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Elastic interaction of oxygen atoms on a graphite surface

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The elastic interaction energy between two oxygen atoms deposited on a graphite basal plane is calculated by atomic *ab initio* simulations and continuum theory of elasticity. The comparison between the results obtained with the two different methods, despite their usual length scale domain of application, is very good; attractive and repulsive behaviors are found. We speculate that this type of interaction could play an important role in the rearrangement of oxygen atoms experimentally observed after a weak oxidation of a graphite surface.

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Elastic interactions of defects play a very important role in the self-organization of matter at an atomic scale in strained nanostructures.[1] The origin of such interactions is due to the fact that microscopic defects (adsorbed atoms,[2] islands,[3] or terraces[4]), deposited on a thick substrate or a thin film, distort the material around them, resulting in a long range deformation. This deformation is due to the relaxation (i.e., the displacement) of each atom of the substrate from its strain free position. As the energy gained by this relaxation depends on the distance between defects, it results in an attractive or a repulsive interaction between them.

To treat this problem, a special continuum model was developed for thin film subtrates.[5] This model describes long range elastic interactions that are found to be attractive or repulsive depending on the geometry of the defects and their relative position. The force distribution, exerted by each defect on its atomic neighbors of the film, is the physical input parameter used by the model. This distribution depends on the nature of the defect and of the material itself. First principles numerical methods *(ab initio)* can calculate such a force distribution and also elastic interaction energy between defects. Thus, in order to gain a deeper understanding of the problem, it is essential to combine continuum modelization and *ab initio* atomic simulations on a specific material.

In this paper, we study the elastic interaction between two oxygen atoms deposited on the same side of a graphite basal plane. Studies on graphite, in the presence of impurities like nitrogen,[6] oxygen,[7] or iron,[8] were recently extensively investigated because of their impact on carbon based materials in aerospace technologies. For our study, the choice of graphite sheet presents mainly three advantages: (i) It is stiff due to the covalent nature of the in-plane chemical bound [the cohesion energy being 7.60 eV (Ref. 9)]. This stiffness prevents any nonlinear behaviors from happening, such as strong displacements (in comparison to the lattice parameter) leading to atomic reconstructions. (ii) The hexagonal symmetry endows carbon basal plane a two-dimensional (2D) isotropic elastic behavior (i.e., characterized by only two elastic constants,[10]) and thus it can be directly comparable with continuum elasticity theory of isotropic media. (iii) Considering that roughly 200 atoms of carbon can be treated by *ab initio* simulations and the 2D structure of a graphite basal plane, we are able to calculate elastic interactions characterized by their typical long range.

The results obtained both by *ab initio* calculations and the continuum model (with the proper force distribution) are compared. The agreement is very good despite the discret nature of matter at such a scale. This validates the use of the continuum model even when defects are separated by only a few inter-atomic distances.

Ab initio calculation. Calculation were performed using the *ab initio* total energy and molecular dynamics program VASP (Vienna Ab initio Simulation Package).[11,12] Ultrasoft Vanderbilt pseudopotentials[11,13] were used to approximate the electron-ion interactions. We expand the wave functions in a plane-wave basis, and bands near the Fermi surface are partially occupied using finite temperature broadening ($\sigma = 0.2$ eV). The slab contains a graphite basal plane of 200 carbon atoms with two oxygen atoms deposited at the surface in the bridge position which is the most stable.[7] Calculations for C and O used energy cutoffs of 211 and 270 eV with only the Γ point and the gradient corrected Perdew-Wang exchange-correlation functional.[14]

The two oxygen atoms are separated by a distance d from each other, they are aligned along two possible perpendicular directions (x,y): the x direction is chosen parallel to a C-C bound (Fig. 1). The z direction is perpendicular to the basal plane. By relaxing only the distance separating each oxygen from the basal plane surface, we obtain the forces applied by each oxygen on its close carbon neighbors (Fig. 1). The distance separating a relaxed oxygen from the plane is 1.41 Å. This configuration is our reference state where the C-C length is noted a.[15] Then, displacing carbons to minimize the total energy leads to a screening of the applied forces by creation of internal stresses. This results in a stretching (in-plane displacements) and a flexing (out-of-plane displacements) of the graphite basal plane. We note E_{relax}, the energy gained by this mechanical relaxation. It is assumed to be the sum of two components,

