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van der Waals attraction between two C_{60} fullerene molecules and physical adsorption of C_{60} on graphite and other substrates

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The van der Waals interaction between two C_{60} fullerene molecules is computed using a discrete-dipole formalism in which C_{60} is viewed as a rigid cluster of 60 polarizable, interacting carbon atoms. The dispersion energy is obtained from the shift in zero-point energy of the ground-state dipolar fluctuations. The intermolecular attraction potential deduced from this approach is compared with the Girifalco potential [J. Chem. Phys. **96**, 858 (1992)] which includes only averaged, pairwise additive interactions. The results are also compared with the potential of two continuum dielectric shells of finite thickness [Ph. Lambin *et al.*, Phys. Rev. B **46**, 1794 (1992)]. The dispersion energy between C_{60} and graphite is also computed with the same discrete-dipole molecular model and by treating the substrate as a continuous dielectric medium. The adsorption energy is compared with the result of summing discrete $1/r^6$ C-C interactions. Similar calculations are presented for a C_{60} molecule on semiconductors (Ge, Si, and GaAs) and insulators (LiF and MgO). Lastly, the substrate-mediated dispersion energy between two adsorbed molecules is discussed. The calculations include all orders of dipole-dipole interactions between the molecules and with the substrate. The comparison with pairwise additive dispersion energies brings out the non-negligible role of many-body contributions.

I. INTRODUCTION

Many thin-film studies involving fullerene layers deposited on a variety of substrates have been conducted in the last few years, as soon as C_{60}, C_{70}, and other fullerenes were discovered[1] and made commonly available.[2] The aim of such studies was manifold: imaging, spectroscopy, structural analysis, transport measurements, etc.[3] Most published works so far concerned films of easily prepared C_{60} fullerite. Only recently films of C_{70},[4] C_{84},[5] and other fullerenes[6] have been successfully grown and characterized. By contrast, the substrate materials investigated were very diverse and ranged from metals,[7–13] semiconductors,[6,14–20] layered materials,[21–28] insulators[29–34] to organic film supports.[35] Some studies were devoted to very thin films, in the sub-monolayer to the monolayer regime. Other concerned multilayers and thick films up to several thousand Å.

The structure of the multilayer films nearly always consists of a stacking of hexagonal close-packed (111) monolayers parallel to the substrate and with about the same density as in bulk C_{60} fullerite. The degree of long-range crystallinity (or the defect density) depends very much on the nature of the substrate, the structure of its surface, the deposition and annealing temperatures, etc. In particular, the actual stacking sequence, whether ordered (fcc or hcp) with occasional or frequent planar defects (faulting, twinning) or completely disordered, is still uncertain. This also reflects the uncertainty on the growth mode, whether layer by layer or by islands. In general, van der Waals epitaxy[36] on weakly bonding substrates, aided by careful annealing, favors highly-ordered films. By contrast, the formation of stronger, chemisorption-like (valence or/and ionic) bonds between the first layer and the substrate (such as Si and some metals) tends to cause the growth of highly disordered films except, possibly, when fortuitously, there is close commensurability of the substrate and the fullerite lattice constants. In any case, it turns out that the structure of the first layer is all important in determining the subsequent film growth. It is, therefore, of major interest to obtain quantitative information on the fullerite-substrate interface.

The equilibrium film structure involves the interactions between the molecules themselves and between the molecules and the substrate. Whereas the former are relatively well understood (from both the experimental and theoretical results) to be predominantly of the van der Waals type, the latter are still largely unexplored and are likely to be highly substrate specific. If one could measure the heat of adsorption of the first molecules arriving at the surface until formation of a monolayer, one would be able to deduce these interactions and perhaps arrive at a better understanding and control of the right conditions for the formation of perfectly ordered films. Unfortunately, after three years of intense fullerene research, there is as yet virtually no experimental determination of adsorption heats.

From the theory side, the rather large number of valence electrons per fullerene makes it difficult to determine the adsorption energy *ab initio*. In addition, the van der Waals interaction which, even on strongly binding substrates, is expected to make a substantial contribution (on account of the molecular nature of the adsorption), is notoriously difficult to predict correctly from *ab initio* methods. As a consequence, one has to consider developing much simpler approaches. For the case of C_{60}

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on graphite, as an example, simply adding C-C pair interactions yields an adsorption energy of about 0.8 eV per molecule,[37] about twice the bond energy of a C_{60} dimer treated on the same pairwise additive footing.[38] While waiting for experimental results to test the reliability of such model predictions, it should be interesting to explore other semi-empirical, more sophicated approaches going beyond the pairwise additivity rule.

