004)] in which the force between the tip and the nanotube was measured in the noncontact mode. The calculations depend on the shape of the tip and whether there is an oxide layer or a layer of amorphous silicon. There is a fair level of agreement between the calculations and measurements for tip-SWNT separations in the range 0.5 to 1.0 nm.

DOI: 10.1103/PhysRevB.72.033410 PACS number(s): 61.46.+w, 34.20.Cf, 68.37.Ps

I. INTRODUCTION

Atomic force microscopes (AFM) now reach atomic resolution and probe forces at sub-nanometer length scales. A quantitative measurement of the forces, as in a recent experiment which operates in the noncontact AFM (NCAFM) mode,[1] relates also to phenomena of adhesion at the microscale and nanoscale.[2,3] One step in validating the interpretation of such measurements is to test whether the inferred forces can be identified with known interactions. The geometry for the silicon AFM tip and the carbon single-walled nanotube (SWNT) in the Ashino *et al.* experiment[1] was relatively simple and the tip-SWNT force was of the magnitude anticipated for van der Waals forces. This has stimulated the present Note, in which the tip-SWNT attractive van der Waals force is calculated using data[4,5] for the bulk electrodynamic response of silicon and graphite. The electrodynamic formulation is adapted to provide estimates for novel configurations.[6]

The SWNT diameter, the dimensions of the AFM tip, and the tip-SWNT separation are all at the nanometer (nm) scale, so the van der Waals forces are in the near-field nonretarded regime. Two frequent approaches to the calculation are (1) to solve the electrodynamic boundary value problem assuming a continuum geometry and using a frequency-dependent dielectric image strength or (2) to use an atom-atom sum or integral[7] of the London–van der Waals energy $-C_6/R^6$, with the coefficient C_6 evaluated using empirical combining rules.[5] Here, data for the bulk dielectric response of graphite, silicon, amorphous silicon, and SiO_2 glass are transformed to give estimates for the dynamic polarizability of the atomic units and these are incorporated into effective C_6 strengths. Finally, the tip-SWNT force is evaluated using models for the tip, allowing for the possible presence of a SiO_2 layer or an amorphous silicon layer.

The calculated van der Waals force at separations 0.5 to 1.0 nm is similar to the experimental force. The experimental force[1] for larger separations is distinctly larger than the calculated force. To improve on the calculations will require more information about the structure and composition of the AFM tip than is known now from the experiment. Further, the force arising from the presence of just one unit of electron charge $|e|$ on the tip is larger than the van der Waals force at separations beyond 1 nm. These comments highlight the requirements to understand quantitatively an experiment that measures forces at the 0.01 nano-Newton (nN) level.

II. CALCULATIONS

A. Effective dynamic polarizabilities

The Clausius-Mossotti relation between polarizability α, number density n and dielectric constant ϵ

$$\frac{\epsilon-1}{\epsilon+2}=4\pi n\alpha/3 \tag{1}$$

is used for generalizations $\alpha(i\omega)$ and $\epsilon(i\omega)$, evaluated at pure imaginary frequencies, which enter in the Casimir-Polder formulation of van der Waals coefficients.[6] The $\epsilon(i\omega)$ is constructed from experimental data[4] for the absorptive component at real frequencies using Kramers-Kronig relations. For the present work, the result of that construction is approximated by Drude-oscillator expressions

$$\frac{\epsilon(i\omega)-1}{\epsilon(i\omega)+1}=\frac{g_0}{1+(\omega/E_s)^2} \tag{2}$$

and

$$n\alpha\,(i\omega)|_a=\,(n\alpha_0)|_a/[1+(\omega/E_a)^2]. \tag{3}$$

The parameters in Eq. (3) are given in terms of those in Eq. (2) by

$$(n\alpha_0)|_a=\frac{(g_0/2\pi)}{1-(g_0/3)};\quad E_a=E_s\sqrt{1-(g_0/3)}. \tag{4}$$

Table I shows the results of this analysis for several materials. The van der Waals coefficient for atoms a and b, using Eq. (3), is $C_6(a,b)=\frac{3}{2}\alpha_a\alpha_b E_a E_b/(E_a+E_b)$.

