Nucleation and growth of single wall carbon nanotubes

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The nucleation and growth of single wall carbon nanotubes from a carbon-saturated catalytic particle surrounded by a single sheet of graphene is described qualitatively by using a very restricted number of elementary processes, namely Stone-Wales defects and carbon bi-interstitials. Energies of the different configurations are estimated by using a Tersoff energy minimization scheme. Such a description is compatible with a broad variety of size or helicity of the tubes. Several mechanisms of growth of the embryos are considered: one of them is made more favourable when the tubes embryos are arranged in an hexagonal network in the graphene plane. All the proposed mechanisms can be indefinitely repeated for the growth of the nanotubes.

I. INTRODUCTION

Since their discovery nearly fifteen years ago, single wall carbon nanotubes (SWNT) have received considerable interest from scientists: they are quite simple nanoscopic objects, with fascinating physical properties; moreover, their potential applications, in the field of nanosciences and nanotechnology, are very promising. But one major challenge is to control the growth of SWNTs, in particular concerning their diameter and helicity. This is the reason why a lot of literature was recently devoted to the understanding of the catalytic nucleation and growth of these tubes.

A typical situation is the high-temperature catalytic growth of SWNTs: small metallic particles of Ni or Co are heated in the presence of carbon, by arc discharge, laser heating or CVD, which causes growth of bundles of SWNTs perpendicular to the surface of the particles. Maiti et al.[1] suggest a general model which seems to get a broad agreement: the metallic particles are oversaturated in carbon, and a graphene layer wraps their surface. Embryos of SWNTs, looking like half-fullerenes, can form on this layer, and subsequently grow from their foot. These authors present molecular-dynamics computations, using a Tersoff-Brener potential, on (11,3) tubes taken as examples.

More recently, other reports on the same subject were published. Gavillet et al.[2] presented a high-resolution transmission electron microscopy study of such a root-growth mechanism, completed by a computer-simulation work using quantum molecular dynamics. The paper by Kanzow et al.[3] is another example of a growth model "in which precipitated graphene sheets detach from the surface of a liquid catalyst particle, forming fullerene-like caps". Gavillet et al.[4] gave an interesting review of experimental and theoretical results on SWNT nucleation and growth; in particular, they stated that "a natural process is to imagine that carbon atoms are incorporated at the root or at the tip where 'defects' necessarily occur: heptagons at the root and pentagons at the tip and/or metal–carbon bonds"; these authors also addressed the role of the catalyst. Recently, Ding et al.[5] presented molecular dynamics calculations on very small iron particles oversaturated with carbon, giving rise to very irregular SWNTs.

The purpose of the present paper is to propose qualitative ideas towards a better understanding of the nucleation and growth of SWNTs. We show that a very small number of elementary defect types are required to build SWNTs from a graphene surface. We also address the case where tubes grow inside a bundle.

II. GENERAL IDEAS AND TOOLS

Our starting point consists in a graphene plane, on which an embryo of SWNT will grow. In order to check the stability and energy of the proposed defect geometries, we performed energy minimizations by using the Tersoff model[6]. We worked mainly with a nearly square portion of the graphene plane of 240 carbon atoms, with periodic boundary conditions in both directions of the plane. We also considered the case of a network of embryos, using for that purpose a diamond-shaped unit cell with suitable periodic boundary conditions. Our energy computations do not pretend to be very precise; they intend to give some indications for comparing different possible configurations.