In the present paper, we first deduce the van der Waals adsorption energy of a C_{60} molecule from the normal modes of 60 dynamical dipoles located at the positions of the carbon atoms of the molecules adsorbed on a semiconductor or an insulator. By the use of a linear-response formalism,[39] we evaluate all orders of dipole-dipole interactions induced by the substrate at the location of the molecule. This technique only demands the dynamical electronic polarizability of the carbon atom and the high-frequency dielectric function of the substrate treated here as a semi-infinite dielectric continuum. These data are in common use in other contexts from which they are available for the present treatment of the van der Walls binding energy. For a molecule having its center 6 Å above a flat surface, the van der Waals energy is found to vary between 0.3–0.6 eV, depending on the nature of the substrate.

The attractive part to the C_{60}-C_{60} interaction energy is next evaluated by the same technique for a pair of molecules adsorbed on a substrate in the parallel configuration. By comparing the pair energy with that of an isolated dimer, we do not find any significant influence of the substrate on the binding energy of the pair. Our dipolar model includes all the many-body terms in the dispersion energy which, as we will see, make a small (of order 10%) contribution to the total energy beyond the usual pairwise additive terms.

The strongest approximation in our approach is in treating the substrate as a continuous medium. This approximation is certainly unrealistic for a system like Si with its dangling bonds and highly reconstructed and corrugated surfaces but should not be too severe for the less reactive surfaces of GaAs and MgO considered below and even less severe for the smooth, unreconstructed metal surfaces. There is no intrinsic difficulties but computational ones in the linear-response formalism in including part of the surface corrugation.[40] This will be reserved for a future, more detailed analysis specialized to specific surfaces and when experimental data become available. The surface corrugation of unreconstructed surfaces is expected to modify our estimated van der Waals energies by 10% at most. However, this corrugation should affect more importantly the repulsive part of the adsorption energies. Surface reconstructions [such as Si(111)7×7 or Au(110)3×1], preexisting or induced by the adsorption,[41] will affect both long-range and short-range interactions but these situations fall outside the scope of the present study.

II. van der WAALS ATTRACTION

It is well known that the van der Waals binding energy arises from the lowering of the zero-point energy of correlated ground-state fluctuations of atomic dipoles as a result of their electromagnetic interactions.[42] This concept, which dates back to the work of London,[43] is now applied to a fullerene molecule in the presence of a solid surface. A C_{60} molecule is viewed as a rigid cluster of 60 polarizable C atoms. A fluctuation $\mathbf{E}(\mathbf{r})e^{-i\omega t}$ of the electric field induces dipoles moments $\mathbf{p}_j e^{-i\omega t}$ on the atoms $j=1,\ldots,N$. These dipoles in turn generate an electric field whose amplitude $\mathbf{E}_i$ on site $\mathbf{r}_i$ is

$$\mathbf{E}_i=\sum_{j\neq i}\underline{T}(\mathbf{r}_i-\mathbf{r}_j)\mathbf{p}_j+\sum_{j}\underline{S}(\mathbf{r}_i,\mathbf{r}_j;\omega)\mathbf{p}_j \ . \tag{1}$$

The first term in Eq. (1) represents the bare field of the dipoles in vacuum whereas the second term is the field induced by the substrate. The latter is assumed to be a linear expression of the source dipoles $\mathbf{p}_j$. Due to the fact that the size of the C_{60} molecule and the adsorption distances are small on the scale of the optical wavelengths, the electromagnetic retardation can be safely neglected throughout. $\underline{T}(\mathbf{r})$ then reduces to the tensor $(3\mathbf{rr}-r^2\underline{I})/r^5$ with $\underline{I}$ the identity matrix. The field propagator $\underline{S}$ induced by the substrate is evaluated in the simplest possible approximation which consists in treating the substrate as a semi-infinite, continuous dielectric medium providing a spatially local response. In this context, the image of electrostatics can be used to obtain

$$\underline{S}(\mathbf{r}_i,\mathbf{r}_j;\omega)=-\frac{\varepsilon(\omega)-1}{\varepsilon(\omega+1}\underline{T}(\mathbf{r}_i-\mathcal{J}\mathbf{r}_j)\mathcal{J} \ , \tag{2}$$

where $\varepsilon(\omega)$ is the local dielectric function of the substrate, and $\mathcal{J}$ is the "imaging" diagonal matrix with elements $(1,1,-1)$, the surface surface having been assumed to be located at $z=0$. Equation (2) simply states that $\underline{S}\mathbf{p}_j$ is the electric field of an image dipole $-(\varepsilon-1)/(\varepsilon+1)\mathcal{J}\mathbf{p}_j$ at the position $\mathcal{J}\mathbf{r}_j$ symmetric of $\mathbf{r}_j$ with respect to the surface plane. This simple dielectric-theory approximation is valid for the physisorption distances (at least 3 Å) relevant to the present systems.