A test of this approximation for graphite[8] is to estimate the C_6 between the carbon atoms using the "atomic" information in Table I. Then $C_6=24$ a.u. for number density $n=1.14\times10^{23}/\mathrm{cm}^3$ and $\alpha_0=7.34$ a.u. This is close to $C_6=4\epsilon\sigma^6=25.0$ a.u. obtained from Steele's Lennard-Jones (12,6) C—C parameters,[9] $\epsilon_{CC}=28$ K and $\sigma=3.40$ Å. Thus

TABLE I. Parameters of the dynamic dielectric screening and polarizability, Eqs. (2)–(4). Energies are in a.u.

Material	g_0	E_s	$n\alpha_0$	E_a
graphite[a]	0.619	0.667	0.124	0.594
silicon[a]	0.84	0.43	0.185	0.365
SiO_2[b]	0.363	0.720	0.0657	0.675
amorphous silicon[c]	0.836	0.37	0.184	0.314

[a] g_0 and E_s from Appendix E of Ref. 5.
[b] SiO_2 glass, from dielectric data tabulated by H. R. Philipp in Ref. 4.
[c] Amorphous silicon with little hydrogen doping, from dielectric data of Pierce and Spicer reviewed by H. Piller in Ref. 4.

the results of the present formulation are likely to be similar to those for alternative combining rule constructions based on the Steele parameters.

Another test is to evaluate the van der Waals energy $-C_3/z^3$ for an atom a at distance z from a semi-infinite planar substrate of atoms b of number density n_b by integrating the atom-atom energy $-C_6(a,b)/R^6$ over the substrate volume. The resulting strength coefficient is denoted C_3(pair) and, using Eqs. (2) and (3), the expressions are

$$C_3(\text{pair}) = \frac{\pi n_b \alpha_b \alpha_a}{4} \frac{E_a E_b}{E_a + E_b}; \quad C_3 = \frac{g_0 \alpha_a}{8} \frac{E_a E_s}{E_a + E_s}. \quad (5)$$

The ratio of the C_3's for a silicon atom interacting with a semi-infinite planar graphite substrate is $C_3/C_3(\text{pair}) = 1.21$, using the data in Table I. This indicates that many-body corrections[6] to the forces calculated in this paper using atom-atom sums are at the level of 20%, which is an acceptable level of accuracy in the current situation.

B. Geometry

The Ashino *et al.* experiment nominally has a conical AFM with hemispherical tip (radius $R=2$ nm) oriented perpendicular to the axis of a graphite SWNT of diameter $d=1.4$ nm. The force was reported as a function of separation D between the tip and the surface of the SWNT. The zero of D was set[1] using a model for the short-range repulsion between the tip and atoms of the SWNT. The SWNT was in a bundle, but the present calculation treats a single SWNT supported on a graphite plane.

The model tip in the calculations has circular symmetry about its axis. The radius as a function of distance ξ along the axis, measured from the join of the hemisphere to a truncated cone, is

$$\rho(\xi) = \sqrt{R^2 - \xi^2}, \quad -R < \xi < 0; = R + \gamma\xi, \quad 0 < \xi. \quad (6)$$

The experimental tips apparently[10] have conical slopes of $\gamma \approx 0.05-0.1$. The value $\gamma=0.1$ is adopted for the work reported here; there are changes of less than 5% when $\gamma=0.05$ is used.[11]

There is some ambiguity about the state of the tip in the measurement. Silicon exposed to air is likely to have a SiO_2 layer of about 1 nm thickness. After cleaning *in situ* by argon ion sputtering,[1] most of the SiO_2 may be replaced by amorphous silicon and the tip itself may be reduced in size. To examine the effects of such uncertainties, the calculations were done for outer tip radii R in the range 1.5–3.0 nm; the tip itself was taken to have two components, a crystalline silicon core, and a shell of SiO_2 or amorphous silicon of thickness $\Delta R = 0.5-1.0$ nm. Because g_0 and E_s for silicon and amorphous silicon are so similar, Table I, replacing silicon by an amorphous silicon layer is expected to make little change in the calculations, and the results for that case are not reported here.