$$E_{relax}(d) = 2E_{self} + E_{int}(d), \tag{1}$$

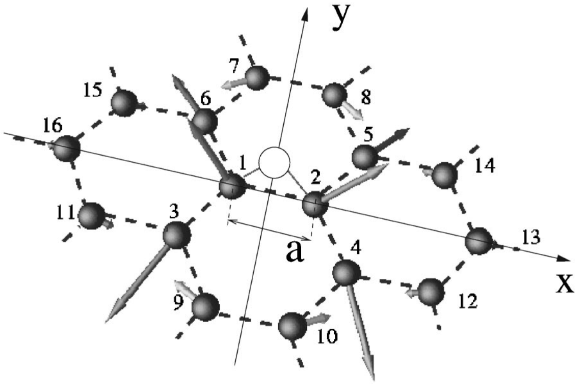

FIG. 1. Forces (arrows) applied on carbon atoms (dark spheres) by an oxygen (represented by an open circle) in the bridge position. The moduli of these forces are tabulated in Table I.

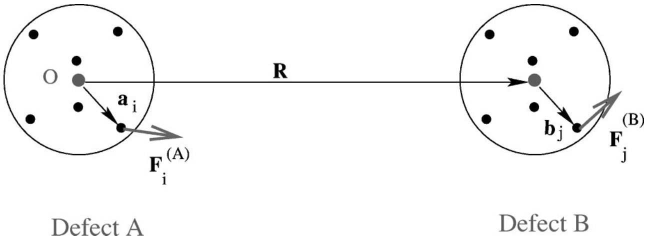

FIG. 2. Two identical defects (A) and (B) separated by a continuous elastic medium. Each defect (open circles) exerts forces on its neighbors (black circles).

where E_{self} is the self-energy associated with the mechanical relaxation of the graphite plane due to the presence of a single oxygen atom, and E_{int} is the part of the relaxation energy that depends on the distance d between oxygens: *it is the elastic interaction energy*. Equation (1) assumes that E_{self} is independent of the distance d between oxygens, i.e., that the force distribution around an oxygen is not too much affected by the other oxygen which is a quite reasonable assumption according to our results. Results are discussed below and compared to the continuum model predictions.

Continuum model. The interaction between localized point defects at a solid surface was mainly investigated with continuum elasticity theory.[2,5] As already presented in Ref. 5, the crystalline layer is treated as a continuum elastic plate with a finite thickness h.[16] The plate is stressed by force distributions localized around each defect. Forces depend on the local symmetry due to the chemical interaction between the substrate and the defect. As we consider mechanical equilibrium situations, the resultant of forces and the total mechanical momentum have to be zero.

An analogy with electrostatics can be made: two electric dipoles interact through a dielectric medium. The dipole momentum (an electric charge times the microscopic typical length) is due to the atomic nature of the matter, but the dipolar interaction energy is calculated assuming a continuous medium between the dipoles.

Let us write the interaction energy E_{int} between two identical localized defects (A) and (B) in the framework of the continuum theory of elasticity. The point defect (A) $[(B)]$ (a foreign oxygen atom in the present case) exerts a set of forces $\{\mathbf{F}_i^{(A)}\}$ $(\{\mathbf{F}_j^{(B)}\})$ on each atom i (j) of its N close neighbors (carbon atoms) located in $\mathbf{a}_i$ for defect (A) $[\mathbf{b}_j$ for defect $(B)]$; see Fig. 2. In order to minimize the total energy, each part of the elastic thin plate (i.e., each carbon atom of the basal plane) relaxes by moving with the displacement $\mathbf{U}(\mathbf{r})$ from its initial stress free position $\mathbf{r}$ (in the reference state). As we use linear elasticity, the displacement at point $\mathbf{r}$ is

$$\mathbf{U}(\mathbf{r})=\mathbf{u}_T^{(A)}(\mathbf{r})+\mathbf{u}_T^{(B)}(\mathbf{r}), \tag{2}$$

where $\mathbf{u}_T^{(A)}(\mathbf{r})$ $[\mathbf{u}_T^{(B)}(\mathbf{r})]$ is the total displacement created at position $\mathbf{r}$ by defect (A) $[(B)]$, i.e., by the set of forces $\{\mathbf{F}_i^{(A)}\}$ $(\{\mathbf{F}_j^{(B)}\})$. The interaction elastic energy can be simply written as[5]

$$E_{int}=-\frac{1}{2}\left[\sum_{i=1}^{N}\mathbf{F}_i^{(A)}\cdot\mathbf{u}_T^{(B)}(\mathbf{a}_i)+\sum_{j=1}^{N}\mathbf{F}_j^{(B)}\cdot\mathbf{u}_T^{(A)}(\mathbf{R}+\mathbf{b}_j)\right], \tag{3}$$

where the origin has been chosen on defect (A), and defect (B) is located in $\mathbf{R}$ (Fig. 2). The defect interdistance is $d=|\mathbf{R}|$.