Inserting $\mathbf{p}_j=\alpha_j(\omega)\mathbf{E}_j$ into the right-hand side of Eq. (1) leads to a set of linear equations for the amplitudes of the fluctuating electric field:

$$\mathbf{E}_i-\sum_{j\neq i}\underline{T}(\mathbf{r}_i-\mathbf{r}_j)\alpha_j(\omega)\mathbf{E}_j-\sum_{j}\underline{S}(\mathbf{r}_i,\mathbf{r}_j;\omega)\alpha_j(\omega)\mathbf{E}_j=0 \ , \quad i=1,\ldots,N \ , \tag{3}$$

where $\alpha_j(\omega)$ is the dynamical polarizability of the atom at the site j. The allowed frequencies ω_q of the coupled dipoles are the zeros of the determinant $\Delta(\omega)$ of the $3N\times3N$ dynamical matrix defined by Eq. (3).

When the dipole eigenmodes of Eq. (3) are quantized, they acquire a zero-point energy given by

$$\mathcal{E}_0=\tfrac{1}{2}\sum_{q}\hbar\omega_q=-(\hbar/4\pi)\int_{-\infty}^{+\infty}\ln[\Delta(i\xi)]d\xi \ , \tag{4}$$

where a well-known theorem of complex analysis has been used to relate the sum of the positive zeros of the analytic function $\Delta(\omega)$ to an integral of its logarithm along the imaginary axis.[42]. The van der Waals energy follows immediately from Eq. (4): the attractive part of the adsorption energy of C_{60} at 0 K is the change of zero-point energy as the molecule comes from infinity to its equilibrium distance to the surface. Note that the results obtained in this way includes the dynamical response of the substrate (not just its static dielectric screening) via the ω dependence of the field propagator $\underline{S}$ in Eq. (2). The same method can be used to evaluate the interaction between two C_{60}'s in free space [$\underline{S}=0$ and $N=120$ in Eq. (3)] or near a solid surface ($\underline{S}\neq 0$ and $N=120$). The way the equations are solved in practice is described in the Appendix. The results are discussed in the following sections.

III. PHYSICAL ADSORPTION OF C_{60} ON GRAPHITE

Graphite is an interesting substrate to begin with as it allows us to compare the results of our calculation with those of a less accurate approach that consists of summing over all C-C pair interactions assumed to be additive. The attractive part to the binding energy of C_{60} can be evaluated by simply adding c_6/r^6 pair potentials with the further simplification that the C atoms in C_{60} are smeared over a sphere.[44] Similarly, the carbons in the graphite substrate are supposed to be distributed on parallel sheets with a uniform planar density σ.[45] The advantage here is that the attraction energy can be expressed analytically[37]

$$U(z_0)=-(N/6)\pi c_6\sigma \sum_{n=0}^{\infty} \frac{3(z_0+nh)^2+R^2}{[(z_0+nh)^2-R^2]^3} , \qquad (5)$$

where h is the interlayer spacing of graphite, R is the radius of the spherical fullerene with N carbons, and z_0 is the distance from the center of the molecule to the outermost graphene layer. This potential for C_{60} is plotted in Fig. 1 against z_0 for two values of the C-C interaction parameter c_6 equal to 15.2 and 20.0 eV Å^6. These were deduced from the static properties of graphite[45] and solid C_{60} fullerite,[44] respectively.

The full circles in Fig. 1 were obtained by applying the discrete-dipole formalism of Sec II. The polarizability of the C atom in the fullerene was represented by a simple isotropic Lorentzian model, $\alpha(\omega)=\alpha_0\omega_0^2/(\omega_0^2-\omega^2)$ with $\alpha_0=1.1$ Å^3 and $\hbar\omega_0=18.15$ eV.[46] Graphite was considered as an isotropic continuum with an effective dielectric function $\varepsilon(\omega)$ of the Drude type.[47] The free surface of the dielectric medium was positioned $h/2$ (one half the interlayer spacing of graphite) above the outermost graphene sheet.[48] In other words, the distance D between the center of C_{60} and the continuum edge in our description is related to the distance z_0 of Eq. (5) through $D=z_0-h/2$. With that choice of the location of the image plane, Eq. (5) with $c_6=15.2$ eV Å^6 (solid curve in Fig. 1) reproduces remarkably well our calculated data points at large separation distances. It underestimates the attraction energy as the distance to the surface decreases and c_6 needs to be raised to about 20 eV Å^6 to reproduce the van der Waals attractive energy at the short adsorption distance $z_0\approx R+h\approx 6.9$ Å (dashed curve in Fig. 1).