The force on the AFM tip includes the van der Waals force arising from the planar graphite that supports the SWNT.[1] This is included here by integrating the $-C_3/z^3$ energy over the "atoms" of the AFM tip (distance $D+d$ from the plane) and using the bulk dielectric function of graphite.

The SWNT is treated as a cylinder of carbon atoms of 2D number density $n = 3.82 \times 10^{15}/\text{cm}^2$. The C_6/R^6 sum for the carbon atoms is evaluated by integrating over a cylindrical surface of radius $d/2$.

The calculations are done as a function of the distance z of the AFM tip from the axis of the SWNT. The force in the experiments is reported as a function of distance D of the tip from the SWNT and so $D \approx z - (d/2)$. The uncertainty in the procedure that sets the zero of D is probably at the level of 0.1 nm. There also is an offset of this order for the effective cylinder boundary after the integration over the SWNT surface.[5]

The integration over the surface of the SWNT and the volume of the AFM tip initially is a calculation in five variables. Three of these are reduced analytically and what remains is a twofold integration, a straightforward numerical task.

C. Results

The results of the calculations are compared with the experimental data in Fig. 1. The abscissa is $Z \equiv z - (d/2)$ for the model calculations and is the reported D for the experiment.[1] As noted above, there is an uncertainty of order 0.1 nm in identifying Z with D.

The X's in Fig. 1 denote the data[1,12] for the total experimental force on the AFM tip, nominally formed of silicon with a hemispherical cap of radius $R=2$ nm. The points are a linear average of the measurements at given D above the carbon and hollow sites of the SWNT. The horizontal arrows indicate the effect of a constant shift of +0.1 nm in D. The open squares show the calculations for a silicon tip shape given by Eq. (6) using $\gamma=0.1$ and $R=2.0$ nm while the open circles have $R=1.5$ nm instead. The filled squares and circles have the same tip shapes, but with the outer 1.0 and 0.5 nm shells, respectively, replaced by SiO_2. All these cases have force magnitudes similar to those of the experiment, but the composite tip cases seem to follow the experimental data better in the range $Z \approx 0.5-1.0$ nm. The contribution of the planar graphite support to the total force increases from 5% at $Z=0.5$ nm to 20% at 1.0 nm and 50% at 2.0 nm.

The experimental force for $D \approx 1-3$ nm was fitted[1] to $F = 0.02/D$, with F in nN and D in nm. The calculated force

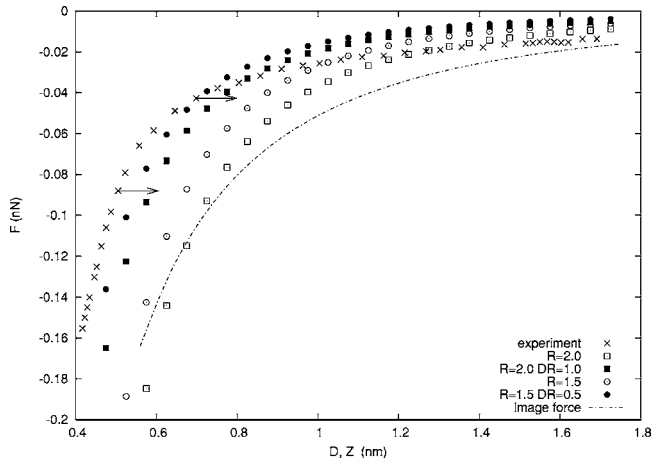

FIG. 1. Force (in nN) as a function of distance (in nm) of the "silicon" AFM tip from the surface of a carbon SWNT of diameter $d=1.4$ nm. The X's denote the experimental data, Ref. 1, and are given as a function of D, which has a zero set by an estimate of the short-range tip-SWNT repulsion. The results of the calculations are shown as a function of the distance Z obtained from the distance z of the tip from the SWNT axis using $Z=z-(d/2)$. The arrows show the effect of a displacement of the origin of D by 0.1 nm. The van der Waals forces are calculated with $\gamma=0.1$. The open squares are for a pure silicon tip with $R=2$ nm and the open circles are for $R=1.5$ nm. The filled symbols have the same shape, but the outer 1.0 (0.5) nm consists of SiO_2 for $R=2.0$ (1.5) nm, respectively. The dot-dash line represents the electrostatic force on a point charge $|e|$ at distance Z from a grounded conducting cylinder of radius $d/2$.