We consider three elementary defects in the graphene plane:

a) the Stone-Wales defect[7] is the simplest possible point defect, which consists in a 90° rotation of a pair of C atoms, with some rearrangement of the C-C bounds: the net result is the transformation of four hexagons into two heptagons and two pentagons. In our configuration, it corresponds to an extra energy of 9.1 eV. This estimate is quite large compared to more precise calculations from *ab initio* approaches[8,9] which give energy values for the Stone-Wales (SW) defect in the 5 to 6 eV range. We use however the Tersoff potential, due to its high simplicity; in spite of its lack of accuracy, we believe that it can be useful for comparing different growth scenarii.

b) the bi-interstitial enables to add extra C atoms to the graphene without generating dangling bonds (which would be the case with single interstitials). Our model for the bi-interstitial consists in adding atoms onto two opposite sides of an hexagon. The net result is again two heptagons and two pentagons, with a different topology

compared to the SW defect. It corresponds to an extra energy of 11.9 eV (this energy is taken as the difference with that of the same number of atoms if they were in a perfect graphene sheet).

c) the last defect is the dislocation. It is composed of a pentagon-heptagon pair[10], the Burgers vector (BV) being perpendicular to the pentagon-heptagon axis. It is quite amusing to note that, in the very different framework of grain growth, Cahn and Padawer pointed out the existence of this defect in a honeycomb network many years ago[11]. Like any dislocation, it is topologically impossible to create ex nihilo such a defect. It can only be created as a pair of dislocations of opposite BV, or (we shall give examples in the following) as a side effect of the evolution of other defects. The energy of an isolated dislocation is known to diverge logarithmically with distance in an infinite crystal; however, in practice, such a divergence being slow, and for a finite size of samples or a finite distance between dislocations, an energy value estimate can often be given. Building two dislocations from such a dislocation pair in our finite graphene sample, we estimate the individual dislocation energy to be about 11 eV.

Elementary dislocation theory teaches that dislocations can glide, along a line in the present 2D configuration: this line is parallel to the Burgers vector, i.e. perpendicular to the pentagon-heptagon axis. It is interesting to note that Fig. 2(a) and (b) of Ref.[12] is an example of the creation and glide of two such dislocations, evidenced in a numerical simulation. In fact, it is quite straightforward that a dislocation can glide by one polygon with a single SW made on one edge of the heptagon. It is worth mentioning that like classical 3D dislocations, two dislocations with opposite BV must attract themselves.

The other defects mentioned before, the SW and the bi-interstials, can also glide: both these defects can be seen as made from two dislocations with opposite BV, which can glide individually.

III. NUCLEATION OF AN EMBRYO

Our model lies on the fact that an embryo is nucleated in the graphene plane, so that it can grow from the foot, perpendicularly to the plane. The cap of the embryo looks like a half-sphere, which means, as many authors remarked, that – from Euler's theorem – it contains exactly 6 pentagons (in reality, topology only dictates that, when the polygons are forced to be heptagons, hexagons or pentagons, the difference between the number of heptagons and pentagons must be 6). As a consequence, there must be exactly 6 heptagons around the foot of the embryo.

We have constructed some embryos by adding bi-interstitials in the graphene plane. For instance, a (12,0) zig-zag embryo could be built by adding 24 interstitials (12 bi-interstitials), which generated 12 new polygons. Such an embryo is shown in Fig. 1. The Tersoff energy
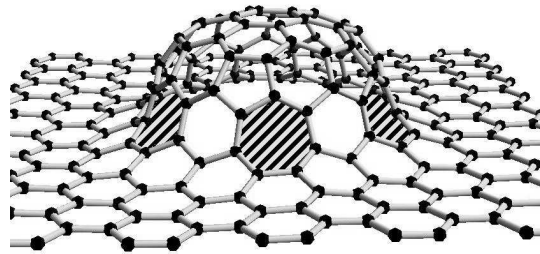

FIG. 1: Embryo of a (12,0) zig-zag SWNT. The heptagons in the foot of the embryo are hatched. We get an extra energy of 28.1 eV.
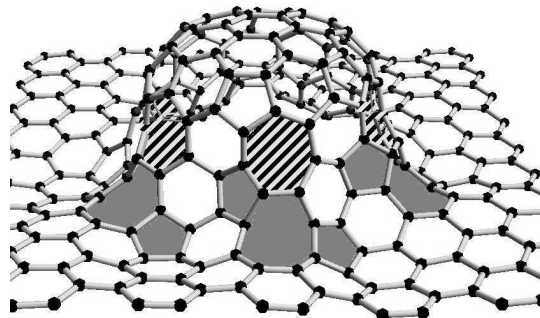

FIG. 2: 24 carbon interstitials are added on the foot of the embryo of a (12,0) SWNT. The heptagons in the foot of the embryo are hatched. The pentagons and octagons are grayed. We get an extra energy of 72.0 eV.

minimization gives an energy of 28.1 eV for this embryo.