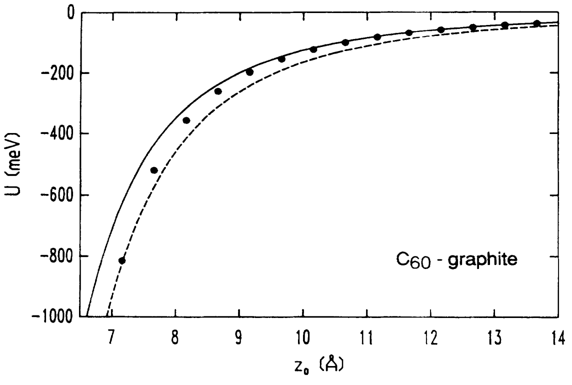

FIG. 1. van der Waals adsorption energy of C_{60} on graphite as a function of the distance z_0 between the center of the molecule and the outermost graphene layer. The closed circles are the results of the discrete-dipole formalism on Sec. II. The two curves were obtained from Eq. (5) with $c_6=15.2$ (solid curve) and 20.0 eV Å^6 (dashed curve) appropriate to graphite and solid C_{60}, respectively.

The discrete-dipole calculations shown in Fig. 1 were performed for a molecule having a pentagon parallel to the surface. By changing the orientation of the molecule while maintaining its center fixed, the attraction energy computed at the adsorption distance of about 7 Å changes by ±1 meV only. In other words, the effect of the atomic corrugation of C_{60} is very small as far as the van der Waals attraction by graphite is concerned and a spherical description of the molecule, in the manner of Girifalco,[44] is very well adapted to this particular problem, provided the pair interaction coefficient c_6 be adjusted to the distance, as indicated in Fig. 1.

IV. C_{60}-C_{60} INTERACTIONS

The attraction energy between two isolated C_{60} molecules has also been computed using similar approaches. The discrete-dipole model, which now includes 120 polarizable carbons on two molecules, yields the data indicated by closed circles in Fig. 2 as a function of the center-to-center distance X_0. The solid curve represents the Girifalco potential[44]

$$U(X_0)=75\frac{c_6}{R^2}\left[\frac{1}{X_0(X_0-2R)^3}+\frac{1}{X_0(X_0+2R)^3}-\frac{2}{X_0^4}\right] \qquad (6)$$

obtained by integrating the pair interaction c_6/r^6 on two spheres of radius $R=3.55$ Å. The interaction parameter was adjusted so as to best fit our calculated data points for $9.5\leq X_0\leq 12$ Å, and this lead us to $c_6=17.0$ eV Å^6 which is intermediate between the two extreme values obtained above for the physical adsorption of C_{60} on graphite.

The dashed curve in Fig. 2 shows the results deduced from yet another approach in which a C_{60} molecule is represented by a dielectric spherical shell of finite thickness. The van der Waals attraction between two such shells is the result of coupling their multipolar electrostatic modes and computing their quantized zero-point energies.[49] This approach demands a dynamical dielectric

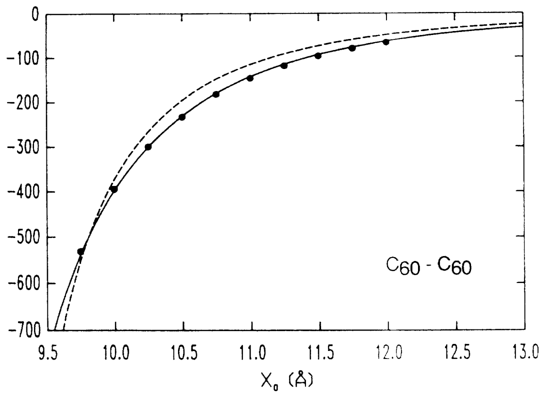

FIG. 2. van der Waals attraction between two C_{60} molecules whose centers are at the distance X_0. The discrete-dipole formalism leads to the data shown by the closed circles. These results are well reproduced by the potential (6) with $c_6 = 17.0$ eV Å^6 (solid curve). The dashed curve shows the attraction energy derived from multipolar charge oscillations in two dielectric spherical shells with parameters appropriate to C_{60} (Ref. 50).