magnitude drops off much more rapidly with increasing distance at these Ds and is about 60% of the experimental value at 2 nm. It is difficult to see how the simple $1/D$ power law dependence might arise for van der Waals forces in this geometry.[7] Further, a force of magnitude of 0.01 nN is indeed very small. One unit of charge can give such a magnitude, but again with a faster decrease with increasing D. The dot-dashed line in Fig. 1 shows the force[13] on a point charge of unit magnitude $|e|$ at a distance Z from a grounded conducting cylinder of radius 0.7 nm, to illustrate the large effect of static charge. However, this does not account for the measured force at 1–3 nm. If the tip shape changed drastically in the experimental processing, to the extent that it became very blunt with $\gamma\approx 1$, the van der Waals force at 2 nm might become of order 0.01 nN.

III. CONCLUSIONS

The present calculations show an encouraging level of agreement with the AFM-SWNT force measured in the recent experiment. The results at intermediate separations 0.5–1.0 nm support the identification of the measured force with a van der Waals force. For a more quantitative analysis, more detailed knowledge of the state of the AFM tip in the measurement and of the distribution of the neighboring SWNTs is needed. Then an extended calculation that included the leading many-body corrections[6] to the pair sums used here would be warranted.

ACKNOWLEDGMENTS

It is a pleasure to thank Professors F. J. Himpsel and M. Eriksson for helpful discussions. This work has been partially supported by the NSF Grant No. DMR0104300.

[1] M. Ashino, A. Schwarz, T. Behnke, and R. Wiesendanger, Phys. Rev. Lett. **93**, 136101 (2004).

[2] J. N. Israelachvili, in *Fundamentals of Friction: Macroscopic and Microscopic Processes*, edited by I. L. Singer and H. M. Pollock (Kluwer, Dordrecht, 1992), pp. 351–385.

[3] R. W. Carpick and J. D. Batteas, in *Handbook of Nanotechnology*, edited by B. Bhushan (Springer, Berlin, 2004), pp. 603–628.

[4] *Handbook of Optical Constants of Solids*, edited by E. D. Palik (Academic, San Diego, 1998), Vol. I.

[5] L. W. Bruch, M. W. Cole, and E. Zaremba, *Physical Adsorption: Forces and Phenomena* (Oxford University Press, Oxford, 1997).

[6] S. M. Gatica, M. W. Cole, and D. Velegol, Nano Lett. **5**, 169 (2005).

[7] F. J. Giessibl, Phys. Rev. B **56**, 16 010 (1997).

[8] The SWNT electronic properties differ from those of a graphene sheet, and in turn from those of bulk graphite, because of the quantization of electron motions around the tube axis. The associated energy scale is about 1 eV and is smaller than the dynamic response 5–10 eV that is the main contribution to the van der Waals energy. A rough estimate is that the magnitude of the modifications to the present calculation might be as much as 25%. For reviews of the electronic properties of the SWNT see C. Dekker, Phys. Today **52** (April), 22 (1999); M. Ouyang, J. L. Huang, and C. M. Lieber, Annu. Rev. Phys. Chem. **53**, 201 (2002).

[9] W. A. Steele, Surf. Sci. **36**, 317 (1973).

[10] Nanosensors, Switzerland, URL www.nanosensors.com

[11] The integral over the conical tip volume is carried to a maximum distance $\xi_m=150$ nm, with ξ as defined in Eq. (6). This is large enough that the calculated force has converged to 1%.

[12] These are the values for the total interaction forces at $D>0.5$ nm. The modeling of short-range forces by Ashino *et al.* (Ref. 1) enters the present work only in setting the origin of the distance D.

[13] F. W. Guy, Proc. of the 1991 IEEE Particle Accelerator Conf., San Francisco, CA, p. 3032, presents the formal solution for the electrostatic potential of a point charge external to a long grounded conducting cylinder.