IV. GROWTH

In order to make the (12,0) embryo grow one row, it is necessary to add 12 hexagons, that is 24 interstitials. There are several possibilities for adding these interstitials.

If the 12 bi-interstitials are added in the 12 polygons (6 hexagons and 6 heptagons) which form the first ring of the embryo, the net result is the growth of the tube without creating any supplementary defect. The final energy of the tube is about 30 eV, which is only slightly more than that of the embryo. Adding the bi-interstitials not at once, but one after the other, the energy increases much more, passing through a maximum of 9 eV above. It is clear that this growing process can be repeated *ad libitum*, making the tube grow indefinitely.

The fact that, in this process, interstitials are not added in the basal graphene plane, but on the side of the embryo, can be questionable if the C atoms come from the inside of the supersaturated metallic particle. We wish thus to suggest here a second possible process.
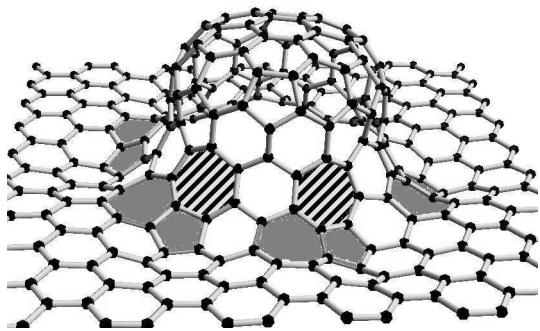
3

FIG. 3: 6 Stone-Wales transforms are made on the pattern shown in Fig. 2. The heptagons in the foot of the embryo are hatched. The dislocations (pentagons plus heptagons) are grayed. We get an extra energy of 52.7 eV.
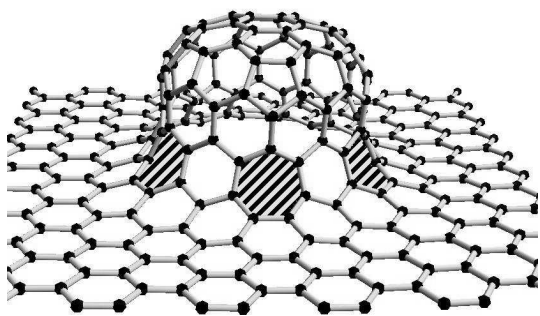

FIG. 4: 6 more Stone-Wales transforms are made on the pattern shown in Fig. 3. The embryo of Fig. 1 has grown of one row. The heptagons in the foot of the embryo are hatched. We get an extra energy of 30.4 eV.

Adding the 12 bi-interstitials in the closest ring of hexagons next to the foot of the embryo gives the arrangement shown in Fig. 2, with an energy of 72.0 eV, which is a much higher value; we discuss this value below. Now, near the foot of the tube, a lot of defects are present: 6 octagons and 12 pentagons (they are grayed in Fig. 2). These defects have to be eliminated by some kind of glide movement in order to get a realistic defect-free growing process. This can be done quite easily, in two steps:

a) the first one is required by the fact that the heptagons, shown hatched in Fig. 2, have to go down back to the foot of the tube. For doing that, 6 SW processes on the bounds between heptagons and octagons are done, which suppress also six of the pentagons and replace the 6 octagons by 6 heptagons: this is clearly shown in Fig. 3. The energy is now 52.7 eV. The net result is a (12,0) tube, grown by one row, plus, near its foot, 6 pentagon-heptagon pairs which are 6 dislocations, with the 6 possible BV values (the sum of these BV is, of course, zero).