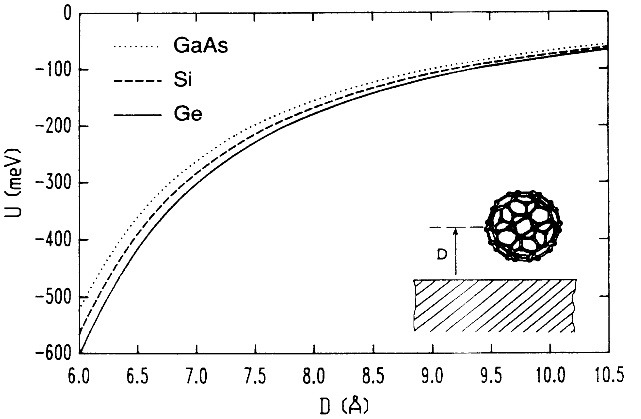

FIG. 3. Variation of the dispersion interaction $U(D)$ between a single C_{60} molecule and a perfectly planar surface of Ge (solid curve), Si (dashed curve), and GaAs (dotted curve). D is the distance from the center of the molecule to the continuum edge of the dielectric medium that represents the substrate.

function appropriate to the valence-electron cloud of fullerene, which in the present application incorporates two resonances at the excitation energies of the π and σ plasmons of sp^2 carbon. These energies were taken, respectively, at 5.0 and 15 eV. The other parameters of the model are the inner and outer radii of the shell, respectively, 2.7 and 4.4 Å.[50] It was necessary to include multipolar modes of order as high as $l = 13$ for the shortest separation distances considered in Fig. 2. At short distances, the potential derived from the multipolar polarization modes of the two shells is harder than those obtained by the two other methods because the shells extend outside the carbon skeleton. This requires the inclusion of higher and higher l values which eventually leads to a diverging potential as the gap between the two shells closes while the carbon frames remain at a finite separation.

When the distance between the two molecules is much larger than the radius of the carbon cages, the attraction energy between them behaves like $U(X_0) \approx -L/X_0^6$. The London constant L deduced from the additive approximation of Eq. (6) is obviously $N^2 c_6$ with $N = 60$ being the number of carbons per molecule. On the other hand, L is also related to the polarizability of the molecule $\alpha_{\rm mol}$ through the Lifshitz formula[51]

$$L = (3\hbar/2\pi)\int_{-\infty}^{+\infty}[\alpha_{\rm mol}(i\xi)]^2 d_{\xi} \; . \qquad (7)$$

Within our discrete-dipole model, $\alpha_{\rm mol}$ depends on the individual polarizability α of carbon in a complicated way. For a sufficiently small α, one can use a power series: $\alpha_{\rm mol} = N\alpha + T_1\alpha^2 + T_2\alpha^3 + \cdots$. The first term is the additive value leading to Girifalco's $L = N^2 c_6$. In the second term, the coefficient T_1 is the sum over all the pairs (i,j) of the dipolar tensors $\underline{T}(\mathbf{r}_i - \mathbf{r}_j)$ and this vanishes in C_{60} for symmetry reasons. The $\underline{T}_2$ coefficient in the series was adjusted numerically so that the exact many-body polarizability of C_{60}, which is obtained by solving for the eigenmodes of our discrete dipole model, be well reproduced by the simple law $\alpha_{\rm mol} = 60\alpha + 26.4\alpha^3$ (in Å^3 units) for $\alpha < 1.1$ Å^3. Evaluating the London constant from Eq. (7) is then reduced to a simple exercise when a Lorentzian model is used for $\alpha(i\xi)$:

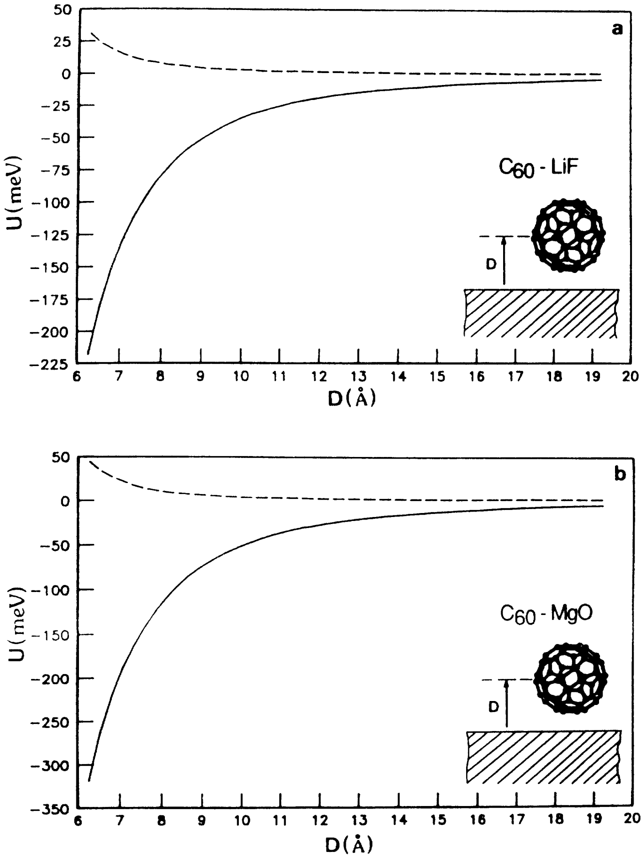

FIG. 4. Dispersion energy between a dielectric substrate and a single C_{60} molecule having its center at a distance D above the surface (solid curves): (a) LiF and (b) MgO. The many-body contributions to the van der Waals energy are visualized by the dashed curves.

$$L=\tfrac{3}{4}\hbar\omega_0\alpha_0^2N^2+\tfrac{5}{4}NT_2\alpha_0^2+\tfrac{63}{128}(T_2\alpha_0^2)^2\ . \tag{8}$$

With the parameters of carbon referred to above,[46] one obtains $L/N^2=29$ eV Å^6. This nonadditive value is nearly twice that of the C-C pair interaction used in the Girifalco additive potential plotted in Fig. 2 ($c_6=17$) at much shorter distances than the asympototic distances considered in the present discussion. This interesting discrepancy stems from the role played by the internal local field within the molecule which enhances the dipole polarizability over the additive value of 60α. At shorter distances, on the other hand, the dipolar term plays a much reduced role[49] in the interaction energy as compared to the contributions of higher and higher multipoles for which the internal molecular field is of decreasing importance, so that the additivity rule holds much better.

V. C_{60} ON OTHER SUBSTRATES

Calculations of the physisorption energy of C_{60} on various substrates were carried out again using the dielectric approximation for the field-propagator $\underline{S}$ of Eq. (1). The dispersion energies obtained for the semiconductors Si, Ge, and GaAs are shown in Fig. 3.[52] Figure 4 illustrates similar results obtained for the insulators LiF and MgO,[53] for which the van der Waals attraction is found to be about twice smaller than with the semiconductors of Fig. 3. This result is a consequence of these insulators having their surface response function $(\varepsilon-1)/(\varepsilon+1)$ at low frequency roughly two times smaller than the one of the semiconductors. Graphite (Fig. 1) is in between these two situations.

In order to assess the importance of the many-body contribution to the physisorption energy of C_{60}, we have subtracted from $U(D)$ the dispersion term linear in both the atomic polarizabilities and the substrate propagator $\underline{S}$, as it is given by McLachlan's equation[54]

$$U_0(D)=-(\hbar/4\pi)\int_{-\infty}^{+\infty}\mathrm{tr}\Big[\alpha(i\xi)\sum_{j,k}\underline{S}(\mathbf{r}_j,\mathbf{r}_k,i\xi)\Big]d\xi\ . \tag{9}$$

This expression is easily evaluated with the dielectric approximation [Eq. (2)]. The dashed curves in Fig. 4 show the results: $U(D)-U_0(D)$ is a repulsive potential (dominated by the triplet interactions) much smaller than the pair attraction. The same also holds true for the semiconductors of Fig. 3 where the many-body contribution is found to be about $0.1|U_0(D)|$ at the distance $D=6$ Å.

The dispersion energy between two fullerenes absorbed in the parallel configuration was also computed. The re-