The Green tensor $\underline{\underline{\mathbf{G}}}(\mathbf{r})$ of the problem is defined by

$$\mathbf{u}(\mathbf{r})=\underline{\underline{\mathbf{G}}}(\mathbf{r})\cdot\mathbf{F}\delta(\mathbf{r}), \tag{4}$$

where $\mathbf{u}(\mathbf{r})$ is the displacement created at a distance $\mathbf{r}$ by a single volumic force $\mathbf{F}\delta(\mathbf{r})$ localized at the origin. Thus the total displacements $\mathbf{u}_T^{(A)}(\mathbf{R}+\mathbf{b}_j)$ and $\mathbf{u}_T^{(B)}(\mathbf{a}_i)$ are given by

$$\mathbf{u}_T^{(A)}(\mathbf{R}+\mathbf{b}_j)=\sum_{i=1}^{N}\underline{\underline{\mathbf{G}}}(\mathbf{R}-\mathbf{a}_i+\mathbf{b}_j)\cdot\mathbf{F}_i^{(A)}\delta(\mathbf{r}-\mathbf{a}_i),$$

$$\mathbf{u}_T^{(B)}(\mathbf{a}_i)=\sum_{j=1}^{N}\underline{\underline{\mathbf{G}}}(-\mathbf{R}+\mathbf{a}_i-\mathbf{b}_j)\cdot\mathbf{F}_j^{(B)}\delta(\mathbf{r}-\mathbf{R}-\mathbf{b}_j). \tag{5}$$

There exist semianalytic expressions for $\underline{\underline{\mathbf{G}}}(\mathbf{r})$ created by a localized force applied at the surface of an elastic and isotropic infinite plate of finite thickness h.[17] These expressions are too involved to be listed here, but were tabulated in Ref. 17. $\underline{\underline{\mathbf{G}}}(\mathbf{r})$ is only parametrized by h, by E (the Young modulus) and by σ (the Poisson coefficient), $E$and σ being the two elastic constants that characterize the isotropic elastic infinite layer. For E and σ we use the standard tabulated values for the graphite basal plane: $E=1.0310^{12}$ Pa and $\sigma=0.17$.[18] The layer thickness h is used as a fitting parameter (see below).

Discussion. A characteristic mechanical behavior of thin plate mechanics is their flexion due to external applied forces. It is well known that it is much easier to bend a plate than to modify its length (by extension, for example). For this reason, a flat plate submitted to localized forces applied on its surfaces deviates from the plane by the vertical displacement $u_z(\mathbf{r})$. For small values of in-plane deformations, the linear equation of equilibrium is such that $\Delta^2 u_z=0$ everywhere exept where the forces are applied,[10,17] Δ being the 2D Laplacian operator $[\Delta=(\partial^2/\partial x^2)+(\partial^2/\partial y^2)]$. Therefore, a plate submitted to a force $F_z\delta(\mathbf{r})$ leads to a typical z dis-

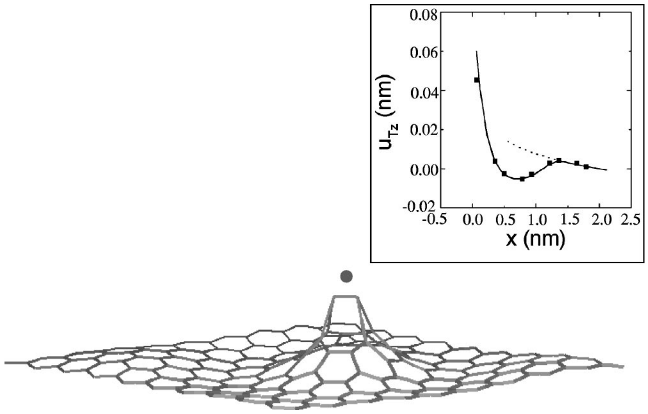

FIG. 3. The relaxed hexagonal lattice of a graphite basal plane in the presence of a single oxygen atom. In order to visualize the deformation, the z direction has been magnified by a factor of 7. Inset: z displacement $u_{Tz}(x,0)$ of carbons, *ab initio* calculated values (squares), continuum prediction (solid curve), and long-range logarithmic behavior (dotted curve).