b) the second step must be performed in order to annihilate these dislocations. This can be done quite simply by 6 new SW processes, which are done on the 6 bounds
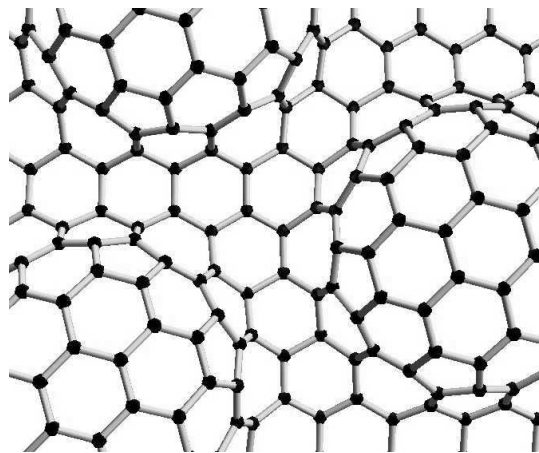

FIG. 5: Embryos of (12,0) SWNTs, seen from above, arranged in an hexagonal network. In this case, the growth is possible without creation of dislocations (see text).

common to two heptagons. After doing this, we are left with a perfect (12,0) tube, with an energy of 30.4 eV (Fig. 4).

It is interesting to address more in detail the problem of the energy values, which seem to be much higher in the second process described above. Reality is more complex: Fig. 2 to 4 show quite clearly what are the steps involved in the tube growth, but they are certainly not the most economical path for this growth. It is much better to do things like the following, from the embryo of Fig. 1:

— introducing 4 interstitials near the foot of the embryo, giving birth to one octagon and two pentagons.

— making a first SW to transform these defects into one dislocation.

— making a second SW to annihilate the dislocation.

— repeating 5 more times these 3 steps, which gives finally the situation depicted in Fig. 4.

We have done this step-to-step process and monitored the energy, whose maximum proved to be of the order of 16 eV above the energy of the perfect embryo. This is a collar energy, substantially higher than the one we have to pass in the first defect-free process (however, the total energy is then about 44 eV, much lower than that of the configuration in Fig. 2). But the second process has the advantage of enabling the addition of carbon interstitials in the graphene basal plane, not on the sides of the embryo.

We finally tried to figure out what can be gained from considering a network of embryos instead of an isolated one. We found that when putting embryos in an suitable hexagonal network (see Fig. 5), the second process described above could be made a little simpler: after addition of 24 interstitials per embryo, step a) described above has to be done in order to bring down the heptagons. But step b), with its 6 SW, is no longer needed: dislocations annihilate 3 by 3, between neighbouring embryos. This simplification corresponds to an interesting gain in energy, the collar value being about 10 eV above

the embryo energy. This is of the same order of magnitude as the first defect-free process. We can also remark that this process of growth of SWNT bundles does not require that all tubes have the same helicity: it is sufficient that the geometry of the 6 created dislocations near the foot of each tube is the same, which is much less restricting.

We point out that it would be interesting to get values for the energy barriers, which the present calculations, taken at equilibrium, do not enable. However, it remains difficult to understand how these growth processes involving very large energies can be efficient in quasi-equilibrium processes. An interesting possibility, considered by several authors[4,9], is that catalytic effects can reduce the energies involved.

V. CONCLUSION

We have shown that the nucleation and growth of carbon nanotubes from a graphene basal plane can be qualitatively described with a small number of elementary processes, each of them corresponding to a moderate amount of energy. Such a description does not depend on the size or helicity of the tubes. Several mechanisms can be considered: one of them is made more favourable when the tubes embryos are arranged in an hexagonal network in the plane. All the proposed mechanisms can be indefinitely repeated, giving rise to a possible endless growth of the nanotubes.

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