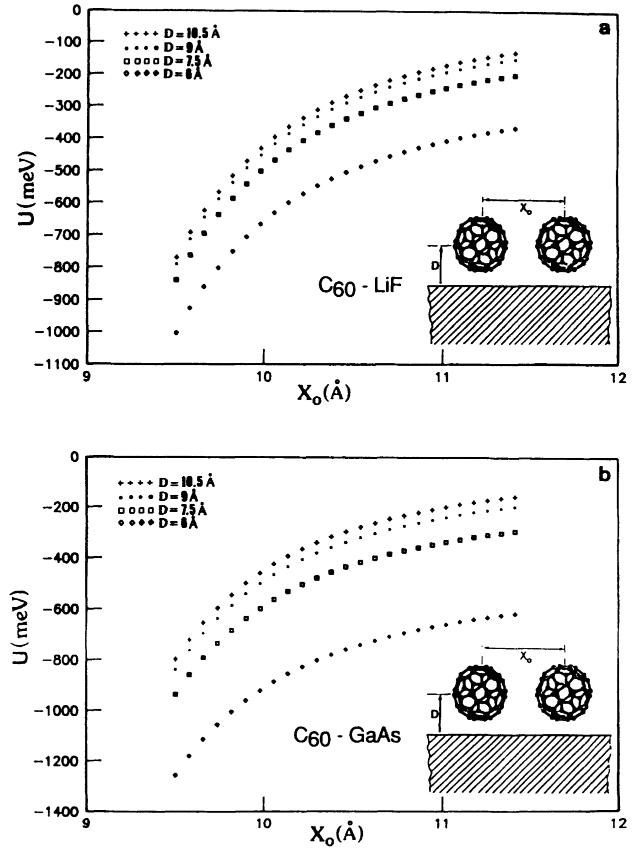

FIG. 5. van der Waals dispersion energy between two C_{60} molecules approaching the surface of (a) LiF and (b) GaAs. X_0 is the separation between the centers and D is the distance of the center of each molecule and the surface ($D=6.0$, 7.5, 9.0, and 10.5 Å). The zero of energy corresponds to the potential of one molecule already adsorbed at the distance D.

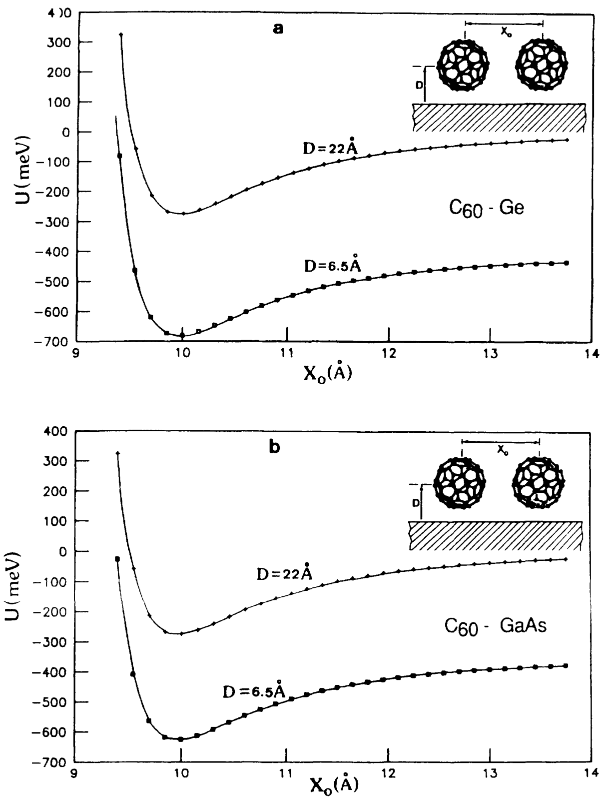

FIG. 6. Total energy curves between two C_{60} molecules interacting with a surface of (a) Ge and (b) GaAs when a short-range repulsive potential is added to the attractive energy. This potential is the sum of c_{12}/r^{12} C-C interactions. The two molecules have their centers at the distance D from the surface ($D=6.5$ and 22 Å).

sults on LiF and GaAs are shown in Figs. 5(a) and 5(b), respectively, as a function of the center-to-center distance X_0. The potential curves obtained for several adsorption distances look as if they were rigidly translated from each other. With a good approximation, the dispersion energy was indeed found to be the sum of the C_{60}-C_{60} interaction in free space and the adsorption energies of the individual molecules. Finally, we have added to the dispersion energies an empirical repulsive potential obtained by summing c_{12}/r^{12} interactions between a pair of carbons not on the same molecule, and using $c_{12}=12.0$ keV Å^{12} for the interaction coefficient.[55] The total energy curves for Ge and GaAs substrates are shown in Fig. 6. There is a minimum of energy around $X_0=10$ Å which closely corresponds to the C_{60}-C_{60} nearest-neighbor distance observed in solid C_{60} fullerite. The binding energy at the equilibrium distance is about 0.3 eV, also in good agreement with the experimental value in fullerite.[56]