placement field $u_z(r) \sim r^2 \ln(r)$ that diverges for large values of r. However, in our case, an oxygen atom has to exert a set of forces (and not a single force) on the graphite plane (Fig. 1) because the total force and the total mechanical momentum have to be zero. Note that, in addition, the force have both in-plane (x,y) and out-of-plane (z) components. The total displacement $u_{Tz}(\mathrm{r})$ created by an oxygen atom at a distance r, is the sum of each displacement created by the main six forces exerted by the defect on the nearest carbon atoms (Fig. 1); these forces preserve the mechanical constraints above mentioned. After simple algebra, for $r \gg h$ and $r \gg a$, this leads to a displacement that behaves as $u_{Tz} \sim \ln(r)$, for which the divergence is indeed negligible for the small systems studied here. Figure 3 shows a lattice of carbon atoms after its relaxation in the presence of a single oxygen. The inset compares the *ab initio* calculated values of the z displacement $u_{Tz}(x,0)$ of carbon atoms with the predictions of a continuous model that uses the forces listed in the Table I. The fitting parameter h is fixed equal to 1.4 Å, which is close to the value of the C-C length (1.43) Å) and of the distance between the oxygen and the graphite plane (1.41 Å). A very good agreement is obtained. At a long distance from the oxygen a logarithmic behavior is indeed obtained (dotted line).

TABLE I. The moduli of forces that are represented in Fig. 1. Numbers represent the carbon atoms on which the force is applied (see Fig. 1). We neglect forces applied on carbon atoms with a number larger than 6.

Carbon atoms	Force modulus (nN)
1, 2	4,00
3, 4, 5, 6	4,05
7, 8, 9, 10	1,53
11, 12, 14, 15	0,91
13, 16	0,74

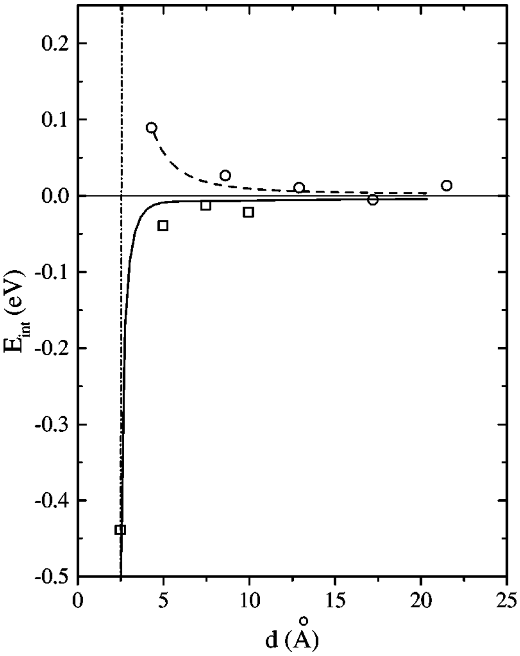

FIG. 4. Variation of E_{int} with the oxygen interdistance d. Circles and squares: *ab initio* calculations; solid and dashed curves: continuum model (using forces given in Table I). E_{int} is both attractive along the y direction (squares and solid curve) and repulsive along the x direction (circles and dashed curve). The vertical dashed line represents a singularity in the Green function due to the overlap of defects in the y direction.

The interaction energy is evaluated with Eq. (1) when using *ab initio* simulations $(2E_{self} = -1.767\ \mathrm{eV})$. It is calculated with Eq. (3) in the framework of continuum theory where applied forces (see Table I) are obtained by *ab initio* simulations. The comparison between the results (Fig. 4) is indeed very nice. Note that we use the same value of h found above. Along the y direction the oxygens attract themselves, while along the x direction they repel each other, a result well predicted by the continuum model. Thus the continuum model can provide reliable results even at an atomic scale. The origin of this good agreement is due to the properties of graphite that are enumerated above. As a consequence, we can speculate that the oxygen atoms deposited on a graphite basal surface could rearrange themselves in an anisotropic way, driven by the elastic attractive/repulsive interactions, thus leading to pattern of oxidation experimentally observed on graphite.[19]

We have shown that elastic interactions between two oxygen atoms on a graphite basal plane can be fruitfully investigated by a combination of first principles simulations and the continuum model. This combination, in that case, is determinant to understanding the mechanical distortion of a specific material at a nanometer scale and to validating the continuum theoretical approaches at such a scale. As a matter of fact, a similarly wide range of validity was found by Bernard and Zunger for two-dimensional semiconductors[20] and by Reich *et al.* for carbon nanotubes.[21] The continuum theory of elasticity for nanometric strain islands in epitaxial growth is also widely used and trusted for studying nanometric strain islands in epitaxial growth, and is the basis for many important results.[22] More generally, we think that other nanoscopic mechanical phenomena can be fruitfully investigated by the complementary use of continuum elasticity and atomistic approaches. This is a promising tool for bridging length scales in the study of mechanical properties of nanometric systems.

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