VI. DISCUSSION AND CONCLUSIONS

The C_{60}-graphite and C_{60}-C_{60} interactions were computed by using a discrete-dipole description of the electron-charge fluctuations in the fullerene. A fairly good agreement with the Girifalco potential was found, but, due to many-body corrections, this simple pair potential could not reproduce the van der Waals energy simultaneously at short and large separation distances with the same c_6 interaction parameter. At short distances, we found that $c_6=20$ eV Å^6 was appropriate for a fullerene adsorbed on graphite (Fig. 1) whereas $c_6=17$ eV Å^6 better reflected our numerical data for the C_{60}-C_{60} attraction potential (Fig. 2). The dispersion energy between C_{60} and selected substrates was computed with the simplifying assumption of a semi-infinite dielectric medium. The van der Waals attraction of a molecule having its center 6 Å above the continuum edge was found to vary in the range 0.3–0.6 eV, depending on the substrate. The triplet and higher many-body interactions lowered the binding energy by approximately 10% at the equilibrium adsorption distances. For two physisorbed C_{60}'s we did not find any significant alteration of the intermolecular interaction by the substrate.

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APPENDIX: COMPUTING THE van der WAALS DISPERSION ENERGY FOR A COMPOSITE SYSTEM

In this appendix, we briefly summarize how the calculation of the dispersion energy between two (or more) C_{60} atoms can be efficiently computed. The technique described below is based on the fact that the physical problem at hand does not require the full information implicitly contained in Eq. (3). Let us recast that equation in a form of a Lippmann-Schwinger equation:[57]

$$\mathbf{E}_i=\mathbf{E}_i^0+\sum_j \underline{S}_{ij}^0\alpha_j\mathbf{E}_j=0\ ,\quad i,j=1,\ldots,N\ . \tag{A1}$$

In the present notations $\underline{S}_{ij}^0$ stands for $\underline{T}(\mathbf{r}_1-\mathbf{r}_j)+\underline{S}(\mathbf{r}_i,\mathbf{r}_j,\omega)$, N is the total number of C atoms, and $\mathbf{E}_i^0$ is a source field (that was set to zero above since our interest was restricted to the eigenmodes of the system). Let us now suppose that $\mathbf{E}_i^0$ is generated by a collection of source dipoles $\mathbf{p}_j^0$. The solution of the set of equations (A1) writes, formally,

$$\mathbf{E}_i=\sum_j \underline{S}_{ij}\mathbf{p}_j^0\ , \tag{A2}$$

where $\underline{S}_{ij}$ is the field susceptibility of the composite system formed by the substrate and the adsorbed molecules. The eigenmodes of the system are the poles of any one of the $\underline{S}_{ij}$ elements and this property establishes the link between field susceptibility and the van der Waals attraction energy.

For any fixed j, the $\underline{S}_{ij}$ elements satisfy a set of linear equations that follow immediately from Eq. (A1) in the form of a Dyson equation:

$$\underline{S}_{ij}=\underline{S}_{ij}^0+\sum_{k=1}^{N}\underline{S}_{ij}^0\alpha_k\underline{S}_{kj}\ . \tag{A3}$$

Suppose now we have m molecules adsorbed and let us denote by $\underline{S}_{ij}^m$ the corresponding field susceptibility. A molecule can represent any subset of n_m adsorbed atoms: in the present context, a molecule could either be a fullerene or any fraction of a fullerene as well. The important point is that the field susceptibility of the system composed of m molecules can be constructed from the field susceptibility of system with $m-1$ molecules:

$$\underline{S}_{ij}^m=\underline{S}_{ij}^{m-1}+\sum_{k=1}^{n_m}\underline{S}_{ik}^{m-1}\alpha_k\underline{S}_{kj}^m\ . \tag{A4}$$

Equation (A4) leads us to an iterative procedure for solving Eq. (A3) which consists in adding the molecules one after the other and computing at each step the corresponding field susceptibilities $\underline{S}_{ij}^1,\underline{S}_{ij}^2,\ldots$. The advantage is that, at the mth step, one only needs to compute the $\underline{S}_{ij}^m$ elements for i and j on the mth molecule and on the atomic sites of the molecules that remains to be added. One indeed does not need to keep track of the molecules adsorbed at the previous steps: their responses are contained in the $\underline{S}_{ik}^{m-1}$ elements. Moreover, computing the $\underline{S}_{ij}^m$ elements from Eq. (A4) requires inverting a matrix of size $3n_m\times 3n_m$, and this can be considerably smaller than the size $3N\times 3N$ of the initial dynamical matrix. How this algorithm can be exploited in computing the van der Waals dispersion interaction in a composite system is detailed in a recent paper by two of the present authors.[58]

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